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#### ABSTRACT

### ANALYSIS OF MUELLER MATRICES OF METAMATERIALS AND MULTIFERROICS

#### by Paul D. Rogers

The optical spectra of complex materials such as magnetic-dielectric media, magnetoelectric and multiferroic crystals, materials with intrinsic chirality, and metamaterials are studied. These media are important both for: (i) their interesting optical effects, such as Negative Index of Refraction (NIR) and impedance matching; and (ii) possible device applications such as switching devices and anti-reflection coatings. Proper characterization of complex materials requires advanced spectroscopic approaches and the development of theoretical models for data analysis. Berreman's  $4 \times 4$  matrix formalism is used to derive forward models for the optical spectra of Reflectivity, Transmission, Rotating Analyzer Ellipsometry (RAE), and Mueller Matrices (MM). The forward models incorporate the relative electric permittivity tensor ( $\mathcal{E}$ ), the relative magnetic permeability tensor ( $\mu$ ), the magneto-electric tensors ( $\alpha$  and  $\alpha'$ ), and the chirality tensors ( $\xi$  and  $\xi'$ ). These models can accommodate various crystal symmetries in both the semi-infinite and thin film configurations. Using non-linear least squares fitting procedures, the forward models can be fitted against experimental optical spectra to determine the tensor parameters, which describe the physical properties of the material.

In the original part of this Thesis, forward models for the Mueller Matrix components of materials with relative magnetic permeability tensor  $\mu \neq 1$  are studied. 4×4 matrix formalism is used to calculate the complex reflection coefficients and the MMs of dielectric-magnetic materials. For materials with simultaneously diagonalizable  $\varepsilon$  and  $\mu$ 

tensors (with coincident principal axes), analytic solutions to the Berreman equation are derived. For the single layer thin film configuration, analytic formulas for the complex reflection and transmission coefficients are derived for orthorhombic symmetry or higher. The separation of the magnetic and dielectric contributions to the optical properties as well as the ability to distinguish materials exhibiting negative index of refraction are demonstrated using simulations of the MM at varying angles of incidence.

Far-infrared spectra of magneto-dielectric Dy<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> garnet (DY-IG) were studied using a combination of transmittance, reflectivity, and rotating analyzer ellipsometry. In addition to purely dielectric and magnetic modes, several hybrid modes with a mixed magnetic and electric dipole activity were observed. Using 4×4 matrix formalism for materials with  $\mu(\omega) \neq 1$ , the experimental optical spectra were modeled and the far-infrared dielectric and magnetic permeability functions were determined. The matching condition  $\mu(\omega_h) \cdot S_e = \varepsilon(\omega_h) \cdot S_m$  for the oscillator strengths  $S_{e(m)}$  explains the observed vanishing of certain hybrid modes at  $\omega_h$  in reflectivity.

Electromagnetic wave propagation and the spectra of optical excitations in complex materials are modeled. Analytical expressions for the complex reflection coefficients of materials with cycloidal magnetic ordering such as  $REMnO_3$  compounds (RE=rare earth) are derived for both semi-infinite and thin film configurations. Simulations for the Negative Index of Refraction (NIR) condition are given and the effect of the magneto-electric tensor on NIR is illustrated. Finally, the MMs of various combinations of material tensor components are illustrated for the dynamic magneto-electric and chirality states and methods to distinguish their contributions are discussed.

## ANALYSIS OF MUELLER MATRICES OF METAMATERIALS AND MULTIFERROICS

by Paul D. Rogers

A Dissertation Submitted to the Faculty of New Jersey Institute of Technology and Rutgers, The State University of New Jersey – Newark in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Applied Physics

**Federated Physics Department** 

May 2011

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## APPROVAL PAGE

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#### CHAPTER 1

#### **INTRODUCTION**

The objective of this Thesis is the analysis of the optical spectra of complex materials. Chapters 1-7 presents the review of necessary background material. This material includes: the magnetic and dielectric properties of matter, multiferroics (including the magneto-electric effect), metamaterials, 4×4 matrix formalism, matrix methods in optics, spectroscopic ellipsometry using synchrotron radiation, and optimization methods for non-linear least squares fitting.

The original results presented in Chapter 8 are published in P. D. Rogers, T. D. Kang, T. Zhou, M. Kotelyanskii, and A. A. Sirenko, "*Mueller matrices for anisotropic metamaterials generated using* 4×4 *matrix formalism*", Thin Solid Films, 519 (2011) 2688-2673 [1], doi: 10.1016/j.tsf.2010.12.066 and have been presented at the ICSE-V Conference in May 2010.

The original results presented in Chapter 9 have been accepted for publication:

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The original results presented in Chapter 10 will be submitted for publication: P. D. Rogers, M. Kotelyanskii, and A. A. Sirenko, "Modeling of electromagnetic wave propagation and spectra of optical excitations in complex media using  $4 \times 4$  matrix formalism."

The Appendices include original results for the derivation of the Adjusted Oscillator Strength Matching condition using two different approaches. The Appendices also provide supplementary material applicable to non-linear least squares fitting and error analysis.

#### **CHAPTER 2**

## OVERVIEW OF THE DIELECTRIC AND MAGNETIC PROPERTIES OF MATTER

#### 2.1 Introduction

This Chapter examines the optical properties of matter when subject to incident electromagnetic radiation. In particular, the theory and models concerning the dielectric permittivity tensor and the magnetic permeability tensor are reviewed. The Chapter concludes with a discussion of how these tensors enter into Maxwell's equations. The majority of theoretical and analytical background for this Chapter is taken from References [3-8].

#### 2.2 Dielectric Properties in an Electromagnetic Field

In the presence of incident electromagnetic radiation, dipole moments are induced at the atomic level. The induced dipole moment  $\vec{p}$  is proportional to the local field  $\vec{E}$  and the net effect of all dipole moments is to produce a polarization field  $\vec{P}$ . This field is defined as the dipole moment per unit volume. In a linear approximation (neglecting nonlinear effects)  $\vec{P}$  is proportional to  $\vec{E}$ :

$$\vec{P} = \varepsilon_0 \chi_e \vec{E} \tag{2.1}$$

The factor  $\chi_e$  is known as the electric susceptibility and is dependent upon the microscopic nature of the material. The vector field  $\vec{E}$  in Eq. (2.1) is the resultant field inside the material. The displacement vector  $\vec{D}$  is defined to be:

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P} \tag{2.2}$$

The source of  $\vec{D}$  is due only to free charges in the system. Its properties will be further discussed in Sections 1.5 and 1.8. Substituting Eq. (2.1) into Eq. (2.2) gives:

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P} = \varepsilon_0 \vec{E} + \varepsilon_0 \chi_e \vec{E} = \varepsilon_0 (1 + \chi_e) \vec{E} = \varepsilon \vec{E}$$
(2.3)

Finally, the relative dielectric constant  $\mathcal{E}_r$  is defined to be:

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} = 1 + \chi_e \tag{2.4}$$

The study of the electric susceptibility  $\chi_e$  including its tensor properties, and especially its spectral dependency, reveals the microscopic properties of the material in question. This is particularly true with respect to its behavior in the presence of incident radiation in proximity to the dipole resonances. Details will be considered in the next Section. In the following Sections, the subscript "r" in will be droped in  $\varepsilon_r$  to keep the formulas more compact.

#### 2.3 Elementary Excitations and the Simple Harmonic Oscillator Model

In the presence of incident radiation having frequency  $\omega$ , the electric susceptibility  $\chi_e$  itself becomes a function of  $\omega$ . This is because the incident radiation interacts with elementary excitations in the material. The four primary groups of elementary excitations are: (a) electronic excitations of valence electrons; (b) ionic or phonon excitations due to lattice vibrations; (c) free carrier excitations and (d) crystal field transitions. For brevity, the coupled excitations, such as plasmons, are excluded from our discussion.

Accordingly, a complete description of the dielectric constant can be written as a sum of the additive contributions:

$$\mathcal{E}_{r}(\omega) = 1 + \chi_{el}(\omega) + \chi_{ph}(\omega) + \chi_{fc}(\omega) + \chi_{CF}(\omega)$$
(2.5)

The frequency-dependent behavior of each of the four contributions to the dielectric constant can be described using, for example, the Simple Harmonic Oscillator (SHO) model. Note, however, that these four types of contributions have strong dispersion in different parts of electromagnetic spectrum. Usually, the off-resonant contributions to the dielectric function are presented with an "infinite value" of the dielectric constant  $\varepsilon_{\infty}$ .

#### **2.3.1 Electronic Excitations of Valence Electrons**

The polarization vector  $\vec{P}$  was introduced as the dipole moment per unit volume. An alternative expression for  $\vec{P}$  which directly incorporates the electronic dipole moment is:

$$\vec{P} = \varepsilon_0 \chi_{el} \vec{E} = N \vec{d} = N q_e \vec{x}$$
(2.6)

In Eq. (2.6), N represents the number of atoms per unit volume,  $\vec{d}$  is the dipole moment at the atomic level,  $q_e$  is the electronic charge, and  $\vec{x}$  represents the distance from the electron to its positively charged nucleus. Eq. (2.6) provides a direct connection between the electronic susceptibility and the  $\vec{x}$  vector. In the presence of an external driving force field, the SHO equation of motion for the valence electron becomes:

$$m_e \frac{\partial^2 \vec{x}}{\partial t^2} = -m_e \omega_0^2 \vec{x} - m_e \gamma \frac{d\vec{x}}{dt} + q_e \overline{E_0} e^{-i\omega t}$$
(2.7)

The first term on the right hand side of Eq. (2.7) is the familiar restoring force term of an harmonic oscillator with  $\omega_0$  representing the electron's natural frequency of motion. The

second term is a damping term and the third term is the external driving force with the incident radiation having frequency  $\omega$ . The solution to Eq. (2.7) is:

$$\vec{x} = \frac{q_e}{m_e} \frac{E_0}{\left(\omega_0^2 - \omega^2 - i\gamma\omega\right)} e^{-i\omega t}$$
(2.8)

Using Eq. (2.6),  $\chi_{el}$  can now be directly calculated as:

$$\chi_{el}(\omega) = \frac{Nq_e^2}{\varepsilon_0 m_e} \frac{1}{(\omega_0^2 - \omega^2 - i\gamma\omega)}$$
(2.9)

The electronic susceptibility is a complex number and is clearly dependent on the frequency of incident radiation  $\omega$  as well as the natural frequency  $\omega_0$  of the valence electron's motion. Stated differently, the electronic susceptibility is dependent upon the relationship between the energy of the incident radiation and the natural energy of the electronic transition. In the case of a free electron, the Schrodinger equation, which describes its wave function, is an eigenvalue equation and therefore admits only discrete forms of the wave function with each having an associated discrete energy level. In other words, there can be many "natural frequencies"  $\omega_0$ . A more comprehensive way of writing Eq. (2.9) is to include all of the natural frequencies in a summation:

$$\chi_{el} = \sum_{j} \frac{P_j^2}{\omega_{0_j}^2 - \omega^2 - i\gamma_j \omega}$$
(2.10)

where,  $P_j$  represents a type of oscillator strength or spectral weighting factor. In the farinfrared (far-IR) part of the spectrum,  $\chi_{el}$  is expected to be frequency independent and can often be combined with the first term of Eq. (2.5) to form  $\varepsilon_{\infty}$ , which is the high frequency dielectric constant.

#### **2.3.2** Ionic or Phonon Excitations due to Lattice Vibrations

Before the application of an external driving force with frequency  $\omega$ , it is a useful exercise to calculate the normal modes of a diatomic lattice in a crystalline structure. Consider planes of alternating ions at u and v having different masses  $M_1$  and  $M_2$ , respectively. Using a SHO model, with s, s-1 and s+1 as indices of adjacent planes; and employing the stiffness coefficient c, the equations of motions for the two ions become:

$$M_{1}\ddot{u}_{s} = c\left(v_{s-1} + v_{s} - 2u_{s}\right)$$

$$M_{2}\ddot{v}_{s} = c\left(u_{s+1} + u_{s} - 2v_{s}\right)$$
(2.11)

To solve Eq. (2.11), it is customary to use a trial solution or 'ansatz' for each of u and v of the form  $u_s = u_0 e^{i(sqa-\omega t)}$  and  $v_s = v_0 e^{i(sqa-\omega t)}$ , where a is the lattice constant, s is the index and q is the wave vector. After these substitutions, a set of homogeneous equations are obtained for  $u_0$  and  $v_0$  which have solutions only if their determinant is set to zero. This produces a solution for  $\omega^2$  of the form:

$$\omega^{2} = c \left( \frac{1}{M_{1}} + \frac{1}{M_{2}} \right) \pm c \sqrt{\left( \frac{1}{M_{1}} + \frac{1}{M_{2}} \right)^{2} - \frac{2}{M_{1}M_{2}} (1 - \cos qa)}$$
(2.12)

As can be seen from equation Eq. (2.12), solutions for  $\omega$  depend upon which sign is taken in front of the square root as well as values for the lattice wave vector q. Due to the periodic nature of the lattice, all available information about lattice behavior is in the first Brillion Zone ("BZ"). Accordingly, we can evaluate Eq. (2.12) both in the long wavelength limit (where  $qa \ll 1$ ) as well as at the zone boundary where  $q = \pi/a$ . The following table illustrates possible values of  $\omega$  in the assumption of  $M_1 > M_2$ .

Branch of Square	Long Wavelength	At BZ boundary	Description of	Name of Mode
Root	Limit(qa << 1)	$(q = \pi / a)$	Ionic Vibration	
$\mathcal{O}_{+}$	$\sqrt{2c\left(\frac{1}{M_1} + \frac{1}{M_2}\right)}$	$\sqrt{\frac{2c}{M_2}}$	Ions vibrate in opposite directions and are optically active	Optical Mode (Transverse-TO or Longitudinal-LO)
<i>@</i> _	$\sqrt{\frac{1}{2}c\frac{1}{M_1+M_2}}qa$	$\sqrt{rac{2c}{M_1}}$	Ions vibrate in the same direction and are not optically active	Acoustic Mode (Transverse-TA or Longitudinal-LA)

**Table 2.1.** Characteristics of the Lattice Vibrations.

Table 2.1 illustrates four interesting properties of the frequency behavior as a function of the underlying wave vector of the lattice vibration. First, the upper branch starts out at with a finite frequency at q=0 and then descends down to the right until its final value at the BZ boundary is achieved. Second, the lower branch starts out at zero frequency when q=0 and moves upwards to the right until its final value is achieved at the BZ boundary. Third, at the BZ boundary, the frequency of the upper branch is always greater than the frequency of the lower branch and an energy gap exists at this point. Fourth, only those modes whose ions vibrate opposite to one another will create an oscillating dipole and therefore become optically active.

The lattice response to an external driving force will now be analyzed. For these purposes, atomic polarization is ignored and focus is on the rigid ion approximation. The response of incident radiation is evaluated for a diatomic crystal having charges  $\pm q_e$ . Eq. (2.11) is again used as the base equation of motion together with an applied electromagnetic field evaluated at the lattice sites (*i.e.*, x = sa). The equations of motion then become:

$$M_{1}\ddot{u}_{s} = c\left(v_{s-1} + v_{s} - 2u_{s}\right) + q_{e}E_{0}e^{i(ska-\omega t)}$$

$$M_{2}\ddot{v}_{s} = c\left(u_{s+1} + u_{s} - 2v_{s}\right) - q_{e}E_{0}e^{i(ska-\omega t)}$$
(2.13)

The ansatz terms  $u_s = u_0 e^{i(sqa-\omega t)}$  and  $v_s = v_0 e^{i(sqa-\omega t)}$  are used to solve Eq. (2.13). For simplification, the lattice and incident wave vectors are phase matched and taken in the long wavelength limit. Accordingly, we set wave vectors q = k = 0 for the purposes of this calculation. A set of homogeneous equations is obtained:

$$-\omega^2 M_1 u_0 = 2cv_0 - 2cu_0 + q_e E_0$$

$$-\omega^2 M_2 v_0 = 2cu_0 - 2cv_0 - q_e E_0$$
(2.14)

We define the reduced mass  $\mu = \frac{1}{M_1} + \frac{1}{M_2}$ ; divide the equations in Eq. (2.14) by  $M_1$ 

and  $M_2$ , respectively; and identify the term  $\sqrt{\frac{2c}{\mu}}$  with  $\omega_{ro}$  (the TO phonon at q=0) to

produce:

$$u_0 - v_0 = \frac{q_e E_0}{\mu} \frac{1}{\omega_{ro}^2 - \omega^2}$$
(2.15)

Combining Eq. (2.15) with Eq. (2.6) gives:

$$P = Nq_{e} \left( u_{0} - v_{0} \right) = \frac{Nq_{e}^{2}E_{0}}{\mu} \frac{1}{\omega_{ro}^{2} - \omega^{2}} = \varepsilon_{0} \chi_{ph} E_{0}$$
(2.16)

The single phonon contribution to the electric susceptibility is given as:

$$\chi_{ph}(\omega) = \frac{Nq_e^2}{\varepsilon_0 \mu} \frac{1}{\omega_{TO}^2 - \omega^2}$$
(2.17)

In crystals, one should take into account that several eigenvalues for  $\omega_{ro}$  are possible (the maximum number of the phonon modes is 3s-3, where s is the number of ions per primitive cell). After the introduction of a damping term in the equations of motion, a more complete expression for  $\chi_{ph}(\omega)$  can be written as:

$$\chi_{ph} = \sum_{k} \frac{N_{k} q_{e}^{2}}{\mu} \frac{1}{\omega_{TO_{k}}^{2} - \omega^{2} - i\omega\gamma_{k}} = \sum_{k} \frac{Q_{k}^{2}}{\omega_{TO_{k}}^{2} - \omega^{2} - i\omega\gamma_{k}}$$
(2.18)

The term  $Q_k^2$  in the numerator can be interpreted as a type of weighting factor in the summation. In this case, it weights the number of molecules in the lattice that are vibrating at the various TO phonon frequencies.

#### 2.3.3 Free Carrier Excitations

The analysis of free carrier excitations follows closely the analysis of the excitations of the valence electrons with the exception of two important features. First, in the case of free carriers, there is no natural restoring force frequency because the free carriers are not bound to a particular nucleus. Second, the summation of various energy levels is not required as in the case of a valence electron. Accordingly, the analog to Eq. (2.9) in the case of free carriers becomes:

$$\chi_{fc} = \frac{-\Omega_p^2}{\omega^2 + i\omega\gamma}$$
(2.19)

Where  $\Omega_p^2 = \frac{N_{fc}q_e^2}{\varepsilon_{core}m^*}$  with  $N_{fc}$  being the free carrier concentration and  $\varepsilon_{core}$  being the

permittivity constant at high frequencies (frequencies above  $\Omega_p$ ).

#### 2.3.4 Crystal Field Transitions

In the presence of a crystal field ("CF'), the wave functions of an ion are changed. Preferred wave function orientations take on lower energy levels and previously degenerate wave functions are split. This process is known as crystal field splitting. An illustration for f orbitals is contained in Fig. 2.1 below.



Figure 2.1 Illustration of Crystal Field Splitting for *f*- orbitals.

The crystal field is an inhomogeneous electrostatic electric field produced by neighboring ions in the lattice. In Lanthanides, the Rare Earth (*RE*) ions are stripped of their outermost 6*s* electrons, which leave the optically active 4*f* electrons inside the 5*s* and 5*p* shell. This shields the 4*f* electrons from the direct effect of the crystal field and the CF effect becomes a perturbation in the Hamiltonian. In Figure 2.1,  $H_{FI}$  refers to the Hamiltonian of the Free Ion,  $H_{LS}$  is the Hamiltonian of the LS coupling and  $H_{CF}$  to the CF. The CF effect is significantly smaller than the spin-lattice interactions which varies as  $Z^4$ , where Z is the number of electrons. Dipolar transitions can then occur between the
lower energy and excited crystal field states. Transition probabilities between the IRactive CF states is analogous to oscillator strength in classical theory [3]. Using the Simple Harmonic Oscillator model, we can now introduce an analogous term for crystal field transitions.

$$\chi_{CF} = \sum_{n} \frac{T_n^2}{\omega_{0_n}^2 - \omega^2 - i\gamma_n \omega}$$
(2.20)

Here, *n* represents the number of allowed transitions due to crystal field splitting. Note, that for a "free" *RE* ion, the center-of-inversion symmetry requires the electric-dipole oscillator strength  $T_n$  to be zero. But in a crystal with the *RE* ion in non-centrosymmetric position, the so-called "forced electic dipole transitions" are allowed between 4f electronic levels due to intermixing between *f* and *d*-orbitals. Still, the magnetic dipole transitions are expected to be dominant between the crystal field levels of *f* electrons for *RE* ions in solids.

### 2.3.5 Summary

A complete expression for the dielectric constant as a function of the frequency  $\omega$  of incident radiation can now be obtained by combining Eqs. (2.5), (2.10), (2.18), (2.19) and (2.20) to produce

$$\mathcal{E}_{r}(\omega) = 1 + \sum_{j} \frac{P_{j}^{2}}{\omega_{0_{j}}^{2} - \omega^{2} + i\gamma_{j}\omega} + \sum_{k} \frac{Q_{k}^{2}}{\omega_{TO_{k}}^{2} - \omega^{2} + i\omega\gamma_{k}} + \frac{\Omega_{p}^{2}}{-\omega^{2} + i\omega\gamma} + \sum_{n} \frac{T_{n}^{2}}{\omega_{0_{n}}^{2} - \omega^{2} - i\gamma_{n}\omega} (2.21)$$

In Eq. (2.21), the second term refers to electronic transitions of the valence electrons, which can be viewed as being independent of frequency in the far infrared region, the third term recognizes phonon contribution to the dielectric function, the fourth term refers

to the contribution of free electrons to the dielectric function, which is not applicable in the case of insulators, and the fifth term refers to crystal field transitions. Eq. (2.21), in the case of an insulator, can be reduced further by combining the first and second terms into the high frequency dielectric constant and eliminating the fourth term to produce:

$$\varepsilon_{r}(\omega) = \varepsilon_{\infty} + \sum_{k} \frac{Q_{k}^{2}}{\omega_{TO_{k}}^{2} - \omega^{2} + i\omega\gamma_{k}} + \sum_{n} \frac{T_{n}^{2}}{\omega_{0_{n}}^{2} - \omega^{2} - i\gamma_{n}\omega}$$
(2.22)

This equation says that for insulators subject to far infrared radiation, the major frequency dependent susceptibility term comes from phonons. The crystal field contribution is usually an order of magnitude weaker. As can be seen, the dielectric constant is a complex number. It consists of a real part and an imaginary part and can be written as.

$$\mathcal{E}_{r}(\omega) = \mathcal{E}_{1}(\omega) + i\mathcal{E}_{2}(\omega) \tag{2.23}$$

In addition to the SHO model, several alternative Dielectric Function Models can be applicable to describe complex behavior of the light propagation in solids. Some of these models have been introduced many decades ago to provide empirical means to model complex interactions between elementary excitations, such as, for example, the phonon-phonon and electron-phonon interactions.

# 2.4 Dielectric Function Models

While the Lorentz, or SHO, model is one of the most popular, other dielectric function models have been developed. These include the Sellmeier and Cauchy models, the Tauc-Lorentz model, the complex Drude model [4], the Coupled Harmonic Oscillator model, and the Pendry model. The Sellmeier model is used for the dielectric function in a region, where the imaginary component of the Lorentz function,  $\varepsilon_2$ , is approximately zero. This

is equivalent to saying that the damping coefficient far from resonance is zero:  $\gamma = 0$ . The expression for the Sellmeier model is:

$$\varepsilon_1 = A + \sum_j \frac{B_j \lambda^2}{\lambda^2 - \lambda_{0j}^2}$$
(2.24)

In Eq. (2.24), A and B, are parameters to be fitted in a data analysis. This model is the most common in the optical glass catalogues for lenses, optical objectives, and optical antireflective coatings .

The Cauchy model is also used in the same spectral region as the Sellmeier model and is derived as a series expansion of the Sellmeier model:

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \dots$$
 (2.25)

In Eq. (2.25), it should be noted that the formula is written in terms of n, the refractive index. Again the letters represent parameters to be fitted against experimental data. For both the Sellmeier and Cauchy models, the imaginary component of the dielectric function is assumed to be zero.

The Tauc-Lorentz model is used to model the dielectric function of amorphous materials. The model is built upon the relationship between  $\varepsilon_2$  and the energy bandgap,  $E_g$ :

$$\varepsilon_2 = A \frac{\left(E_n - E_g\right)^2}{E_n^2} \tag{2.26}$$

In Eq. (2.26),  $E_n$  represents the photon energy. The final expression for  $\varepsilon_1$  is quite complicated as it is derived from the Kramers-Kronig (KK) relations which will be discussed later in this section.

$$\varepsilon(\omega) = \varepsilon_{\infty} \left( 1 - \frac{\Omega_p^2}{\omega^2 - i\omega\gamma} \right)$$
(2.27)

In Eq. (2.27),  $\varepsilon_{\infty}$  is the high frequency dielectric constant and  $\Omega_p$  is the plasma frequency.

The Coupled Harmonic Oscillator (CHO) model treats the Lorentz model as a partial fraction decomposition [5]:

$$\varepsilon(\omega) = \varepsilon_{\infty} \prod_{i}^{N} \frac{\omega_{LOi}^{2} - \omega^{2} - i\omega\gamma_{LOi}}{\omega_{TOi}^{2} - \omega^{2} - i\omega\gamma_{TOi}}$$
(2.28)

In Eq. (2.28),  $\omega_{TOi}$  and  $\omega_{LOi}$  are the natural frequencies associated with the transverse optical and longitudinal optical phonons and  $\mathcal{E}_{\infty}$  is the dielectric constant far above the resonances.

The Kramers-Kronig relations describe the coupling between  $\mathcal{E}_1$  and  $\mathcal{E}_2$ :

$$\varepsilon_{1}(\omega) = 1 + \frac{2}{\pi} P_{0}^{\infty} \frac{\omega' \varepsilon_{2}(\omega')}{\omega'^{2} - \omega^{2}} d\omega'$$

$$\varepsilon_{2}(\omega) = \frac{-2\omega}{\pi} P_{0}^{\infty} \frac{\varepsilon_{1}(\omega') - 1}{\omega'^{2} - \omega^{2}} d\omega'$$
(2.29)

In Eq. (2.29), *P* refers to the Cauchy principal value of the integral. This equation says that if  $\varepsilon_2(\omega)$  is known throughout the entire spectrum, then  $\varepsilon_1(\omega)$  can be calculated using the above equations. The Lorentz, CHO, Tauc-Lorentz , and Drude models automatically satisfy the KK relations. Since the Sellmeier and Cauchy models assumed that  $\varepsilon_2(\omega) = 0$ , they are not KK compatible [4].

The Pendry model for the dielectric function is not common, but it is widely accepted for modeling of magnetic succeptibilities in the analysis of metamaterials. In the static limit of  $\omega = 0$ , magnetic succeptibility  $\mu(0)$  is expected to be close to 1, while at the resonance a Lorentzian oscillator shape is desired. Both requirements can be achieved using the following function:

$$\mu(\omega) = 1 + \frac{A_e \omega^2}{\omega_{m0}^2 - \omega^2 - i\omega\gamma_m}$$
(2.29)

where  $\omega_{m0} >> \gamma_m$ . The Pendry model is sometimes known as the Adjusted Oscillator model [6].

# 2.5 The Dielectric Tensor $\hat{\varepsilon}(\omega)$

In describing the theory of the dielectric function in Section 1.2, it was assumed that the polarization vector  $\vec{P}$  as defined in Eq. (2.1) was in the direction of the electric field. However, this need not be the case in low-symmetry crystals or anisotropic materials. For example, a material which has a built-in dipole moment will have a  $\vec{P}$  vector different from the direction of an arbitrarily applied field. The same argument can be applied to the displacement vector  $\vec{D}$  and its relationship to  $\vec{E}$  as derived in Eq. (2.3):  $\vec{D} = \hat{\epsilon}\vec{E}$ . Accordingly, a more accurate description of  $\epsilon$  should be as a second ranked tensor in order to reflect the possible anisotropic nature of a medium. The dielectric tensor can now be written as:

$$\hat{\varepsilon} = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{pmatrix}$$
(2.30)

The dielectric tensor is a symmetric tensor [7]. It can, therefore, be diagonalized in a certain coordinate system and a set of principal axes x-y-z should be determined. Such a tensor would have the form:

$$\hat{\varepsilon} = \begin{pmatrix} \varepsilon_{xx} & 0 & 0 \\ 0 & \varepsilon_{yy} & 0 \\ 0 & 0 & \varepsilon_{zz} \end{pmatrix}$$
(2.31)

If  $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz}$ , the material is said to be isotropic. If the diagonal tensor components are not equal, the material is anisotropic.

The dielectric constant displays certain dispersion characteristics within a medium and its value depends on the frequency of the applied field. Accordingly, the dielectric tensor should be written with each component being a function of frequency:

$$\hat{\varepsilon} = \begin{pmatrix} \varepsilon_{xx}(\omega) & \varepsilon_{xy}(\omega) & \varepsilon_{xz}(\omega) \\ \varepsilon_{yx}(\omega) & \varepsilon_{yy}(\omega) & \varepsilon_{yz}(\omega) \\ \varepsilon_{zx}(\omega) & \varepsilon_{zy}(\omega) & \varepsilon_{zz}(\omega) \end{pmatrix}$$
(2.32)

Eq. (2.31) also becomes a function of frequency and therefore the associated principal axes will also be frequency dependent. This characteristic is called the dispersion of the axes [7].

#### 2.6 Magnetic Properties in an Electromagnetic Field

A material's magnetic properties are highly influenced by the magnetic moment of atoms, which constitute the material on a microscopic level. The magnetic moment of a free atom is affected by (a) the spins of its electrons; (b) their orbital angular momentum; and (c) induced magnetic moments which serve to counteract changes in magnetic flux in the system [8]. In addition, in much the same way that an applied electric field can induce lattice vibrations or phonons, an applied magnetic field can induce magnetic spin waves called magnons. Both the magnetic moment and magnon effects of an applied field are frequency dependent and will influence a material's magnetic permeability. These effects can be described in the following equation:

$$\mu(\omega) = 1 + \chi_{md}(\omega) + \chi_{sw}(\omega) \tag{2.33}$$

The subscript *md* refers to the net effect of magnetic dipole transitions and the subscript *sw* refers to the spin wave or magnon contribution. The two magnetic susceptibility terms will now be described.

### 2.7 Contributions to Magnetic Susceptibility

# 2.7.1 Magnetic Dipole Contributions to Magnetic Susceptibility

Quantum mechanics is needed to precisely describe the interaction of magnetic moments and spin waves subject to an externally applied field. The magnetic moment of an atom is dependent upon the aggregate spin and orbital angular momentum state of its electrons. With  $\vec{\mu} = g\mu_B \vec{J}$  (with  $\vec{\mu}$  being the magnetic moment of an atom,  $\mu_B$  the Bohr magneton, g the Lande factor,  $\vec{J}$  being the total of the atom's orbital and spin angular momenta) and  $\vec{M} = N\vec{\mu}$  (with  $\vec{M}$  being the magnetic moment per unit volume and N being the number of atoms per unit volume) the expression for magnetic susceptibility has the form:

$$\chi_{magnetic} = \mu_0 \frac{\vec{M}}{\vec{B}} = \sum_i \mu_0 N_i g \,\mu_b J_i \tag{2.34}$$

Accordingly, the magnetic susceptibility of a material subjected to an external field involves understanding the possible configurations of  $J_i$  along with the number  $N_i$  of atoms that could have such a configuration. Magnetic states can change as a result of absorption or emission of energy quanta in interaction with an applied field. Quantum mechanics is used to calculate the probability of allowed transitions between such states.

Hund's rules are used to estimate the ground state of an ion with many electrons [9]. Rule #1 states that the electron wave functions should be arranged so as to maximize *S*, the spin angular momentum. This is necessary because of the Pauli Exclusion Principle, which prevents electrons with parallel spins from occupying the same orbital. Rule #2 states that given the configuration established with the first rule, the electron wave functions should be arranged so as to maximize *L*, the orbital angular momentum. The basic principle used in this rule is that electrons orbiting in the same direction are less likely to run into each other with the result that the Coulomb energy can be minimized. Hund's 3rd rule says that the value of *J* can be found using J = |L-S| if the shell is less than half full and J = |L+S| if the shell is more than half full. The ground state is then summarized as  ${}^{2S+1}L_J$ . As an example, which we will consider in detail in Chapter 8, the ground state of Dy<sup>3+</sup> is estimated in Table 2.2 using Hund's rules.

Tab	le 2.2	The ground	l state of	f Dy <sup>y+</sup>	using	Hund'	s rul	les.
-----	--------	------------	------------	--------------------	-------	-------	-------	------

$m_l$	$\uparrow$	$\downarrow$
3	•	•
2	•	•
1	•	
0	•	
-1	•	
-2	•	
-3	•	

Dy<sup>3+</sup> has an outer shell  $4f^9$ . Since l=3, the first seven electrons are positioned with spin up while the remaining two are positioned with spin down. This satisfies rule #1. Rule #2 is satisfied if the two spin down electrons occupy the highest  $m_l$  orbitals. This configuration results in  $S = \frac{5}{2}$  and L=5 (written as the letter H in spectroscopic notation). The shell is more than half full so  $J = \left|\frac{5}{2} + 5\right| = \frac{15}{2}$ . Accordingly, the symbol for the ground state of  $Dy^{3+}$  is  ${}^{6}H_{15/2}$ . The ground state for Ho<sup>3+</sup> can also be easily determined using Table 1.1. With one more electron than  $Dy^{3+}$ , its ground state is  ${}^{5}I_8$ .

It is interesting to use Hund's rules to estimate the crystal field effect on the electron configuration of transition metal ions. For example, in a crystal field, the  $Fe^{2+}$  ion, which has a  $3d^6$  shell, splits into 3-fold lower energy orbitals and 2-fold higher energy orbitals. The term pairing energy is used to describe the amount of energy it takes to have two electrons occupy the same orbital. If the crystal field energy is less than the pairing energy then the first five electrons will each occupy one orbital. This sixth electron will then share one lower level orbital with another electron. This is known as the high spin configuration. On the other hand, if the crystal field energy is higher than the pairing energy, then all six electrons will occupy the three lower orbitals. This is known as the low spin configuration. In some cases, spin-flip transitions can occur when subject to incident radiation [9].

In general terms, Hund's rules do not say anything about the higher excited magnetic states. Transitions to these states are governed by quantum mechanical selection rules. For example, for the case of *RE* ions, all electric dipole transitions are forbidden due to

parity. This applies to the case where the force field has a center of symmetry. However, if this symmetry requirement is broken, such as in the case of a crystal field in noncentrosymmetric crystals, then three possible transitions are allowed: (i) a forced electric dipole transition; (ii) a magnetic dipole transition; and (iii) an electric quadrupole transition [10]. The latter is usually very weak in the far-IR spectral range and have never been reported in literature. The discrete nature of the electronic transitions motivates the use of the SHO model for magnetic dipole transitions just as we did in the case of electric dipole transitions in a crystal field. One model to describe the contribution of magnetic dipole transitions to magnetic susceptibility is to assume that the magnetic dipole response of a crystal consists of a collection of Lorentzian oscillators. Using this approach, the following equation describes the magnetic dipole contribution to magnetic susceptibility [11]:

$$\mu(\omega) = 1 + \sum_{j} \frac{f_{j}}{\omega_{j}^{2} - \omega^{2} - i\gamma_{j}\omega}$$
(2.35)

In (2.35),  $f_j$  is the oscillator strength of a given magnetic resonance,  $\omega_j$  is the frequency of a given resonance and  $\gamma_j$  is the relaxation rate of that resonance.

### 2.7.2 Spin Wave Contributions to Magnetic Susceptibility

In Section 2.3.2 elementary excitations due to phonon or lattice vibrations were examined. Natural frequencies for these lattice vibrations were calculated using systems of coupled equations. By setting the determinant of these systems of equations equal to zero, it was found that only certain frequencies (*i.e.* eigenvalues) were permitted. These eigenvalues correspond to quantized energy levels for the lattice vibrations. These are

called phonons. In a similar way, the spin states of nearest neighbor electrons can influence one another and form systems of coupled equations. In a manner similar to phonons, disturbances in spin alignments can be expected to propagate through a crystal lattice and would do so with only certain allowed levels of frequency and therefore energy. These quantized spin waves are called magnons.

**2.7.2.1 Ferromagnetic Magnons.** Ferromagnetic magnons deal with the excitation of spin waves in which all spins are pointing in the same direction. The equations of motion for the spin wave can be derived by starting with the interaction Hamiltonian for the spin of the p<sup>th</sup> electron [8]:

$$U = -2J\vec{\mathbf{S}}_{\mathbf{p}} \cdot \left(\vec{\mathbf{S}}_{\mathbf{p}-1} + \vec{\mathbf{S}}_{\mathbf{p}+1}\right)$$
(2.36)

Here *J* is the exchange integral from quantum mechanics and  $\hbar \vec{\mathbf{S}}_{p}$  is the angular momentum of the spin at the *p*<sup>th</sup> site. Using the magnetic moment at the *p*<sup>th</sup> site to be  $\vec{\mu}_{p} = g\mu_{B}\vec{\mathbf{S}}_{p}$ , Eq. (2.36) can be rearranged as:

$$\vec{\mu}_{\mathbf{p}} \cdot \left[ \left( \frac{-2J}{g \mu_B} \right) \left( \vec{\mathbf{S}}_{\mathbf{p}-1} + \vec{\mathbf{S}}_{\mathbf{p}+1} \right) \right]$$
(2.37)

The second bracketed term in Eq. (2.37) is called  $\vec{B}_{p}$  which is the effective magnetic field that acts on the  $p^{\text{th}}$  spin. Using the principal from mechanics that the rate of change of angular momentum equals the torque, the following differential equation can be produced:

$$\frac{d\mathbf{S}_{\mathbf{p}}}{dt} = \left(\frac{2J}{\hbar}\right) \left(\vec{\mathbf{S}}_{\mathbf{p}} \times \vec{\mathbf{S}}_{\mathbf{p}-1} + \vec{\mathbf{S}}_{\mathbf{p}} \times \vec{\mathbf{S}}_{\mathbf{p}+1}\right)$$
(2.38)

This time derivative will produce three separate equations in Cartesian coordinates. As Kittel points out, for very small excitations it is assumed that  $S_p^z = S$  and that terms of the form  $S^x S^y$  can be ignored [8]. Using these assumptions we get:

$$\frac{dS_{p}^{x}}{dt} = (2JS / \hbar) (2S_{p}^{y} - S_{p-1}^{y} - S_{p+1}^{y})$$

$$\frac{dS_{p}^{y}}{dt} = (2JS / \hbar) (2S_{p}^{x} - S_{p-1}^{x} - S_{p+1}^{x})$$

$$\frac{dS_{p}^{z}}{dt} = 0$$
(2.39)

The third equation above simply says that the *z* component of the spin is a constant that does not change in time. The first two equations form a system of coupled equations. Together, these imply that spin will precess about the *z* axis and the phase of this precession will change from the  $p^{\text{th}}$  to the  $p+1^{\text{th}}$  electron. An alternative derivation of Eq. (2.39) can be produced by employing the Pauli spin exchange operator [12]. In this manner, the small change in spin precession will propagate like a wave through the lattice. This motivates a solution of the form  $S_p^x = ue^{i(pka-\omega t)}$  and  $S_p^y = ve^{i(pka-\omega t)}$ . Inserting these ansatz into Eq. (2.39) and taking the determinant of the coupled set of equations to be zero leads to[8]:

$$\hbar\omega = 4JS(1 - \cos ka) \tag{2.40}$$

In the long wavelength limit, where  $ka \ll 1$ , this reduces to the dispersion relationship:

$$\hbar\omega \cong (2JSa^2)k^2 \tag{2.41}$$

It is interesting to note that, in the long wavelength limit, the frequency of magnons is proportional to the square of the wave vector, while for acoustic phonons frequency is directly proportional to the wave vector. There is a possibility for the two modes to couple and interfere [13]. Note, however, that the ferromagnetic magnons, in the absence of external magnetic field, cannot be studied using far-IR spectroscopy due to nearly zero energy value, which corresponds to the k-vector of far-IR light.

**2.7.2.2 Antiferromagnetic Magnons.** Antiferromagnetic magnon excitations occur when nearest neighbor ions have opposite spin. This ordering can be visualized with two equivalent intersecting lattices with each lattice having alternating spin. Just as in the case of a ferromagnetic magnon, three directional equations of motion can be derived. Also, as in the case of phonons arising from a diatomic lattice, the equations of motion for the nearest neighbor are coupled. When an external field is applied to the material, Eq. (2.38) becomes:

$$\frac{d\mathbf{S}_{\mathbf{p}}}{dt} = \left(\frac{2J}{\hbar}\right) \left(\mathbf{\vec{S}}_{\mathbf{p}} \times \mathbf{\vec{S}}_{\mathbf{p}-1} + \mathbf{\vec{S}}_{\mathbf{p}} \times \mathbf{\vec{S}}_{\mathbf{p}+1}\right) - \frac{g\mu_{b}}{\hbar} \left(\mathbf{\vec{S}}_{\mathbf{p}} \times \mathbf{\vec{B}}_{\mathbf{ext}}\right)$$
(2.42)

In working through Eq. (2.42), we assume that all even numbered lattice sites have spin up and all odd numbered lattice sites have spin down. In addition, we assume that the external magnetic field is polarized in the z direction. In order to reduce the dimensionality of the analysis, the variable  $\mathbf{S}^+ = \mathbf{S}^x + i\mathbf{S}^y$  is introduced [8]. When considering nearest neighbor interactions, the exchange integral J becomes negative. Using this definition of  $\mathbf{S}^+$ , the following set of coupled equations are obtained:

$$\frac{d\mathbf{S}_{2p}^{+}}{dt} = \frac{2iJ\mathbf{S}}{\hbar} \Big( 2\mathbf{S}_{2p}^{+} + \mathbf{S}_{2p-1}^{+} + \mathbf{S}_{2p+1}^{+} \Big) + \frac{ig\mu_{B}}{\hbar} \mathbf{S}_{2p}^{+} \mathbf{B}_{z_{2p}}$$

$$\frac{d\mathbf{S}_{2p+1}^{+}}{dt} = \frac{-2iJ\mathbf{S}}{\hbar} \Big( 2\mathbf{S}_{2p+1}^{+} + \mathbf{S}_{2p}^{+} + \mathbf{S}_{2p+2}^{+} \Big) + \frac{ig\mu_{B}}{\hbar} \mathbf{S}_{2p+1}^{+} \mathbf{B}_{z_{2p}}$$
(2.43)

Using the ansatz  $S_{2p}^+ = ue^{i(2pka-\omega t)}$ ,  $S_{2p+1}^+ = ve^{i((2p+1)ka-\omega t)}$  and  $\mathbf{B}_z = B_{0z}e^{i(2pqa-\omega t)}$  and with the

definitions 
$$\omega_{exch} = \frac{-4JS}{\hbar}$$
 and  $\gamma = \frac{-g\mu_B e^{i(2\,pqa-\omega t)}}{\hbar}$ , Eq. (2.43) produces another set of

coupled equations:

$$u\left(\omega_{exch} - \omega + \gamma B_{0_z}\right) + v\left(\omega_{exch}\cos(ka)\right) = 0\right)$$

$$u\left(\omega_{exch}\cos(ka)\right) + v\left(\omega_{exch} + \omega - \gamma B_{0_z}\right) = 0$$
(2.44)

Setting the determinant of this system of equations equal to zero produces frequency for normal modes as follows:

$$\omega = \gamma B_{0_z} \pm \frac{2JS}{\hbar} ak \tag{2.45}$$

Eq. (2.45) is an important result. It demonstrates that for the antiferromagnetic case, the dispersion relationship is linear in k. Resonance is expected to occur when incident frequencies are near those of the normal modes with the frequency  $\omega_m$ . The discrete nature of normal modes again motivates the use of the SHO model to describe the susceptibility contribution of magnons and the following equation will be used for this purpose.

$$\chi_{magnon} = \sum_{m_{sw}} \frac{S_j}{\omega_m^2 - \omega^2 - i\gamma_m \omega}$$
(2.46)

**2.7.2.3 Ferrimagnetism and Kaplan-Kittel Modes.** In the preceding discussion on antiferromagnetic modes, it was assumed that the two sublattices of opposite spins were equivalent. However, if the two sublattices are not identical then it is possible that a net magnetization appears. Since the sublattices are not identical in ferrimagnetic materials,

such as *RE*-iron garnets (see Chapter 9), it is possible that their spontaneous magnetizations will have different temperature dependencies and, in general, the magnetism in ferrimagnetics can be quite complicated. At a certain temperature one sublattice can dominate and therefore its magnetization is most pronounced. The opposite can be true in a different temperature range. It is possible that at a certain temperature, known as the compensation temperature, the net magnetization can be reduced to zero [9].

One group of ferrimagnetic materials is the garnets which have the chemical composition:  $RE_3Fe_5O_{12}$  where RE is the trivalent Rare Earth atom. These materials are also known as Rare Earth Iron Garnets or RE-IG. As explained in Blundell [9], the crystal structure is cubic but the unit cell is complex. Three of the Fe<sup>3+</sup> ions are on tetrahedral sites, two are on octahedral sites and the  $RE^{3+}$  ions are on dodecahedral sites. Kang *et al.* [14] describe the structure for Tb<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> in more detail. The Tb<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> crystals form a cubic structure. Tb<sup>3+</sup> ions with the ground state  ${}^{7}F_{6}$  are in the 24*d* dodecahedral sites with the local orthorhombic symmetry  $222(D_2)$ . There are several nonequivalent Tb ions in each unit cell with the same surrounding field but the axes are inclined to each other. This has the overall effect of producing an average cubic symmetry. Fe<sup>3+</sup> ions occupy two sites: 16a octahedral sites with the  $\overline{3}(C_{3i})$  symmetry and 24c tetrahedral sites with the  $\overline{4}(S_4)$  symmetry. Below the transition temperature of  $T_N \approx 550K$ , the iron spins are ordered in a ferrimagnetic structure with the spins aligned in the [1 1 1] direction. Among six possible exchange interactions between spins in three different magnetic subsystems, only two dominate. The main magnetic superexchange interaction is between Fe in two different sites: spins of Fe in the tetrahedral site are antiparallel to those of the octahedral site. Another important interaction is between Tb and Fe in the tetrahedral site resulting in the Tb spins to be antiparallel to Fe moments in the tetrahedral sties, and, hence, antiparallel to the net magnetic moment of Fe. Below approximately 150K, a rhombohedral distortion of the cubic cell causes the canting of Tb spins, which is usually described as a "double umbrella structure." The symmetry of the Tb<sup>3+</sup> is lowered from 222(D<sub>2</sub>) tetragonal to 2(C<sub>2</sub>) monoclinic. Note that Tb<sup>3+</sup> is not at the center of inversion, which is important for the future discussion of the selection rules for the crystal-field transitions.

Also as explained in Kang *et al.*, in addition to phonons and crystal-field excitations, the far-IR spectra of ferrimagnetic materials can exhibit magnetic excitations related to the spins of iron and RE ions, such as magnons. An acoustic ferrimagnetic mode that corresponds to the strongest superexchange Fe-Fe interaction falls in a very low-frequency range. The Fe-Tb ferrimagnetic interaction reveals itself in the measured far-IR spectral range. If one considers only the interaction between the *RE* and the combined Fe subsystems, then two optical magnetic modes should appear. One is the Kaplan-Kittel (KK) mode  $\Omega_M$ , which corresponds to the exchange between two magnetic subsystems. Another one  $\Omega_{LF}$  corresponds to precession of the RE moments in the effective field imposed by the iron magnetization. The zone-center energies of these modes are:

$$\Omega_{M}(T) = \lambda_{ex}\mu_{B} \lfloor g_{Fe}M_{Tb}(T) - g_{Tb}M_{Fe} \rfloor$$

$$\Omega_{LF} = \lambda_{ex}\mu_{B}g_{Tb}M_{Fe}$$
(2.47)

where  $\mu_B$  is the Bohr magneton,  $\lambda_{ex}$  is the exchange constant,  $g_{Fe,Tb}$  are the corresponding g factors,  $M_{Tb}$  is the Tb sublattice magnetization, and  $M_{Fe}$  is the combined Fe magnetization.

# 2.7.3 Summary

A complete expression for the magnetic permeability as a function of the frequency  $\omega$  of incident radiation can now be obtained:

$$\mu(\omega) = 1 + \sum_{l_{md}} \frac{R_l}{\omega_l^2 - \omega^2 - i\gamma_l \omega} + \sum_{m_{sv}} \frac{S_m}{\omega_m^2 - \omega^2 - i\gamma_m \omega}$$
(2.48)

In the above equation the second term incorporates magnetic dipole transitions and the third term incorporates the effects of spin waves or magnons. As with the dielectric permittivity tensor,  $\mu(\omega)$  is also a symmetric tensor:

$$\hat{\mu} = \begin{pmatrix} \mu_{xx} & 0 & 0 \\ 0 & \mu_{yy} & 0 \\ 0 & 0 & \mu_{zz} \end{pmatrix}$$
(2.48)

As seen in Eq. (2.48), the magnetic permeability of a material is a complex number. It consists of a real and imaginary part and can be written as:

$$\mu(\omega) = \mu_1(\omega) + i\mu_2(\omega) \tag{2.49}$$

#### 2.8 Maxwell's Equations

Electromagnetic phenomena in the absence of currents and charges are described by Maxwell's equations [15]:

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \qquad \nabla \times \vec{H} = \frac{\partial \vec{D}}{\partial t}$$

$$\nabla \cdot \vec{D} = 0 \qquad \nabla \cdot \vec{B} = 0$$
(2.50)

These are calculated without taking into consideration any induced polarization charges or currents. An equation for the displacement vector  $\vec{D}$  has already been given in equation (2.3) as  $\vec{D} = \varepsilon_0 (1 + \chi_e) \vec{E} = \varepsilon \vec{E}$ . A completely symmetric equation is available to describe  $\vec{B}$ , the magnetic induction vector. It is given by:

$$\vec{B} = \mu_0 \left( \vec{H} + \vec{M} \right) = \mu_0 (1 + \chi_m) \vec{H} = \mu \vec{H}$$
(2.51)

Together with bi-anisotropic tensors  $\rho$  and  $\rho'$ , which will be described in more detail later, Eq. (2.3) and Eq. (2.51) form the constitutive relations for the material.

A complete description of electromagnetic wave propagation in a complex anisotropic medium is made possible using Berreman's matrix equation [16]:

$$\begin{pmatrix} 0 & -curl \\ curl & 0 \end{pmatrix} \begin{pmatrix} \vec{E} \\ \vec{H} \end{pmatrix} = i \frac{\omega}{c} \begin{pmatrix} \hat{\varepsilon} & \hat{\rho} \\ \hat{\rho}' & \hat{\mu} \end{pmatrix} \begin{pmatrix} \vec{E} \\ \vec{H} \end{pmatrix}$$
(2.52)

In Eq. (2.52), *curl* represents the  $3\times3$  matrix operator. The first matrix on the right hand side is a  $6\times6$  matrix called the optical matrix **M**. This matrix contains all of the information contained in the constitutive relations and completely describes the anisotropic properties of the material including chirality and magneto-electric effects [17].

# **2.9 Chapter Summary**

In this Chapter we described the properties of the  $\hat{\varepsilon}$  and  $\hat{\mu}$  tensors. The symmetry and optical effects related to the case of  $\hat{\varepsilon}$  anisotropy and  $\mu = 1$  is rather a "common knowledge" in the community of the far-IR spectroscopy of solid state materials. We have been described this case in this introductory Chapter with the goal to present a

complete picture, define symbols, explain models, and to make a clear link to the optical properties of magnetic materials. The problem of the light propagation in magnetic materials with  $\mu \neq 1$  is already a specialized field that has been the focus of theoretical and experimental research in the last 10 years. The obvious conceptual complication arises from the fact that there is no theoretical relationship between the  $\hat{\varepsilon}$  and  $\hat{\mu}$  tensors. Without an assumption about their dispersion, it is impossible to de-couple the  $\varepsilon(\omega)$  and  $\mu(\omega)$  complex functions based on a single optical measurement of either transmission or reflectivity spectra. Still, the earlier work using far-IR and neutron spectroscopies built a solid foundation to understanding of magnetic materials in the frequency range below 100 cm<sup>-1</sup>, where  $\mu \neq 1$  and  $\varepsilon(\omega) \approx Const$ .

In contrast, the properties of the  $\rho$  and  $\rho'$  tensors, and especially their frequency dependence, are far less known theoretically compared to that for the  $\varepsilon$  and  $\mu$  tensors. Our knowledge of their symmetries and frequency dependence is practically "terra incognita". In recent years there is a tremendous interest regarding the optical properties of metamaterials and multiferroic crystals. One can say that the key to understanding of the magneto-electric coupling and the light propagation in the materials with Negative Index of Refraction (NIR) and in materials with chirality is hidden in the non-trivial relationships between the  $\rho$  and  $\rho'$  tensors in Eq. (2.52), which has no obvious connection to the  $\varepsilon$  and  $\mu$  tensors. In the next Chapter we will discuss the general ideas about the  $\rho$  and  $\rho'$  tensors, mostly obtained from the specialized literature in the field of metamaterials and multiferroic materials. The analytical and numerical solutions to the problem of light propagation in a magneto-electric medium with chirality and the connection between the "measurable" infrared spectra and the  $\varepsilon$ ,  $\mu$ ,  $\rho$  and  $\rho$ ' tensors is the central part of this Thesis.

#### **CHAPTER 3**

# MULTIFERROICS AND METAMATERIALS

# **3.1 Introduction**

In this chapter, multiferroic materials and metamaterials are examined. These materials are chosen for analysis because they are characterized with a magnetic permeability,  $\mu \neq 1$  and the  $\rho$  and  $\rho'$  tensors, which describe bi-anisotropic behavior, may not be equal to zero.

The study of complex materials is motivated both by their interesting physics as well as for possible device applications. For multiferroics, a proper understanding of the origin of both the electric and magnetic order inside the material is of fundamental importance. In addition, for multiferroic crystals with certain symmetries, it is possible for the magneto-electric (ME) effect to occur whereby electric polarization can be induced with the application of a magnetic field; and magnetization can be induced with the application of an electric field [18]. Phenomenon such as the ME effect suggest that multiferroic materials can have application for novel switching devices where, for example, magnetic memory could be addressed electronically [19]. Further, in the dynamic state, multiferroic materials allow for the possibility of electromagnons which enable the transfer of a portion of the spectral weight of magnons to hybridization with phonons at the same resonant frequency<sup>\*</sup>. Metamaterials, on the other hand, are artificial materials which allow for independent control of electric and magnetic field components [20]. When their design permits simultaneously negative dielectric permittivity and magnetic permeability, it is possible to achieve negative index of refraction (NIR). Under

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conditions of NIR, light takes on a 'left-handed' behavior and the propagating wave is refracted to the left of normal in the metamaterial. This allows for possibility of novel optical devices such as cloaking devices which 'bend' light around an object.

### 3.2 Multiferroic Materials and the Magneto-Electric Effect

# 3.2.1 Definition

The strict definition of a multiferroic material is one that combines any two or more of the primary ferroic orders in one phase: ferroelectric, ferromagnetic and ferroelastic. The more common definition, however, is to include only simultaneously ferroelectric and ferromagnetic orders. Ferroelectric ordering refers to the spontaneous ordering of electric dipole moments in a material; ferromagnetism refers to the spontaneous ordering of orbital and spin magnetic moments [19]. Magneto-electric coupling is a separate effect which most often occurs in, but is not restricted to, multiferroic materials. The following Venn diagram illustrates the relationships among these terms [21]:



**Figure 3.1** Relationships among polarization, multiferroic and magneto-electric effects. (Source: Ref [21]).

#### 3.2.2 Background

The possibility for the magneto-electric effect was known in the 1950's and early 1960's through the pioneering work of Landau and Lifshitz [22], Dzyaloshinskii [23] and Astrov [24] Landau and Lifshitz addressed the possibility of linear coupling between the electric and magnetic fields in a medium. Dzyaloshinskii proved that anti-ferromagnetic  $Cr_2O_3$  had a magnetic symmetry that should theoretically allow the ME effect and Astrov actually showed the effect experimentally in  $Cr_2O_3$  in the following year. Other early efforts at studying multiferroics and the magneto-electric effect are covered by O'Dell (see Ref. [25]). Classification as a multiferroic material requires that two types of ordering, ferroelectric and ferromagnetic, coexist in the same phase. The term multiferroic has been attributed to the work of Hans Schmid [26] whose work, interestingly, was funded by the Swiss Post Office [27]. Building on this early work, multiferroics and the magneto-electric effect are now topics of a high level of interest. There are at least four main reasons for this strong interest [19, 21]. First, in 2000, Hill [28] wrote a paper claiming that the conditions for multiferroic materials are actually quite rare. This challenge spawned a huge interest in finding new multiferroics. Second, advances in experimental techniques have increased the availability of multiferroic materials for study. Modern methods for crystal growth allow for precise control over crystalline perfection with the result that large enough samples for measurement can be produced [27]. Third, discoveries in 2003 relating to bismuth ferrite, BiFeO<sub>3</sub>, and TbMnO<sub>3</sub> showed the differing origins of the multiferroic effect. Even at room temperature Bismuth ferrite is both anti-ferromagnetic and ferroelectric and, therefore, is clearly a multiferroic wherein these two order coexist. Studies of TbMnO<sub>3</sub> again showed

coincident ferromagnetic and ferroelectric effects but this time with the ferroelectricity being caused by the magnetism. Fourth, there is a possibility for new devices including 4-state logic systems, new electrical switching technologies, and optical recording and memory devices.

### **3.2.3 Classification of Multiferroic Materials**

The two major categories of multiferroic materials are proper (or Type I) and improper (or Type II) ones. The difference in nomenclature relates to the origin of the ferroelectric effect in the material. Before going in to further detail regarding the classification, it is worthwhile to explore the apparent contradiction in having coincident ferroelectric and ferromagnetic orders. Most ferroelectrics are transition metal oxides with the transition metal having an empty d shell. Covalent bonding is formed between the negatively-charged oxygen ions and the anions and cations inside the periodic crystal. The ionic shift from the centrosymmetric position accounts for the polarization effect. Magnetism, on the other hand, requires a partially filled d shell as a source for the net spin effect in order to produce a magnetic moment. In general terms, ferroelectricity and ferromagnetism should therefore be mutually exclusive [29]. However, as discussed previously, these coincident orders have been found experimentally suggesting that a deeper explanation is needed for the source of coincident ordering in a multiferroic. The two categories of Type I (proper) and Type II (improper) address this need.

Type I multiferroics are generally good ferroelectrics but the coupling between magnetism and ferroelectricity is weak. An example of this is the perovskite structure bismuth ferrite, BiFeO<sub>3</sub>, referred to previously. In this structure, Fe<sup>3+</sup> has 5 3*d* electrons which account for the magnetism. The Bi<sup>3+</sup> ion has two electrons on the 6*s* orbital which

form a lone pair that moves away from the centrosymmetric position in its surrounding oxygen. This accounts for the ferroelectricity. The fact that these orders arise from two separate and distinct ions accounts for the resultant weak coupling between the two effects of ferroelectricity and magnetism. This weak coupling has been observed experimentally with  $\varepsilon$  showing only a slight anomaly at  $T_{FM}$ , the ferromagnetic transition temperature [30]. Ferroelectricity arising from charge ordering and geometric tilting are also included in the Type I category.

Type II multiferroics are also referred to as magnetic multiferroics because (i) ferroelectricity exists only in a magnetically ordered state; and (ii) it is caused by either spiral or collinear magnetic structures, with the spiral structure being the most common [19]. In the 1970's, R. Newnham *et al.*, proposed that a non-centrosymmetric magnetic ordering could produce an electric polarization  $\vec{P}$ . The Figure below, from Ref. [27], shows atoms symmetric about 'x' but the spins are not which leads to a net polarization. This effect has been observed in the *RE*-manganites Tb(Dy)MnO<sub>3</sub> and Tb(Dy)Mn<sub>2</sub>O<sub>5</sub>. In



Figure 3.2 Non-centrosymmetric magnetic order produces a net polarization. (Source: Ref. [27]).

TbMnO<sub>3</sub> below  $T_{N1}$ =41 K, the magnetic structure is sinusoidal which results in no net magnetic moment and no ferroelectricity. However, below  $T_{N2}$ =28 K, the Mn spins change to cycloidal order due to magnetic frustration in which competing interactions between spins preclude simple magnetic order [29]. A polarization is produced in this phase as a result of spin-orbit coupling. The polarization is proportional to  $\vec{Q} \times \vec{e}$ , where  $\vec{Q}$  is the wave vector associated with the spiral and  $\vec{e}$  is the spin rotation axis [19]. Upon application of an external magnetic field in Tb(Dy)Mn<sub>2</sub>O<sub>5</sub>, the polarization vector was seen to rotate by 90° [31]. The second group of Type II multiferroics is characterized by ferroelectricity being induced due to collinear magnetic ordering. Polarization appears in these materials as a result of exchange striction because the magnetic coupling varies with atomic positions. An example of this multiferroic is Ca<sub>3</sub>CoMnO<sub>6</sub> which consists of one dimensional chains of alternating Co<sup>2+</sup> and Mn<sup>4+</sup> ions. At high temperatures, the distances between the ions are the same but at low temperatures, there is asymmetry in magnetic order which causes a distortion in the bonds. As a result, the material becomes ferroelectric [19].

# **3.2.4 Magneto-Electric Effect and Symmetry**

The inclusion of the magneto-electric effect into tensors  $\rho$  and  $\rho'$ , force a decision about how to construct the constitutive relations for the complex material. There are two choices of basis vectors to use:  $(\vec{E}, \vec{H})$  and  $(\vec{E}, \vec{B})$ . For the  $(\vec{E}, \vec{H})$  basis, Dzyaloshinskii obtained the constitutive relations in the following form:

$$D^{\alpha} = \varepsilon^{\alpha\beta} E_{\beta} + \alpha^{\alpha\beta} H_{\beta}$$

$$B^{\alpha} = \alpha^{\beta\alpha} E_{\beta} + \mu^{\alpha\beta} H_{\beta}$$
(3.1)

Note that in Eq. (3.1) we use a new notation,  $\hat{\alpha}$  tensor, for the pure magneto-electric effect. As we will explain in the following, the  $\hat{\alpha}$  tensor is an additive component of the more general  $\rho$  and  $\rho'$  tensors. As explained in O'Dell book [25], the  $(\vec{E}, \vec{H})$  basis has

a number of advantages. For a non magneto-electric material, the constitutive relations can easily be substituted into Maxwell's Equations (see Eq. (2.50)). The two vectors both share the same boundary condition that their tangential components must be continuous. The Poynting vector is also made up of the cross product of these two vectors.

On the other hand, it has been pointed out that this basis creates some difficulty. In Eq. (3.1),  $\vec{B}$  and  $\vec{E}$  are connected through the magneto-electric tensor. However, Maxwell's equations already connect these two vectors. Similar situation is for  $\vec{D}$  and  $\vec{H}$ . The  $(\vec{E}, \vec{B})$  basis solves this problem. The constitutive relations in this basis are:

$$D^{\alpha} = \varepsilon^{\alpha\beta} E_{\beta} + \beta^{\alpha\beta} B_{\beta}$$

$$H^{\alpha} = \beta^{\beta\alpha} E_{\beta} + \tilde{\mu}^{\alpha\beta} B_{\beta}$$
(3.2)

As explained by O'Dell, it is important to note that these two sets of equations are not simply different ways of writing the same thing. For example,  $\varepsilon^{\alpha\beta}$  is the permittivity tensor measured under conditions of constant  $\vec{H}$  in Eq. (3.1) while it is measured under conditions of constant  $\vec{B}$  in Eq. (3.2). The  $\tilde{\mu}$  tensor has a meaning of  $\hat{\mu}^{-1}$ . This definition requires an elaborate procedure for recovering of the  $\hat{\mu}$  tensor components based on the measured values of the  $\tilde{\mu}$  tensor.

There has been much debate as to which basis to use in discussing the magneto-electric effect and both are in use in present day literature. For the remainder of this Thesis, we have chosen to use the  $(\vec{E}, \vec{H})$  or Dzyaloshinskii basis. This basis is the one used in Berreman's 4×4 matrix formalism which is a powerful tool to analyze wave propagation in complex media. This formalism will be discussed in more detail in the next Chapter.

The tensors  $\rho$  and  $\rho'$  will always refer to the  $(\vec{E}, \vec{H})$  basis. Unless otherwise stated, the  $\alpha$  tensor will also refer to the  $(\vec{E}, \vec{H})$  basis.

Equations describing the magneto-electric effect can be derived from the expression for the free energy F of the system [21]:

$$-F(E,H) = \frac{1}{2}\varepsilon_{0}\varepsilon_{ij}E_{i}E_{j} + \frac{1}{2}\mu_{0}\mu_{ij}H_{i}H_{j} + \alpha_{ij}E_{i}H_{j} + \frac{1}{2}\beta_{ijk}E_{i}H_{j}H_{k} + \frac{1}{2}\gamma_{ijk}H_{i}E_{j}E_{k} + \dots (3.3)$$

In Eq. (3.3),  $\alpha_{ij}$  is the linear magneto-electric coupling tensor, while  $\beta_{ijk}$  and  $\gamma_{ijk}$  are tensors that describe higher order magneto-electric effects. To establish  $P_i(H_j)$  and  $M_i(E_j)$ , differentiation of F with respect to  $E_i$  and  $H_j$  is required:

$$P_{i} = \alpha_{ij}H_{j} + \frac{\beta_{ijk}}{2}H_{j}H_{k} + \dots$$

$$\mu_{0}M_{i} = \alpha_{ji}E_{j} + \frac{\gamma_{ijk}}{2}E_{j}E_{k} + \dots$$
(3.4)

Eerenstein *et al.* [21] point out that, for thermodynamic reasons,  $\alpha_{ij}$  is bounded by the geometric mean of the diagonalized permittivity and permeability tensors:

$$\alpha_{ij}^2 \le \varepsilon_0 \mu_0 \varepsilon_{ii} \mu_{jj} \tag{3.5}$$

 $\alpha_{ij}$  is an asymmetric second ranked tensor that is a function of temperature *T*. It changes sign under space inversion or time reversal, and therefore is invariant under simultaneous space and time inversion. Note that the two  $\alpha$  terms in Eq. (3.1) are the transpose of each other. This relationship is true for the static case ( $\omega = 0$ ) but may not necessarily hold at each frequency  $\omega$  for the dynamic case [32], where more complicated transfers of the spectral weightings of magnons and phonons are involved. O'Dell has shown that ME effect ( $\alpha \neq 0$ ) can exist only in material systems that do not have a center of inversion and no time-inversion symmetry. That means, ME crystals allow a simultaneous presence of magnetization (that destroys time-reversal) and electric polarization (that obviously destroys the center of inversion). The role of symmetry is critical in determining which crystals can display the magneto-electric effect. Crystal symmetry, for example, determines the form of each of the  $\varepsilon, \mu, \alpha, \beta$ , and  $\gamma$  tensors in Eq. (3.3). Neumann's principle states that the symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal. This principle makes a clear connection between the physical properties of a crystal and the material tensor which describes those properties. The point group of a crystal is the group of macroscopic symmetry elements that its structure possesses. A detailed treatment of this subject is found in Ref. [33]. There are 58 magnetic point groups which allow the linear ME effect ( $\alpha \neq 0$ ) [18]. O'Dell presented a simplified and elegant way to analyze the possible forms of the magneto-electric tensor,  $\alpha$ , given knowledge of the form of the electric and magnetic susceptibility tensors. This treatment has been further developed by H. Schmid and J. Rivera in Refs. [34] and [18]. For the purpose of illustration, two of the examples worked through by O'Dell will be presented here. The first deals with the symmetry of the magnetic point group **mm2** which incorporates the three symmetry transformations  $\overline{2}_x$ ,  $\overline{2}_y$  and  $2_z$ . **mm2** will be recognized as the crystal class associated with orthorhombic symmetry [33]. The next Figure illustrates O'Dell's explanation for the form of the electric and magnetic susceptibility tensors that are consistent with the three symmetry transformations:



**Figure 3.3.** Magnetic and electric susceptibility tensors associated with orthorhombic symmetry transformations. (Source:[25]).

In Figure 3.3, the notation is that followed by Nye. The symbol • indicates a tensor element that is allowed by symmetry, while the symbol  $\cdot$  indicates a tensor element that is forbidden. Each • is taken to be independent unless otherwise indicated by a joining line  $\bullet - \bullet$ .  $\bullet - \circ$  indicates elements of equal magnitude but of opposite sign. In Figure 3.3, the first three tensors are associated with each of the three symmetry transformations. The fourth tensor is the only tensor which is consistent with all three. It is well known that all orthorhombic crystals have a tensor of this form. Using symmetry tables, O'Dell further explains that the magneto-electric tensors which are consistent with the three symmetry transformations are:

(.	•	•	(•	•	· )(•	•	. `		(•	•	• )
•	•		•	•	•    •	•	•	$\Rightarrow$	•	•	
	•	.)	(.	•		•	• )		(.	•	.)

**Figure 3.4** Magneto-electric susceptibility tensors associated with orthorhombic symmetry transformations. (Source:[25]).

In Figure 3.4, the fourth tensor on the right is the only tensor that is consistent will all three symmetry transformations. Accordingly, the magneto-electric tensor associated with crystals of orthorhombic symmetry will not be orthorhombic itself but rather will consists of two independent off-diagonal elements.

The second example concerns crystals having hexagonal symmetry which contain all of the symmetry transformations  $\overline{2}_z$  or  $\underline{2}_z$  together with  $3_z$  and  $\overline{3}_z$ . Following an analysis similar to the above, the compatible magneto-electric tensors must be of the form:

(•		•		(•	•	• )		(•	•	• )
		•		0	٠		$\Rightarrow$			
(•	•	• )	and	(.		•)		(.	•	.)

Figure 3.5 Forms of the magneto-electric tensor associated with hexagonal crystal symmetry. (Source: [25]).

In Figure 3.5, in the second tensor on the right, the two upper diagonal elements are equal in magnitude while the two upper off diagonal elements are equal in magnitude but opposite in sign. As can be seen in Figure 3.5, there is no tensor which can simultaneously meet both of these tensor symmetries. Accordingly, the *linear* magneto-electric effect in hexagonal crystals is strictly forbidden by symmetry reasons. This includes the entire class of hexagonal rare earth manganites of the form *RE*MnO<sub>3</sub> (*RE*=Ho-Lu, Y). In these materials, ferroelectricity appears below the lattice transition, which enlarges the unit cell and is induced by a *non-linear* coupling to nonpolar lattice distortions [29]. As further evidence of the non-linear effect for this class of materials, Fiebig *et al.* reported on the spatial maps of coupled antiferromagnetic and ferroelectric domains in YMnO3, obtained by imaging with optical second harmonic generation. The coupling originates from an interaction between magnetic and electric domain walls, which leads to a configuration that is dominated by the ferroelectromagnetic product of the order parameters [35]. This has been referred to as a landmark study in multiferroics

[21]. Finally, as derived by O'Dell, there are three cubic point groups,  $\underline{4}32$ , 43m and  $\underline{m}3m$ , whose magneto-electric tensors are symmetry forbidden.

#### **3.2.5 Further Work in Multiferroics**

The current knowledge of multiferroics and the magneto-electric effect suggests a number of possible avenues for further work. The connection between cycloidal ordering and an induced polarization points to further work in the study of domain walls, magnetic vortices and spin waves (magnons) [19]. Eerenstein *et al.* emphasize the continued importance of developing a clear understanding of magnetic point group symmetries as these are vital to the analysis and prediction of magneto-electric effects [21]. In addition, they suggest the investigation of strain as providing a coupling mechanism for ferroelectric and ferromagnetic effects in a multiferroic. The study of dynamical properties and elementary excitations will also be important. This includes the possibility of electromagnons. Finally, the whole area of artificial multiferroics is a possibility by combining materials in multilayers or in self organized nano structures. This is also suggestive of metamaterials which will be described next.

# 3.3. Metamaterials

#### **3.3.1 Introduction**

In Greek, the term "meta" means "beyond" and, in this sense, metamaterials are artificial materials, which are intended to go beyond the usual electromagnetic properties of materials at the atomic scale. A metamaterial is an artificial crystal in which man-made

structures replace the microscopic atoms of natural materials [6]. A metamaterial has a lattice constant *a* much smaller than  $\lambda$ , the wavelength of incident radiation. As fabrication processes have improved, it is possible for a metamaterial to become almost indistinguishable from a continuous material. One of the unique properties of metamaterials is the simultaneous electric and magnetic response to incident electromagnetic radiation in the near optical region. For natural materials, magnetic coupling in this frequency region is very weak with the result that for all practical purposes  $\mu = 1$ . In contrast, metamaterials can have magnetic resonances at the optical frequencies  $\mu(\omega) \neq 1$ , thus creating a possibility for simultaneously negative  $\varepsilon$  and  $\mu$ . This condition is required for NIR, which is the basis for a large number of interesting electromagnetic effects including left handed behavior, transformational optics, and a variety of non-linear responses [20].

### **3.3.2 Theoretical Development**

The modern era of metamaterials and the study of NIR is usually attributed to the work of Veselago in 1968 [36] who explored the properties of materials with simultaneously negative  $\varepsilon$  and  $\mu$ . It is useful to examine the nature of

$$\mathbf{Re}(n) = 0, \underbrace{\mathbf{IV}}_{n < 0} \xrightarrow{\mathbf{I}}_{n > 0} \underbrace{\mathbf{I}}_{n > 0} \xrightarrow{\mathbf{IV}}_{\mathbf{I}} \varepsilon$$

$$\mathbf{III}_{n < 0} \qquad \mathbf{III}_{\text{Re}(n) = 0, \text{Im}(n) \neq 0}$$

Figure 3.6. Quadrants for analysis of  $\varepsilon$  and  $\mu$ . (Source: Ref. [37]). electromagnetic wave propagation in each of the quadrants in Figure 3.6 [37]. An oscillating electromagnetic wave incident normally on a medium is described with the

exponential  $e^{ikz} = e^{i\left(n\frac{\omega}{c}\right)^2}$  where  $n = \sqrt{\varepsilon\mu}$  with forward propagation in the positive z direction. In quadrant I,  $\varepsilon > 0$  and  $\mu > 0$ , with the result that n is a real number. The wave will propagate in the material in an oscillating fashion. In quadrant II,  $\varepsilon < 0$  and  $\mu > 0$ , with the result that n will be a purely imaginary number causing the exponential to become negative. This describes a decaying or evanescent wave, which will not propagate in the material. In quadrant III,  $\varepsilon < 0$  and  $\mu < 0$ , with the result that n will be real and negative. The wave will still propagate in an oscillatory fashion but with a negative wave vector. This suggests that the phase velocity will be opposite to that of the wave in quadrant II. Finally, in quadrant IV,  $\varepsilon > 0$  and  $\mu < 0$  resulting in the same outcome as for quadrant II. The wave in quadrant IV will decay exponentially and will not propagate in the material. This brief overview points to the fact that in order for NIR to occur, both  $\varepsilon$  and  $\mu$  must be simultaneously negative. In addition, the changes to the wave vector result in interesting propagation properties under the NIR condition.

Veselago used energy arguments to explain that simultaneously negative  $\varepsilon$  and  $\mu$  can only be realized if there is frequency dispersion [36]. In the absence of dispersion with simultaneously negative  $\varepsilon$  and  $\mu$ , energy would be negative as given by:

$$W = \varepsilon E^2 + \mu H^2 \tag{3.6}$$

With dispersion, the energy relation becomes:

$$W = \frac{\partial (\varepsilon \omega)}{\partial \omega} E^2 + \frac{\partial (\mu \omega)}{\partial \omega} H^2$$
(3.7)

When  $\varepsilon$  and  $\mu$  are simultaneously negative, for Eq. (3.7) to be positive, the partial derivatives need to be positive. This necessarily requires that  $\varepsilon$  and  $\mu$  depend on frequency.

### **3.3.3 Materials Development**

It was not until 1999 that Sir John Pendry devised a method by which these conditions could be created artificially using a split ring resonator (SRR) structure [38]. The following year, D. R. Smith and colleagues successfully used this structure to create a composite material in the lab which displayed the predicted negative response functions [39]. Figure 2.5 below illustrates the SRR structure used by D. R. Smith.



Figure 3.7. SRR structure used to create first NIR conditions. (Source, Ref. [39])

In Figure 3.7, two rings of copper, each having a gap, were placed one inside the other. The dimensions were c=.8 mm, d=.2 mm and r=1.5mm. Incident radiation with a time varying magnetic field parallel to the axis of the rings was applied. The induced current created an additional magnetic field parallel to the incident field. The gap in the wires acted as a capacitor thereby setting up an LC circuit which resonated at approximately 4.85 GHz. The concentric placement of the wires allowed for additional capacitance and

ultimately an enhancement of the effect. In the experiment, D. R. Smith *et al.* demonstrated simultaneously negative dielectric permittivity and magnetic permeability. This discovery spawned a great deal of interest and work in creating metamaterials which could demonstrate NIR at higher and higher frequencies. Initially, most of the effort revolved around reducing the size of the SRR structures. However, due to a kinetic inductance effect, the SRR resonance frequency saturates at small sizes and new metamaterial structures were required to reach higher frequencies. Various architectures for metamaterials were developed including paired nano-rods, nano-strips and a fishnet structure which included nano-strips layered on a metallic substrate. The result of this work was that in a short four year period between the beginning of 2004 and the end of 2007, the demonstrated frequencies for NIR went from 10 GHz to 500 THz [40], practically to the visible range. This exponential growth has since leveled off due to a metal's finite plasma frequency, which ultimately imposes a limit on the resonance frequency [20].

With metamaterials, the interesting situation whereby an applied magnetic field may give rise to polarization,  $\vec{P}$ , and an applied electric field may give rise to a magnetization,  $\vec{M}$ , presents some similarities to the magneto-electric effect in multiferroics. For metamaterials, this configuration can be described using Maxwell's equations:

$$D = \varepsilon E + i\xi H$$

$$\vec{B} = -i\xi \vec{E} + \mu \vec{H}$$
(3.8)

In Eq. (3.8),  $\xi$  is the chirality parameter, which is another additive component for the  $\hat{\rho}$ and  $\hat{\rho}'$  tensors. It can be shown that the eigenvector solutions for this electromagnetic wave are left and right circularly polarized light [41]. It has been demonstrated that
metamaterials built with helical inclusions show strong circular dichroism. This result is in addition to the numerous other optical effects that metamaterials are responsible for.

#### **3.3.4 Optical Effects**

Two interesting optical effects for metamaterials will now be discussed. Without a doubt, the most interesting observable for a NIR material is the left handed behavior of wave propagation. Instead of radiation being refracted to the right of normal in a material, the wave is refracted left of normal. The wave vector, which becomes negative under NIR conditions, now points upwards. Accordingly, the phase velocity is also in the upward direction. The direction of energy flow, on the other hand, as given by the Poynting vector  $\vec{S}$ , remains directed downwards and into the material. Therefore, under NIR, the phase velocity and group velocity are oppositely directed. In the NIR medium,  $\vec{k}$ ,  $\vec{E}$  and  $\vec{H}$  form a left handed coordinate system.

Another property of materials with  $\mu \neq 1$  is the concept of impedance matching. Here, impedance is defined as  $Z = \sqrt{\frac{\mu}{\varepsilon}}$ . Pursuant to the laws of reflection of a magnetic material, when the impedance of the incident medium matches that of the material all reflection will vanish. In this sense, the material itself will become invisible. For example, if the incident medium is vacuum, then the condition for impedance matching is that  $\varepsilon = \mu$  inside the material. Given that both  $\varepsilon$  and  $\mu$  are complex functions, it is quite difficult to engineer a material where both the real and imaginary parts of each response function will exactly match. However, Grigorenko did see this result experimentally in 2005 [42]. Grigorenko showed that for a thin film on a substrate, under the impedance matching condition, only reflection from the substrate boundary could be observed. More recently, the study of transformation optics has developed which uses a mathematical approach similar to that of general relativity wherein the response functions become functions of  $\vec{r}$ . Using this approach, the condition  $\varepsilon(\vec{r}) = \mu(\vec{r})$  guarantees that the wave impedance is equal to the vacuum impedance which results in the vanishing reflection phenomenon [20].

## **3.4 Summary Comments and Research Direction**

Before we proceed to the next Chapter, we should reconcile Eq. (2.52), Eq. (3.4)(a) and Eq. (3.8). In Eq. (2.50):

$$\begin{pmatrix} \vec{D} \\ \vec{B} \end{pmatrix} = \begin{pmatrix} \hat{\varepsilon} & \hat{\rho} \\ \hat{\rho}' & \hat{\mu} \end{pmatrix} \begin{pmatrix} \vec{E} \\ \vec{H} \end{pmatrix}$$

the  $\hat{\rho}$  and  $\hat{\rho}'$  tensors describe a general effect of the mutual dynamic coupling between electricity and magnetism. We will limit our further consideration to the case of ME and chirality contributions to  $\hat{\rho}$  and  $\hat{\rho}'$  so that these two effects are additive as follows

$$\hat{\rho} = \hat{\alpha} + j \cdot \hat{\xi}$$

$$\hat{\rho}' = \hat{\alpha}' - j \cdot \hat{\xi}^{T}$$
(3.9)

One can see that the ME effect is described by the complex tensor  $\hat{\alpha}$ , as it was presented in Eq. (3.1). According to Dzyaloshinskii, the corresponding ME contribution to  $\hat{\rho}'$ should be a "transpose" complex tensor:  $\hat{\alpha}' = \hat{\alpha}^T$ . This requirement follows from the Dzyaloshinsky's definition of  $\hat{\alpha}$  in the static case:

$$\alpha_{ij} = \frac{\partial^2 F}{\partial E_i \partial H_i} \tag{3.10}$$

At present, however, this requirement of  $\hat{\alpha}' = \hat{\alpha}^T$  is under depate in literature for optical frequencies. So, in the following theoretical analysis we won't implement this restriction keeping a general notation for  $\hat{\rho}$  and  $\hat{\rho}'$  tensors. In any case, both  $\hat{\alpha}$  and  $\hat{\alpha}'$  have the same sign of their complex parts. The physical interpretation for this requirement is that the oscillators in  $\hat{\alpha}$  and  $\hat{\alpha}'$  should absorb light in the transmission experiments. Both tensors,  $\hat{\xi}$  and  $\hat{\alpha}$ , can have both, real and imaginary parts, so  $\hat{\rho}$  and  $\hat{\rho}'$  are NOT expected to be the complex-conjugate-transpose for each other [43].

In contrast to  $\hat{\alpha}$ , the chirality contribution  $i \cdot \hat{\xi}$  has its transpose and complex conjugate counterpart that contributes to  $\hat{\rho}': -i \cdot \hat{\xi}^T$ . For isotropic materials, Georgieva [41] showed that the chirality parameter  $\xi$ , which originated from  $\partial \vec{H}/\partial t$  and  $\partial \vec{E}/\partial t$  terms in the Maxwell equations, is an odd function of  $\omega: \xi \sim \omega$ . In the case of a crystal, it hard to imagine that the chirality effect won't have a resonant behavior. Here we propose to use the following model to describe the dispersion behavior of chirality

$$\xi(\omega) = \omega^2 \cdot \frac{A_{ch}}{\omega_{ch0}^2 - \omega^2 - i\omega\gamma_{ch}}$$
(3.10)

that gives  $\xi(0) \to 0$ ,  $\xi(\infty) \to 0$  and can have both a strong enhancement and even a change of a sign in the vicinity of the resonance when  $\omega \to \omega_{ch0}$ .

In the general case of magneto-electric medium with chirality, the formal description based on Eq. (2.52) can include an endless number of possible combinations between the  $\hat{\varepsilon}(\omega)$ ,  $\hat{\mu}(\omega)$ ,  $\hat{\rho}(\omega)$  and  $\hat{\rho}'(\omega)$  tensors. For simplicity, we will always assume that the same oscillator that appears in several tensors at the same resonant frequency  $\omega_0$  should have the same value of the decay parameter  $\gamma$ . This means that the anisotropy of the dispersive tensor functions  $\hat{\varepsilon}(\omega)$ ,  $\hat{\mu}(\omega)$ ,  $\hat{\rho}(\omega)$  and  $\hat{\rho}'(\omega)$  can be described by the nondispersive tensors of the corresponding oscillator strengths for all excitations. An exact symmetry of the materials system can, of course, further reduce the number of non-zero oscillator strengths that describe  $\hat{\varepsilon}(\omega)$ ,  $\hat{\mu}(\omega)$ ,  $\hat{\rho}(\omega)$  and  $\hat{\rho}'(\omega)$  tensors, so some of those tensors could become equal to  $\hat{1}$  or zero. However, in a real experimental situation, the symmetry is not always known in advance and the goal of the future optical experiments is exactly opposite: we aim to determine the symmetry of the material based on the polarization analysis of the transmitted and reflected light. Thus, the primary focus of this Theses is on analysis of the polarization of the optical spectra for materials with  $\hat{\mu}(\omega) \neq 1$ ,  $\hat{\rho}(\omega) \neq 0$  and  $\hat{\rho}'(\omega) \neq 0$ .

In the following Chapters we will study the following possible situations with certain elementary excitations contributing to the different tensors.

One of them is an "electromagnon" excitation that according to our understanding is an oscillator that appears simultaneously in the  $\hat{\mu}(\omega)$  tensor as a magnon and also contributes to  $\vec{D}$  through its appearance in  $\hat{\alpha}(\omega)$  tensor (the "electro-" part). It is also possible to imagine its counterpart: an electric dipole that contributes to  $\vec{B}$  through its appearance in the  $\hat{\alpha}'(\omega)$  tensor. In the following analysis, we will study the difference between these two types of electromagnons.

Another situation can be realized in a material with a weak ME effect,  $(\hat{\alpha} = 0, \hat{\xi} = 0)$ , but with strongly overlapping electric- and magnetic dipoles in  $\hat{\varepsilon}(\omega)$  and  $\hat{\mu}(\omega)$  tensors that form "hybrid modes". The angular dependence of the MM spectra in metamaterials that is considered in Chapter 8 also belongs to this case of a simultaneous appearance of the elementary excitations (or resonances) in both  $\hat{\varepsilon}(\omega)$  and  $\hat{\mu}(\omega)$  tensors. We observed this case in RE-IG crystals and will present their theoretical and experimental studies in Chapter 9. It is also possible to imagine a combination of a magnon  $[\hat{\mu}(\omega) \neq 1]$  and a chiral excitation  $[\hat{\xi}(\omega) \neq 0]$  at the same frequency. We will call these excitations "chiromagnons". The corresponding spectra are analyzed in Chapter 10.

The last case to be consider in this Thesis is a coexistence of the chiral and ME excitations at the same frequency as a magnon in the  $\hat{\alpha}(\omega)$  tensor and chiral excitation in  $\hat{\xi}$  tensor.

It is obvious that traditional Transmission or Reflectivity measurements won't be able reveal all details for  $\hat{\varepsilon}(\omega)$ ,  $\hat{\mu}(\omega)$ ,  $\hat{\rho}(\omega)$  and  $\hat{\rho}'(\omega)$  tensors. Even the most advanced approach, the Muller Matrix ellipsometry, that measures 16 independent functions of the 4×4 matrix, may not be always helpful due to the entangled contributions of  $\hat{\varepsilon}(\omega)$ ,  $\hat{\mu}(\omega)$ ,  $\hat{\rho}(\omega)$  and  $\hat{\rho}'(\omega)$  tensors to the *observable* optical spectra. In this Thesis, we will calculate the MM spectra and Poynting vectors, at the resonance frequencies and combine these studies with analysis of their angular dependencies. The properties of semi-infinite crystals will be compared to the thin films grown on isotropic substrates.

### **CHAPTER 4**

## **4×4 MATRIX FORMALISM**

## **4.1 Introduction**

The main challenge to the analysis of materials with non-zero  $\varepsilon$ ,  $\mu$ ,  $\rho$  and  $\rho'$ tensors is the vast number of possible tensor symmetries in the bulk crystals and thin films. The task of obtaining analytical solutions for all possible configurations appears daunting. In this thesis, a *simple medium* is defined to have isotropic  $\varepsilon$  and  $\mu$  tensors but no magneto-electric activity. A complex medium will refer to all other possible tensor symmetries and allowed tensor combinations [34]. Fortunately,  $4 \times 4$  matrix formalism, as developed by Berreman[16], provides for an accurate and systematic method of obtaining numerical, and in some cases, analytic solutions for electromagnetic wave propagation in both simple and complex media. A complete description of electromagnetic wave propagation in a complex medium is made possible using Berreman's matrix equation in Eq. (2.52). In this Chapter, we analyze a simple medium in order to illustrate this formalism. In other words, we chose a medium with isotropic  $\varepsilon$ and  $\mu$  tensors that is also non bi-anisotropic ( $\rho = \rho' = 0$ ). 4×4 matrix formalism is used to calculate the complex reflection coefficients and Poynting Vectors in a semi-infinite configuration. We also use the results of  $4 \times 4$  matrix formalism to explain the interesting property of impedance matching at the surface of a magnetic material. The two main references for this Chapter are Ref. [16] and Ref. [17].

## 4.2 The Procedure

The Berreman equation describing electromagnetic wave propagation in a crystal is:

$$\frac{d\psi}{dz} = i\frac{\omega}{c}\tilde{\Delta}\psi,\tag{4.1}$$

where  $\psi$  is a an array of the transverse components of the electromagnetic wave  $[E_x, H_y, E_y, -H_x]^T$  in the medium. Fig. 3.1 illustrates the refraction of light incident in the x-z plane propagating forward in an anisotropic dielectric-magnetic material.



**Figure 4.1** Wave vector diagram of refracted waves propagating in an anisotropic dielectric-magnetic medium.

For a crystal with isotropic symmetry having principal axes parallel to the x, y and z

coordinate axes,  $\tilde{\Delta}$  in Eq. (4.1) is a 4×4 matrix [16]:

$$\tilde{\Delta} = \begin{pmatrix} 0 & \mu - \frac{N_0^2 \sin(\theta_0)^2}{\varepsilon} & 0 & 0 \\ \varepsilon & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu \\ 0 & 0 & \varepsilon - \frac{N_0^2 \sin(\theta_0)^2}{\mu} & 0 \end{pmatrix}$$
(4.2)

Inserting Eq. (4.2) into Eq. (4.1) returns four exact solutions of the form  $\psi_l(z) = \psi_l(0)e^{iq_l z}$  with l = 1, 2, 3 or 4, two for each of the *p* and *s* polarization states.  $\theta_0$  is the angle of incidence while p(s) refers to radiation parallel (perpendicular) to the plane of incidence.  $q_{zp}$  and  $q_{zs}$  are the eigenvalues associated with *p* and *s* polarizations, respectively and constitute the *z* components of the wave vectors in the medium. These are:

$$q_{zp} = \pm \frac{\omega}{c} \sqrt{\varepsilon} \sqrt{\mu} - \frac{N_0^2 \sin^2(\theta_0)}{\varepsilon}$$

$$q_{zs} = \pm \frac{\omega}{c} \sqrt{\mu} \sqrt{\varepsilon} - \frac{N_0^2 \sin^2(\theta_0)}{\mu}$$
(4.3)

The positive eigenvalues are associated with the two forward propagating waves. Fig. 4.1 shows  $q_{zp}$  and  $q_{zs}$  for an anisotropic medium. In the case of an isotropic medium, it is clear from Eq. (4.3) that the *z* components of both polarized waves are identical. The *x* components of the wave vector are also constant for all of the incident and refracted waves. The complete wave vectors for each of the *p* and *s* polarization states can be written as:

$$\vec{k}_{p} = \left( \left( \frac{\omega}{c} \right) N_{0} \sin\left(\theta_{0}\right), 0, \frac{\omega}{c} \sqrt{\varepsilon} \sqrt{\mu - \frac{N_{0}^{2} \sin^{2}\left(\theta_{0}\right)}{\varepsilon}} \right)$$

$$\vec{k}_{s} = \left( \left( \frac{\omega}{c} \right) N_{0} \sin\left(\theta_{0}\right), 0, \frac{\omega}{c} \sqrt{\mu} \sqrt{\varepsilon - \frac{N_{0}^{2} \sin^{2}\left(\theta_{0}\right)}{\mu}} \right)$$

$$(4.4)$$

The two *k* vectors in Eq. (4.4) identify the direction of propagation of the waves associated with each polarization. It is clear that they are identical, which is an important characteristic of an isotropic medium. We note further that characteristic is true for any value of the angle of incidence (AOI). This means that the refracted waves in Fig. 4.1 would be superimposed. On the other hand, as will be shown in detail later, for an anisotropic medium, the two *k* vectors will not be identical and will therefore diverge as they propagate forward (downward) into the medium. This phenomenon is known as birefringence and is evidenced by two separate forward propagating electromagnetic waves. It is through Eq. (4.3) (eigenvalues of the Berreman equation) that information about the optical properties of the medium [17] enters into the calculation of the complex reflection coefficients and, in turn, the Mueller Matrix (MM) elements. (Mueller Matrices will be discussed in detail in the next Chapter.) We note that the  $\varepsilon$  and  $\mu$  tensors are important components of the constitutive relations discussed in Chapter 1.

## 4.3 Eigenvector Solutions and the Reflectance Matrix

Each eigenvalue solution has an associated eigenvector. The eigenvectors are calculated by solving:

$$\left(\frac{\omega}{c}\tilde{\Delta} - qI\right)\Psi(0) = 0 \tag{4.5}$$

$$\begin{pmatrix} 1 & 0 & 1 & 0 \\ \frac{\sqrt{\varepsilon}}{\sqrt{\mu} - \frac{N_0^2 \sin(\theta_0)^2}{\varepsilon}} & 0 & -\frac{\sqrt{\varepsilon}}{\sqrt{\mu} - \frac{N_0^2 \sin(\theta_0)^2}{\varepsilon}} & 0 \\ 0 & 1 & 0 & 1 \\ 0 & \frac{\sqrt{\varepsilon} - \frac{N_0^2 \sin(\theta_0)^2}{\mu}}{\sqrt{\mu}} & 0 & -\frac{\sqrt{\varepsilon} - \frac{N_0^2 \sin(\theta_0)^2}{\mu}}{\sqrt{\mu}} \end{pmatrix}$$
(4.6)

In Eq.(4.6), the eigenvectors in columns 1 and 2 represent forward propagating waves while those in columns three and four represent backward propagating waves. For an isotropic medium there is really no neeed to use separate nomenclature for polarizations. The eigenvectors in columns one and three are associated with the  $q_{zp}$  eigenvalue and represent p polarized radiation. A complete description of this wave involves multiplication by  $e^{\pm iq_{zp}z}$ . Similarly, the eigenvectors in columns two and four are associated with the  $q_{zp}$  eigenvalue and represent s polarized radiation. A complete description of this wave also involves multiplication by  $e^{\pm iq_{zp}z}$ . For a semi-infinite material, the two eigenvectors representing the forward propagating waves are used to calculate the complex reflection coefficients for p and s polarized radiation. The procedure for calculating the complex reflection coefficients involves matching the tangential components of the incident and reflected  $\vec{E}$  and  $\vec{H}$  fields to a linear combination of the two eigenvectors calculated at the common interface located at z = 0[16],[17]. For a semi-infinite medium, only the two forward propagating waves are used in these calculations. Using the two eigenvector solutions for the forward propagating waves taken from Eq.(4.6), two *S* matrices are derived:

$$S_{1} = \cos(\theta_{0}) \begin{pmatrix} \psi_{11} & \psi_{12} \\ \frac{\psi_{41}}{N_{0}} & \frac{\psi_{42}}{N_{0}} \end{pmatrix}^{-1}$$

$$S_{2} = \begin{pmatrix} \frac{\psi_{21}}{N_{0}} & \frac{\psi_{22}}{N_{0}} \\ \psi_{31} & \psi_{32} \end{pmatrix}$$
(4.7)

The Reflectance matrix, or Jones matrix is then calculated as:

$$R = (S_1 + S_2)^{-1} (S_2 - S_1)$$
(4.8)

The complex reflection coefficients for the isotropic case are (note there are no offdiagonal elements):

$$r_{pp} = \frac{\varepsilon k_{z0} - N_0^2 q_{zp}}{\varepsilon k_{z0} + N_0^2 q_{zp}}$$

$$r_{ss} = \frac{\mu k_{z0} - q_{zs}}{\mu k_{z0} + q_{zs}}$$
(4.9)

In Eq. (4.9),  $k_{z0} = \frac{\omega}{c} N_0 \cos(\theta_0)$  and  $N_0$  are the *z* component of the wave vector and index of refraction in the incident medium.  $r_{pp}$  and  $r_{ss}$  are complex numbers for each frequency of light. Multiplication by their complex conjugate is required to produce measureable reflection intensities.

### 4.4 The Poynting Vector

The eigenvectors in Eq. (4.6) can also be used to calculate the Poynting vector for each of the p and s polarized radiation states. This procedure first requires recapture of the zcomponents of the  $\vec{E}$  and  $\vec{H}$  fields which were originally suppressed in the Berreman equations in order to reduce from a  $6\times6$  to a  $4\times4$  formalism. By solving the two algebraic equations associated with the initial Berreman matrices, for isotropic symmetry the solutions for the z components are:

$$E_{z} = -\frac{H_{y}N_{0}\sin(\theta_{0})}{\varepsilon}$$

$$H_{z} = \frac{E_{y}N_{0}\sin(\theta_{0})}{\mu}$$
(4.10)

Eq. (4.10) can be applied to each of the p and s polarization states. Since the terms in

Eq. (4.6) recur frequently in this analysis, we define  $\zeta = \sqrt{\varepsilon - \frac{N_0^2 \sin(\theta_0)^2}{\mu}}$  and

 $\eta = \sqrt{\mu - \frac{N_0^2 \sin(\theta_0)^2}{\varepsilon}}$ . First consider *p* polarization. Here,  $H_z$  becomes zero and the

vector fields are:

$$\vec{E} = E_x \left( 1, 0, \frac{-\sqrt{\varepsilon}N_0 \sin(\theta_0)}{\varepsilon \eta} \right) e^{iq_{zp}z}$$

$$\vec{H} = E_x \left( 0, \frac{\sqrt{\varepsilon}}{\eta}, 0 \right) e^{iq_{zp}z}$$
(4.11)

The fields in Eq. (4.11) now permit the calculation of the Poynting vector,  $\vec{S} = \frac{1}{2} (\vec{E} \times \vec{H}^*)$ applicable to *p* polarization:

$$\vec{S}_{p} = \frac{1}{2} \left| E_{x} \right|^{2} \left( \left| \frac{\sqrt{\varepsilon}}{\eta} \right|^{2} \frac{N_{0} \sin(\theta_{0})}{\varepsilon}, 0, \left( \frac{\sqrt{\varepsilon}}{\eta} \right)^{*} \right)$$
(4.12)

where the asterisks, \*, represents the complex conjugate operation. From Eq. (4.12), the tangent of the Poynting vector angle in the medium is:

$$\tan\left(\theta_{\bar{s}}\right)_{p} = \frac{\sqrt{\varepsilon}N_{0}\sin\left(\theta_{0}\right)}{\varepsilon\eta}$$
(4.13)

From Eq. (4.4), the tangent of the *k* vector angle in the medium is:

$$\tan\left(\theta_{\tilde{k}}\right)_{p} = \frac{N_{0}\sin\left(\theta_{0}\right)}{\sqrt{\varepsilon}\eta}$$
(4.14)

The expressions in Eq. (4.13) and Eq. (4.14) are identical. This analysis points out the well known observation that for a crystal with isotropic symmetry, the direction of the wave vector is identical to that of the energy flow as given by the Poynting vector. For *s* polarization,  $E_z$  is zero and the fields become:

$$\vec{E} = E_y(0,1,0)e^{iq_{zz}z}$$

$$\vec{H} = E_y\left(-\frac{\varsigma}{\sqrt{\mu}}, 0, \frac{N_0 \sin(\theta_0)}{\mu}\right)e^{iq_{zz}z}$$

$$(4.15)$$

and the Poynting vector for *s* polarization is found to be:

$$\vec{S} = \frac{1}{2} \left| E_y \right|^2 \left( \left| \frac{N_0 \sin(\theta_0)}{\mu} \right|^*, 0, \left| \frac{\varsigma}{\sqrt{\mu}} \right|^* \right)$$
(4.16)

From Eq. (4.16), the tangent of the Poynting vector angle for s polarization is:

$$\tan\left(\theta_{\bar{s}}\right)_{s} = \frac{\sqrt{\mu}N_{0}\sin\left(\theta_{0}\right)}{\mu\varsigma}$$
(4.17)

and from Eq. (4.4), the tangent of the k vector angle for s polarization is calculated to be:

$$\tan\left(\theta_{\bar{k}}\right)_{s} = \frac{N_{0}\sin\left(\theta_{0}\right)}{\sqrt{\mu_{\varsigma}}}$$

$$(4.18)$$

Again, the expressions in Eq. (4.17) and Eq. (4.18) are identical. Accordingly, for the *s* polarized state, the direction of wave propagation in the crystal and the direction of energy flow are coincident. Furthermore, since  $\sqrt{\mu\varsigma} = \sqrt{\epsilon\eta}$ , all four wave vectors and Poynting Vectors will be coincident.

#### 4.5 Impedance Matching

Complex reflection coefficients stated in this formalism have been used in the study of media with indefinite permittivity and permeability tensors [44]. These results, obtained from  $4 \times 4$  matrix formalism, also allow for the immediate analysis of the intriguing property of impedance matching. From Eq. (4.9), at normal incidence,  $r_{pp}$  is zero when  $N_0 = \sqrt{\varepsilon/\mu}$ . A similar result can be obtained for the *s* polarization. These relationships are known as the impedance matching condition. It provides the condition for zero reflection at normal incidence even though the indices of refraction of the incident medium  $(N_0)$  and the index of refraction of the material ( $\sqrt{\varepsilon\mu}$ ) are completely different. With incidence from vacuum, this condition is satisfied if  $\varepsilon = \mu$ . Aside from a trivial case for vacuum, when both  $\varepsilon$  and  $\mu$  are unity, this is only possible if the material is magnetic and provides confirmation that the material has magnetic permeability  $\mu \neq 1$ . In practice, it is difficult to achieve impedance matching because both the real and

imaginary parts of the dielectric and magnetic tensors must be identical. Evidence of impedance matching in metamaterials was found by Grigorenko *et al.* in 2005 [42]. Application of the Berreman's method to bi-anisotropic medium will be considered in Chapter 10.

## **CHAPTER 5**

## MATRIX METHODS IN OPTICS

## **5.1 Introduction**

This Chapter will introduce matrix methods in optics. We will focus on the Stokes vector, Jones matrices, Mueller matrices, and the Poincare sphere. The majority of theoretical and analytical background for this Chapter is taken form the following references [46-48]:

## **5.2 The Stokes Polarization Parameters**

The study of the Stokes polarization parameters begins with the introduction of a pair of plane waves that are orthogonal to each other at a point in space.

$$E_{x}(t) = E_{0x}(t)\cos(\omega t - kz + \delta_{x})$$
(5.1)

$$E_{y}(t) = E_{0y}(t)\cos(\omega t - kz + \delta_{y})$$
(5.2)

Taking z=0, defining  $\delta = \delta_y - \delta_x$ , and eliminating  $\omega t$  in the equations, gives the equation for the familiar polarization ellipse:

$$\frac{E_x^2(t)}{E_{0x}^2} + \frac{E_y^2(t)}{E_{0y}^2} - \frac{2E_x(t)E_y(t)}{E_{0x}E_{0y}}\cos(\delta) = \sin^2(\delta)$$
(5.3)

We are interested in representing Eq. (5.3) in terms of *observables* for a field of a monochromatic radiation. This requires that the time dependent terms in Eq. (5.3) be time averaged to produce:

$$\frac{\left\langle E_x^2(t) \right\rangle}{E_{0x}^2} + \frac{\left\langle E_y^2(t) \right\rangle}{E_{0y}^2} - \frac{2\left\langle E_x(t)E_y(t) \right\rangle}{E_{0x}E_{0y}} \cos(\delta) = \sin^2(\delta)$$
where
$$\left\langle E_x(t)E_y(t) \right\rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T E_x(t)E_y(t)dt$$
(5.4)

After integration over the time domain and with some simple algebraic manipulation, Eq. (5.4) yields:

$$\left(E_{0x}^{2} + E_{0y}^{2}\right)^{2} - \left(E_{0x}^{2} - E_{0y}^{2}\right)^{2} - \left(2E_{0x}E_{0y}\cos(\delta)\right)^{2} = \left(2E_{0x}E_{0y}\sin(\delta)\right)^{2}$$
(5.5)

Eq. (5.5) is an important equation and is written in terms of intensities, which are real observables. All of the equations inside the brackets are therefore real and can be measured in optical experiments. In fact, the equations inside the brackets are taken to be the Stokes polarization parameters and are used to form the elements of the Stokes vector representation of light as follows:

$$S = \begin{pmatrix} S_{0} \\ S_{1} \\ S_{2} \\ S_{3} \end{pmatrix} = \begin{pmatrix} E_{0x}^{2} + E_{0y}^{2} \\ E_{0x}^{2} - E_{0y}^{2} \\ 2E_{0x}E_{0y}\cos(\delta) \\ 2E_{0x}E_{0y}\sin(\delta) \end{pmatrix}$$
(5.6)

 $S_0$  is identified with the total intensity of light.  $S_1$  is identified with the amount of that light that is horizontally or vertically polarized.  $S_2$  is identified with the amount of light that is polarized linearly at angles of  $\pm 45^\circ$ .  $S_3$  is identified with the amount of light that is left or right circularly polarized. In discussing circular polarization, we will be using the convention that light is right circularly polarized if it is moving clockwise when looking into the direction of the source of the oncoming light.

With the definitions in Eq. (5.6), Eq. (5.5) can be rewritten more simply as:

$$S_0^2 = S_1^2 + S_2^2 + S_3^2 \tag{5.7}$$

Eq. (5.7) is the identity for completely polarized light. Since unpolarized light has intensity but no net polarization attributes (*i.e.*  $S_1 = S_2 = S_3 = 0$ ), Eq. (5.7) can be stated more generally as the Stokes inequality for any state of polarized and unpolarized light:

$$S_0^2 \ge S_1^2 + S_2^2 + S_3^2 \tag{5.8}$$

Eq. (5.8) shows that the intensity of incident light is at least equal to the intensity of the embedded polarized light and may include unpolarized light as well.

According to Eq. (5.6), a complete description of the polarization of light can be understood in terms of the relative amplitudes and phase difference between the orthogonal elements of light that were first introduced in Eq. (5.1) and Eq. (5.2). The following table gives a useful guide to the description of the more common polarization states of light.

<b>Polarization</b>	<u>Amplitude</u>	<u>Phase</u>	<b>Total Intensity</b>	Stokes Vector
State	Relationship	Relationship		
Linear	$E_{0y} = 0$	n/a	$I_0 = E_{0x}^2$	$\begin{pmatrix} 1 \end{pmatrix}$
Polarized Light				S-I
(LHP)				$ S - I_0   0 $
				$\left( 0\right)$
Linear	$E_{0x} = 0$	n/a	$I_0 = E_{0y}^2$	$\begin{pmatrix} 1 \end{pmatrix}$
Vertically Polorized Light				$\mathbf{S} = \mathbf{I} \begin{bmatrix} -1 \end{bmatrix}$
(LVP)				$S = I_0   0  $
				$\left( 0 \right)$
Linear $+45^{\circ}$	$E_{0x} = E_{0y} = E_0$	$\delta = 0$	$I_0 = 2E_0^2$	(1)
Polarized Light				$\mathbf{S} = \mathbf{I} \begin{bmatrix} 0 \end{bmatrix}$
(L+45)				$S = I_0   1  $
				$\left( 0\right)$
Linear $-45^{\circ}$	$E_{0x} = E_{0y} = E_0$	$\delta = 180^{\circ}$	$I_0 = 2E_0^2$	$\begin{pmatrix} 1 \end{pmatrix}$
Polarized Light				$S = I \begin{bmatrix} 0 \\ 0 \end{bmatrix}$
(L-43)				$ S - I_0  - 1 $
				$\left( 0 \right)$
Right	$E_{0x} = E_{0y} = E_0$	$\delta = 90^{\circ}$	$I_0 = 2E_0^2$	(1)
Circularly Polarized Light				$\mathbf{S} = \mathbf{I} \begin{bmatrix} 0 \end{bmatrix}$
(RCP)				$ S - I_0   0 $
				(1)
Left Circularly	$E_{0x} = E_{0y} = E_0$	$\delta = -90^{\circ}$	$I_0 = 2E_0^2$	$\begin{pmatrix} 1 \end{pmatrix}$
(I CP)				S - I = 0
				0  =  0
				$\left(-1\right)$

 Table 5.1 Stokes vectors of various polarization states of light.

It was stated earlier that in order to produce the Stokes polarization parameters, it was necessary to go through the time averaging integration process. However, the same results can be achieved if we were to focus on real optical amplitudes only. Eq. (5.1) and Eq. (5.2) can be rewritten as:

$$E_{x}(t) = E_{0x}e^{i(\omega t + \delta_{x})} = E_{x}e^{i\omega t}$$

$$E_{y}(t) = E_{0y}e^{i(\omega t + \delta_{y})} = E_{y}e^{i\omega t}$$
(5.9)
where
$$E_{x} = E_{0x}e^{i\delta_{x}}$$

$$E_{y} = E_{0y}e^{i\delta_{y}}$$

The Stokes polarization parameters can now be obtained from:

$$S_{0} = E_{x}E_{x}^{*} + E_{y}E_{y}^{*}$$

$$S_{1} = E_{x}E_{x}^{*} - E_{y}E_{y}^{*}$$

$$S_{2} = E_{x}E_{y}^{*} + E_{y}E_{x}^{*}$$

$$S_{3} = i\left(E_{x}E_{y}^{*} - E_{y}E_{x}^{*}\right)$$
(5.10)

Inserting the identities from Eq. (5.9) into Eq. (5.10) will be shown to give the familiar Stokes polarization parameters.

# 5.3 The Poincare' Sphere

The Poincare' Sphere is a useful visualization of the Stokes polarization parameters. In discussions of the traditional polarization ellipse, the angle of rotation  $\psi$  and the ellipticity angle  $\chi$  of the ellipse are introduced through the following equations:

$$\tan 2\psi = \frac{2E_{0x}E_{0y}\cos\delta}{E_{0x}^2 - E_{0y}^2}$$
(5.11)
$$\sin 2\chi = \frac{2E_{0x}E_{0y}\sin\delta}{E_{0x}^2 + E_{0y}^2}$$

terms of  $S_0, \psi, \chi$  as follows:

$$S = S_0 \begin{pmatrix} 1 \\ \cos 2\chi \cos 2\psi \\ \cos 2\chi \sin 2\psi \\ \sin 2\psi \end{pmatrix}$$
(5.12)

Eq. (5.12) looks very similar to the construct of a sphere in Cartesian coordinates where:

$$x = r \sin \theta \cos \phi$$
  

$$y = r \sin \theta \sin \phi$$
  

$$z = r \cos \theta$$
  
(5.13)

In fact, Eq. (5.12) can be described in spherical terms by assigning  $\theta = 90^{0} - 2\chi$  and  $\phi = 2\psi$ . The Poincare' sphere can now be represented by the following diagram:



Figure 5.1 The Poincare' Sphere

In interpreting positions on the Poincare' sphere, it can be seen that the vector along  $S_1$  will represent light that is horizontally polarized. Similarly, the vector along  $S_2$  will represent light that is polarized at a +45<sup>o</sup> angle, and a vector along  $S_3$  will represent light that is completely right circularly polarized. Other points on the surface of the sphere would represent combinations of various polarization states. Opposite points on the sphere represent orthogonal states.

#### **5.4 Mueller Matrices**

Mueller matrices are useful to describe the interaction of polarized light with elements that can change the state of the incident polarization. Specifically, if S' describes the state of an emergent beam of light, it can be expressed as a linear combination of the previous basis  $S_0, S_1, S_2$  and  $S_3$  of the incident beam. In terms of matrix algebra, this new vector can be written as:

$$\begin{pmatrix} S_{0}^{'} \\ S_{1}^{'} \\ S_{2}^{'} \\ S_{3}^{'} \end{pmatrix} = \begin{pmatrix} m_{11} & m_{12} & m_{13} & m_{14} \\ m_{21} & m_{22} & m_{23} & m_{24} \\ m_{31} & m_{32} & m_{33} & m_{34} \\ m_{41} & m_{42} & m_{43} & m_{44} \end{pmatrix} \begin{pmatrix} S_{0} \\ S_{1} \\ S_{2} \\ S_{3} \end{pmatrix}$$
(5.14)

#### **5.4.1** The Mueller Matrix of a Polarizer

Consider components of an incident beam  $E_x$  and  $E_y$ . Once the beam emerges from a polarizer, its new components are  $E'_x$  and  $E'_y$  which are both parallel to the original axes. With  $0 \le p_x$ ,  $p_y \le 1$ , the fields can be represented as:

$$E'_{x} = p_{x}E_{x}$$

$$(5.15)$$

$$E'_{y} = p_{y}E_{y}$$

Using Eq. (5.10) to describe both S and S', it can be shown that:

$$\begin{pmatrix} S_{0}^{'} \\ S_{1}^{'} \\ S_{2}^{'} \\ S_{3}^{'} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} p_{x}^{2} + p_{y}^{2} & p_{x}^{2} - p_{y}^{2} & 0 & 0 \\ p_{x}^{2} - p_{y}^{2} & p_{x}^{2} + p_{y}^{2} & 0 & 0 \\ 0 & 0 & 2p_{x}p_{y} & 0 \\ 0 & 0 & 0 & 2p_{x}p_{y} \end{pmatrix} \begin{pmatrix} S_{0} \\ S_{1} \\ S_{2} \\ S_{3} \end{pmatrix}$$
(5.16)

For the case of an ideal horizontal polarizer, we have  $p_x = 1$  and  $p_y = 0$ . Accordingly, the Mueller matrix becomes:

Similarly, for the case of an ideal vertical polarizer, we have  $p_x = 0$  and  $p_y = 1$  to produce the Mueller matrix for an ideal vertical polarizer:

# 5.4.2 The Mueller Matrix of a Retarder

Retarders introduce a phase shift between the orthogonal elements of the incident field. Consider  $E'_x(z,t) = e^{+i\phi/2}E_x(z,t)$  and  $E'_y(z,t) = e^{-i\phi/2}E_y(z,t)$  so that a phase shift of  $\phi$  is introduced between the orthogonal components. Again using Eq. (5.10), it can be shown that:

$$S_{0}^{'} = S_{0}$$

$$S_{1}^{'} = S_{1}$$

$$S_{2}^{'} = S_{2} \cos \phi + S_{3} \sin \phi$$

$$S_{3}^{'} = -S_{2} \sin \phi + S_{3} \cos \phi$$
(5.19)

Accordingly, the matrix representation for a retarder can be written as:

$$\begin{pmatrix} S_{0}^{'} \\ S_{1}^{'} \\ S_{2}^{'} \\ S_{3}^{'} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \cos\phi & \sin\phi \\ 0 & 0 & -\sin\phi & \cos\phi \end{pmatrix} \begin{pmatrix} S_{0} \\ S_{1} \\ S_{2} \\ S_{3} \end{pmatrix}$$
(5.20)

The Mueller matrix for a quarter wave retarder ( $\phi = 90^{\circ}$ ) from Eq. (5.20) is easily seen to be:

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$$
(5.21)

From mechanics, we understand that for a rotated coordinate system  $E'_x = E_x \cos\theta + E_y \sin\theta$  and  $E'_y = -E_x \sin\theta + E_y \cos\theta$ . Once again, using Eq.(5.10), the

Mueller matrix for a rotator can be derived as:

$$M(2\theta) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos 2\theta & \sin 2\theta & 0 \\ 0 & -\sin 2\theta & \cos 2\theta & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$
(5.22)

The following are Mueller matrices for some ideal common optical elements:

$\frac{1}{2}$	$\begin{pmatrix} 1\\1\\0\\0 \end{pmatrix}$	1 1 0	0 0 0	°)	Linear polarizer (Horizontal Transmission)	$\begin{pmatrix} 1\\0\\0\\0\\0 \end{pmatrix}$	0 1 0 0	0 0 0 1	$\begin{pmatrix} 0 \\ 0 \\ -1 \\ 0 \end{pmatrix}$	Quarter wave plate (fast-axis vertical)
$\frac{1}{2}$	$\begin{pmatrix} 1\\ -1\\ 0\\ 0 \end{pmatrix}$		-1 1 0	00000	0 0 0 0 0	$\begin{pmatrix} 1\\0\\0\\0\\0 \end{pmatrix}$	0 1 0 0	0 0 0 -1	0 0 1 0)	Quarter wave plate (fast-ævis horizontal)
$\frac{1}{2}$	$\begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \end{pmatrix}$	0 0 0	1 0 1 0	°)	Linear polarizer (+45° Transmission)	$\begin{pmatrix} 1\\0\\0\\0\\0 \end{pmatrix}$	0 1 0 0	$0 \\ 0 \\ -1 \\ 0$	0 0 0	Half wave plate (fast-axis vertical)
$\frac{1}{2}$	$\begin{pmatrix} 1\\ 0\\ -1\\ 0 \end{pmatrix}$	0 0 0 0		-1 0 1 0	0 0 0 0	$\frac{1}{4} \begin{pmatrix} 1\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\$		0 0 1 0 0 1 0 0	0	Attenuating filter (25% Transmission)

Figure 5.2 Mueller Matrices of Ideal Optical Elements. (Source: [45]).

## 5.5 Polarization Transformations using Mueller Matrices

Virtually any form of polarization can be created using the Mueller matrices applicable to polarizers, retarders and rotators. For example, using only a rotated polarizer and rotated retarder, completely elliptically polarized light can be created having any desired orientation and ellipticity from any incident beam of arbitrary polarization [45]. The Mueller matrix calculus for the transformation of an incident beam with arbitrary Stokes

vector  $\mathbf{S}$  through a rotated ideal linear polarizer and subsequently through an ideal nonrated retarder is given by the following matrix equation:

$$\begin{pmatrix} S_{0} \\ S_{1} \\ S_{2} \\ S_{3} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \cos\phi & \sin\phi \\ 0 & 0 & -\sin\phi & \cos\phi \end{pmatrix} \begin{pmatrix} 1 & \cos 2\theta & \sin 2\theta & 0 \\ \cos 2\theta & \cos^{2} 2\theta & \sin 2\theta \cos 2\theta & 0 \\ \sin 2\theta & \sin 2\theta \cos 2\theta & \sin^{2} 2\theta & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} S_{0} \\ S_{1} \\ S_{2} \\ S_{3} \end{pmatrix} (5.23)$$

The first matrix on the RHS is the MM for an ideal non-rotated retarder and the second matrix on the RHS is that of the MM for a rotated ideal linear polarizer. Working through the matrix algebra produces the following solution for the Stokes vector of the emergent beam:

$$\begin{pmatrix} S_{0}^{'} \\ S_{1}^{'} \\ S_{2}^{'} \\ S_{3}^{'} \end{pmatrix} = \frac{1}{2} \left( S_{0} + S_{1} \cos 2\theta + S_{2} \sin 2\theta \right) \begin{pmatrix} 1 \\ \cos 2\theta \\ \cos \phi \sin 2\theta \\ -\sin \phi \sin 2\theta \end{pmatrix}$$
(5.24)

Eq. (5.24) can be easily identified as being the Stokes vector associated with complete elliptical polarization. By adjusting the rotation angle and phase shift parameters, elliptically polarized light of any orientation and ellipticity can be produced.

## 5.6 Mueller Matrix Formalism for an Ideal Ellipsometer

Ellipsometry is concerned with measuring and analyzing the elliptical polarization of light. In recent years, the practice has focused on the measurement of the complex index of refraction as well as the measurement of the thickness of thin films [45]. In general terms, the set up of an ellipsometer consists of a light source together with a polarization state generator (PSG). Together, these constitute to formulate the incident beam which is sent towards a sample at a certain angle of incidence. The reflected beam then goes

through a polarization state analyzer (PSA) and then onto a detector. The PSG consists of a linear polarizer and retarder. The PSA consists of a linear analyzer with an optional retarder. The Stokes vector and Mueller Matrix formalism for this set up is as follows:

$$\mathbf{S}_{final} = \mathbf{P}_{2}\mathbf{R}_{2}(\theta)\mathbf{M}\mathbf{R}_{1}(\theta)\mathbf{P}_{1}\mathbf{S}_{initial}$$
(5.25)

In Eq. (5.25),  $\mathbf{S}_{initial}$  and  $\mathbf{S}_{final}$  are the initial and final Stokes vectors, respectively.  $\mathbf{P}_1$  and  $\mathbf{R}_1(\theta)$  are the Mueller matrices of the first polarizer and retarder through which the initial beam traverses.  $\mathbf{P}_2$  and  $\mathbf{R}_2(\theta)$  are the Mueller matrices of the second polarizer and retarder through which the reflected beam traverses.  $\mathbf{M}$  is the Mueller matrix of the sample itself. It is this quantity that needs to be determined. From the construction of this Mueller matrix, the electro-optical and magneto-optical properties of the sample can be deduced.

Ellipsometry seeks to relate the amplitude and phase of an incident and reflected beam[45]. A complex relative amplitude attenuation factor is defined as:

$$\tilde{\rho} = \frac{r_{pp}}{r_{ss}} = \left(\frac{\mathbf{R}_{\mathbf{p}} / \mathbf{E}_{\mathbf{p}}}{\mathbf{R}_{\mathbf{s}} / \mathbf{E}_{\mathbf{s}}}\right) e^{i(\beta - \alpha)} = \tan \psi e^{i\Delta}$$
(5.26)

In Eq. (5.26), **R** refers to the reflected beam and **E** refers to the incident beam. The subscripts p and s refer to parallel and perpendicular polarizations, respectively. The term  $\tan \psi$  refers to the change in amplitude ratio and the term containing  $\Delta$  refers to the change in phase. Equation (5.26) can be related to the optical constants  $(n, \kappa)$  and thickness (d) of the sample in the following equation:

$$\tilde{\rho} = \tan \psi e^{i\Delta} = f(n, \kappa, d) \tag{5.27}$$

Eq. (5.27) is known as the *fundamental equation of ellipsometry*.

Consider an incident beam  $\mathbf{S} = \mathbf{R}_1(\theta)\mathbf{P}_1\mathbf{S}_{initial}$ . That is, this is a beam incident upon the sample material after having been transformed by the PSG in the ellipsometer. Using the Stokes vector formalism of Eq. (5.10), the components of this incident beam can be derived from:

$$\mathbf{S}_{0}^{'} = \mathbf{E}_{s}\mathbf{E}_{s}^{*} + \mathbf{E}_{p}\mathbf{E}_{p}^{*}$$

$$\mathbf{S}_{1}^{'} = \mathbf{E}_{s}\mathbf{E}_{s}^{*} - \mathbf{E}_{p}\mathbf{E}_{p}^{*}$$

$$\mathbf{S}_{2}^{'} = \mathbf{E}_{s}\mathbf{E}_{p}^{*} + \mathbf{E}_{p}\mathbf{E}_{s}^{*}$$

$$\mathbf{S}_{3}^{'} = i(\mathbf{E}_{s}\mathbf{E}_{p}^{*} - \mathbf{E}_{p}\mathbf{E}_{s}^{*})$$
(5.28)

The Stokes vector for the reflected beam is given as:

$$\mathbf{S}_{0}^{*} = \mathbf{R}_{s}\mathbf{R}_{s}^{*} + \mathbf{R}_{p}\mathbf{R}_{p}^{*}$$

$$\mathbf{S}_{1}^{*} = \mathbf{R}_{s}\mathbf{R}_{s}^{*} - \mathbf{R}_{p}\mathbf{R}_{p}^{*}$$

$$\mathbf{S}_{2}^{*} = \mathbf{R}_{s}\mathbf{R}_{p}^{*} + \mathbf{R}_{p}\mathbf{R}_{s}^{*}$$

$$\mathbf{S}_{3}^{*} = i(\mathbf{R}_{s}\mathbf{R}_{p}^{*} - \mathbf{R}_{p}\mathbf{R}_{s}^{*})$$
(5.29)

Upon the restatement of the **R** factors in Eq. (5.29) in terms of the appropriate reflection coefficients, the Mueller matrix which transforms the incident beam into the reflected beam is given in the following equation [45].

$$\begin{pmatrix} \mathbf{S}_{0}^{*} \\ \mathbf{S}_{1}^{*} \\ \mathbf{S}_{2}^{*} \\ \mathbf{S}_{3}^{*} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} \left( \left| r_{pp} \right|^{2} + \left| r_{ss} \right|^{2} \right) & \left( \left| r_{ss} \right|^{2} - \left| r_{pp} \right|^{2} \right) & 0 & 0 \\ \left( \left| r_{ss} \right|^{2} - \left| r_{pp} \right|^{2} \right) & \left( \left| r_{pp} \right|^{2} + \left| r_{ss} \right|^{2} \right) & 0 & 0 \\ 0 & 0 & r_{ss} r_{pp}^{*} + r_{pp} r_{ss}^{*} & -i \left( r_{ss} r_{pp}^{*} - r_{pp} r_{ss}^{*} \right) \\ 0 & 0 & i \left( r_{ss} r_{pp}^{*} - r_{pp} r_{ss}^{*} \right) & r_{ss} r_{pp}^{*} + r_{pp} r_{ss}^{*} \end{pmatrix} \begin{pmatrix} \mathbf{S}_{0} \\ \mathbf{S}_{1}^{*} \\ \mathbf{S}_{2}^{*} \\ \mathbf{S}_{3}^{*} \end{pmatrix} (5.30)$$

In Eq. (5.30)  $R_p = r_{pp}$  and  $R_s = r_{ss}$  and so on. Using the relationships in Eq. (5.26), this Mueller matrix can also be expressed in terms of the standard ellipsometric parameters  $\psi$ and  $\Delta$ :

$$\begin{pmatrix} \mathbf{S}_{0}^{*} \\ \mathbf{S}_{1}^{*} \\ \mathbf{S}_{2}^{*} \\ \mathbf{S}_{3}^{*} \end{pmatrix} = \frac{r_{s}r_{s}^{*}}{2} \begin{pmatrix} 1 + \tan^{2}\psi & 1 - \tan^{2}\psi & 0 & 0 \\ 1 - \tan^{2}\psi & 1 + \tan^{2}\psi & 0 & 0 \\ 0 & 0 & 2\tan\psi\cos\Delta & 2\tan\psi\sin\Delta \\ 0 & 0 & -2\tan\psi\sin\Delta & 2\tan\psi\cos\Delta \end{pmatrix} \begin{pmatrix} \mathbf{S}_{0}^{*} \\ \mathbf{S}_{1}^{*} \\ \mathbf{S}_{2}^{*} \\ \mathbf{S}_{3}^{*} \end{pmatrix}$$
(5.31)

Eq. (5.31) is applicable for the case where the magnetic permeability  $\mu$  is equal to 1. If the sample were to behave as an ideal polarizer, it is expected that  $\Delta = 0$ . That is, there should be no phase shift for such an optical element. Moreover, if  $\psi = 0$  and there is no  $\mathbf{R}_{p}$  component then no attenuation is expected. With these two constraints, (5.31) reduces to:

It can easily be seen that Eq. (5.32) is identical to Eq. (5.17) which is the Mueller matrix for an ideal linear polarizer. Similarly, if  $\tan^2 \psi = 1$  and  $\Delta = \phi$  then the Mueller matrix in Eq. (5.31) reduces to:

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \cos\phi & \sin\phi \\ 0 & 0 & -\sin\phi & \cos\phi \end{pmatrix}$$
(5.33)

It can easily be seen that Eq. (5.33) is identical to the Mueller matrix in Eq. (5.20) which is that for an ideal compensator or retarder.  $\tan^2 \psi = 1$  confirms there is no attenuation for the retarder.

## 5.7 Mueller Matrix Formalism for Cross Polarizations - r<sub>sp</sub>, r<sub>ps</sub>

In the case cross polarization occurs, s polarizations will be transformed into p polarizations and vice versa. In this instance, the Mueller Matrix in Eq. (5.30) needs to be expanded to include off diagonal terms. The applicable MM that includes these terms is given as [46].

$$\begin{pmatrix} \mathbf{S}_{0}^{*} \\ \mathbf{S}_{1}^{*} \\ \mathbf{S}_{2}^{*} \\ \mathbf{S}_{3}^{*} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} \left( \left| r_{pp} \right|^{2} + \left| r_{ss} \right|^{2} + \left| r_{ps} \right|^{2} \right) & \frac{1}{2} \left( \left| r_{pp} \right|^{2} - \left| r_{ss} \right|^{2} - \left| r_{sp} \right|^{2} + \left| r_{ps} \right|^{2} \right) & \Re \left( r_{pp} r_{sp}^{*} + r_{ss}^{*} r_{ps} \right) & \Im \left( r_{pp} r_{sp}^{*} + r_{ss}^{*} r_{ps} \right) \\ \frac{1}{2} \left( \left| r_{pp} \right|^{2} - \left| r_{ss} \right|^{2} + \left| r_{sp} \right|^{2} - \left| r_{ss} \right|^{2} - \left| r_{ss} \right|^{2} - \left| r_{ss} \right|^{2} - \left| r_{ps} \right|^{2} \right) & \Re \left( r_{pp} r_{sp}^{*} - r_{ss}^{*} r_{ps} \right) & \Im \left( r_{pp} r_{sp}^{*} - r_{ss}^{*} r_{ps} \right) \\ \frac{1}{2} \left( \left| r_{pp} \right|^{2} + \left| r_{ss} \right|^{2} - \left| r_{ps} \right|^{2} \right) & \frac{1}{2} \left( \left| r_{pp} \right|^{2} + \left| r_{ss} \right|^{2} - \left| r_{ps} \right|^{2} \right) & \Re \left( r_{pp} r_{sp}^{*} - r_{ss}^{*} r_{ps} \right) & \Im \left( r_{pp} r_{sp}^{*} - r_{ss}^{*} r_{ps} \right) \\ \frac{\Re \left( r_{pp} r_{ps}^{*} + r_{ss}^{*} r_{sp} \right) & \Re \left( r_{pp} r_{ps}^{*} - r_{ss}^{*} r_{sp} \right) & \Re \left( r_{pp} r_{ss}^{*} + r_{ps}^{*} r_{sp} \right) & \Im \left( r_{pp} r_{ss}^{*} - r_{ps}^{*} r_{sp} \right) \\ -\Im \left( r_{pp} r_{ps}^{*} + r_{ss}^{*} r_{sp} \right) & -\Im \left( r_{pp} r_{ps}^{*} - r_{ss}^{*} r_{sp} \right) & -\Im \left( r_{pp} r_{ps}^{*} - r_{ps}^{*} r_{sp} \right) & \Re \left( r_{pp} r_{ss}^{*} - r_{ps}^{*} r_{sp} \right) \\ (5.34) \end{array}$$

In the case where there are no cross polarization terms, the upper right and lower left quadrants in Eq. (5.34) will have null entries and the format can be seen to be identical to that of the Mueller matrix of the ideal ellipsometer given in Eq. (5.30) with the  $\mathbf{S}_{1}^{'}$  component being defined, in terms of intensities, to be  $I_{p} - I_{s}$ .

#### 5.8 The Jones Vector and Jones Matrices

As discussed section 5.4, Mueller Matrices provide an excellent formalism for the analysis of intensities of incoming and emergent light. When it comes to the analysis of amplitude superposition, it is often better to use the Jones vector and Jones matrix formalisms. The Jones formalism can only be used with polarized light. The Jones column matrix, or the Jones vector, is a column matrix with two components describing

the electric field of each of its orthogonal constituents. The Jones vector for elliptically polarized light is as follows:

$$\mathbf{E} = \begin{pmatrix} E_x \\ E_y \end{pmatrix} = \begin{pmatrix} E_{0x} e^{i\delta_x} \\ E_{0y} e^{i\delta_y} \end{pmatrix}$$
(5.35)

The intensity is defined as  $\mathbf{I} = \mathbf{E}^{\dagger} \mathbf{E}$ , with  $\mathbf{E}^{\dagger}$  representing the conjugate transpose of the Jones vector. Accordingly, the intensity of the Jones vector described in Eq. (5.35) is:

$$\left( E_x^* E_y^* \right) \begin{pmatrix} E_x \\ E_y \end{pmatrix} = E_{0x}^2 + E_{0y}^2 = E_0^2$$
 (5.36)

To obtain a normalization condition we set  $E_0^2$  equal to 1. As in the case of the Stokes vector, various forms of polarization can be described from the amplitude and phase relationships between the orthogonal components of the Jones vector. These are given in the following table:

Polarization State	Amplitude Relationship	Phase Polationship	<b>Total Intensity</b>	Jones Vector	
Linear Horizontally Polarized Light (LHP)	$E_{0y} = 0$	n/a	$I_0 = E_{0x}^2$	$\begin{pmatrix} 1\\ 0 \end{pmatrix}$	
Linear Vertically Polarized Light (LVP)	$E_{0x} = 0$	n/a	$I_0 = E_{0y}^2$	$\begin{pmatrix} 0\\1 \end{pmatrix}$	
Linear +45 <sup>°</sup> Polarized Light (L +45)	$E_{0x} = E_{0y} = E_0$	$\delta = 0$	$I_0 = 2E_0^2$	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$	
Linear -45 <sup>°</sup> Polarized Light (L -45)	$E_{0x} = E_{0y} = E_0$	$\delta = 180^{\circ}$	$I_0 = 2E_0^2$	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$	

Table 5.2 Jones vector description of polarization states. (Source: Ref. [45]).

			· /	
Right	$E_{0x} = E_{0y} = E_0$	$\delta = 90^{\circ}$	$I_0 = 2E_0^2$	1(1)
Circularly			0	$\overline{\sqrt{2}}$
Polarized Light				$\sqrt{2} \left( \pm i \right)$
(RCP)				
Left Circularly	$E_{0x} = E_{0y} = E_0$	$\delta = -90^{\circ}$	$I_0 = 2E_0^2$	1(1)
Polarized Light	0,4 0,9 0		0 0	$\left  \frac{1}{\sqrt{2}} \right $
(LCP)				$\sqrt{2} \left( -l \right)$

Table 5.2 Jones vector description of polarization states. (continued)

A Jones matrix can be defined as the matrix of transforming factors that takes an incident Jones vector into an emergent one,  $\mathbf{E}' = \mathbf{J}\mathbf{E}$ . In matrix algebra, this can be stated as:

$$\begin{pmatrix} E'_{x} \\ E'_{y} \end{pmatrix} = \begin{pmatrix} j_{xx} & j_{xy} \\ j_{yx} & j_{yy} \end{pmatrix} \begin{pmatrix} E_{x} \\ E_{y} \end{pmatrix}$$
(5.37)

For a polarizer, we recall the transformation definitions contained in Eq. (5.15), where  $0 \le p_x, p_y \le 1$ :

$$E'_{x} = p_{x}E_{x}$$
$$E'_{y} = p_{y}E_{y}$$

Accordingly, the Jones vector and Jones matrix representation of (5.15) can be written as:

$$\begin{pmatrix} E'_{x} \\ E'_{y} \end{pmatrix} = \begin{pmatrix} p_{x} & 0 \\ 0 & p_{y} \end{pmatrix} \begin{pmatrix} E_{x} \\ E_{y} \end{pmatrix}$$
(5.38)

An ideal linear horizontal polarizer would have  $p_x = 1$  and  $p_y = 0$  and the Jones matrix

would become  $\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$ . Similarly, an ideal vertical polarizer would have a Jones matrix

of the form 
$$\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$
. The Jones matrix for a retarder is of the form  $\begin{pmatrix} e^{i\phi/2} & 0 \\ 0 & e^{-i\phi/2} \end{pmatrix}$ . For

example, the Jones matrix for a quarter wave retarder would be:

$$\mathbf{J}_{R}\left(\frac{\lambda}{4}\right) = \begin{pmatrix} e^{i(\pi/2)/2} & 0\\ 0 & e^{-i(\pi/2)/2} \end{pmatrix} = e^{i\pi/4} \begin{pmatrix} 1 & 0\\ 0 & -i \end{pmatrix}$$
(5.39)

Equation (5.39) shows that the Jones matrix can be complex. Finally, the Jones matrix for

a rotation is of the form 
$$\begin{pmatrix} \cos\theta & \sin\theta\\ -\sin\theta & \cos\theta \end{pmatrix}$$
.

In the original Chapters we will present results of the Muller matrix calculations. Our numerical approach allows to produce practically any desired characteristics of the bi-anisotropic medium, such as Mueller and Jones matrices, as well as reflectivity and transmittivity.

## **CHAPTER 6**

# FULL MUELLER MATRIX SPECTROSCOPIC ELLIPSOMETRY IN THE FAR INFRARED USING SYNCHROTRON RADIATION

### **6.1 Introduction**

Spectroscopic ellipsometry (SE) uses changes in the polarization state of incident, reflected and transmitted radiation to characterize the properties of materials. The term ellipsometry originates from the observation that most materials cause incident polarizations to become elliptical upon reflection or transmission [45]. The term spectroscopic addresses the fact that many of the excitations in a material are subject to dispersion. The study of polarization changes then requires analysis over a spectral range of incident frequencies which encompass the excitation resonance. SE has a number of advantages for the characterization of materials [4]. Most importantly, it is a nondestructive measurement. This is particularly important in the study of materials, such as multiferroics, which require advanced and time consuming crystal growth techniques. Under these circumstances, it is clearly advantageous for a single sample to be used multiple times. SE is highly precise and is capable of measuring film thickness to approximately 0.01 nm. In addition, SE is an extremely fast measurement tool. In fact, the combination of precision with speed, has made SE an indispensable tool to the semiconductor industry by allowing real time feedback in *insitu* fabrication processes. One disadvantage of SE is that it is an indirect technique, which requires optical models to characterize the response functions of the material.

The output of a SE measurement can be the ellipsometry parameters  $\psi$  and  $\Delta$  and/or a partial or full Mueller Matrix. Recall that the ellipsometry parameters are connected to the Jones matrix components  $r_s$  and  $r_p$  through the equation:

$$\frac{r_p}{r_s} = \tan \psi e^{i\Delta} \tag{6.1}$$

For materials with low crystal symmetry or that display excitations in multiple response functions, the off-diagonal Jones matrix elements can be non-zero. Under these conditions, a proper characterization of the material is often difficult using  $\psi$  and  $\Delta$ only. On the other hand, all 16 elements of the Mueller Matrix (MM) are populated, enabling a more direct connection between SE output and complicated crystal symmetries or response function combinations:

$$\begin{pmatrix} \frac{1}{2} \left( \left| r_{pp} \right|^{2} + \left| r_{ss} \right|^{2} + \left| r_{sp} \right|^{2} + \left| r_{ps} \right|^{2} \right) & \frac{1}{2} \left( \left| r_{pp} \right|^{2} - \left| r_{ss} \right|^{2} - \left| r_{sp} \right|^{2} + \left| r_{ps} \right|^{2} \right) & \Re \left( r_{pp} r_{sp}^{*} + r_{ss}^{*} r_{ps} \right) \\ \frac{1}{2} \left( \left| r_{pp} \right|^{2} - \left| r_{ss} \right|^{2} + \left| r_{sp} \right|^{2} - \left| r_{ps} \right|^{2} \right) & \frac{1}{2} \left( \left| r_{pp} \right|^{2} + \left| r_{ss} \right|^{2} - \left| r_{ps} \right|^{2} \right) & \Re \left( r_{pp} r_{sp}^{*} - r_{ss}^{*} r_{ps} \right) \\ \Re \left( r_{pp} r_{ps}^{*} + r_{ss}^{*} r_{sp} \right) & \Re \left( r_{pp} r_{ps}^{*} - r_{ss}^{*} r_{sp} \right) & \Re \left( r_{pp} r_{ss}^{*} + r_{ps}^{*} r_{sp} \right) & \Im \left( r_{pp} r_{ss}^{*} - r_{ps}^{*} r_{sp} \right) \\ -\Im \left( r_{pp} r_{ps}^{*} + r_{ss}^{*} r_{sp} \right) & -\Im \left( r_{pp} r_{ps}^{*} - r_{ss}^{*} r_{sp} \right) & -\Im \left( r_{pp} r_{ss}^{*} + r_{ps}^{*} r_{sp} \right) & \Re \left( r_{pp} r_{ss}^{*} - r_{ps}^{*} r_{sp} \right) \\ (6.2) \end{array}$$

Eq. (6.2) points to the need for developing an experimental setup which can measure all elements of the Mueller Matrix. In this chapter, the set up for a full Mueller Matrix spectroscopic ellipsometer using far infrared synchrotron radiation is discussed.

# **6.2 Experimental Setup**

# **6.2.1 Theory of Operations**

As discussed in the previous chapter, Mueller Matrices are generated through various combinations of optical elements in the polarization state generator (PSG) and polarization state analyzer (PSA) stages of an ellipsometer. Figure 6.1 illustrates how these combinations influence the MM [4, 45, 47].



Figure 6.1 Relationship between PSG and PSA components and MM elements. (Source: [4]).

As indicate in Figure 6.1, in order to generate all 16 elements of the MM, both the PSG and PSA stages of the ellipsometer must contain polarizer and rotating compensator elements. These elements are illustrated in Figure 6.2.


**Figure 6.2** Schematics of a full MM ellipsometer with rotating polarizers and retarders in the PSG and PSA sections.

Figure 6.2 is the illustration for a full MM ellipsometer recently completed at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). Light captured from the synchrotron source is directed through an interferometer and then onto the PSG which consists of a rotating polarizer and compensator combination. This produces incident light of known polarization as indicated by the full Stokes vector,  $S_{IN}$ . This incident light is then directed at an oblique angle of incidence,  $\theta$ , onto a sample housed in a cryostat. In SE experiments,  $\theta$  is often chosen to be near the Brewster angle of the material in order to maximize amplitude and phase differences between p and s polarization states. Upon emerging from the cryostat, the reflected light now has a different polarization to that of the incident beam. It enters the PSA section of the ellipsometer which also consists of a combination of rotating analyzers and retarders. Light emerging from the PSA stage can also be identified with a full Stokes vector,  $S_{oUT}$ . The exiting light is directed to a bolometer which detects the intensity of the reflected light. Recall that this intensity is also the  $S_0$  component of  $S_{oUT}$ . For both the PSG and

PSA sections of the ellipsometer, given the possibility for losses and dispersion, the optical elements must be designed specifically for efficient operation in the far infrared. Isolation of the MM for the sample,  $\hat{M}_{SAMPLE}$ , is achieved using the matrix methods outlined in the previous chapter. Applying matrix multiplication, in order, gives:

$$I = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}^{T} \hat{M}_{PSA} \hat{M}_{sample} \hat{M}_{PSG} \vec{S}_{incident};$$
(6.3)

In Eq. (6.3), *I* is the intensity measurement obtained in the bolometer.  $\hat{M}_{PSG}\vec{S}_{incident}$  form a 4×1 vector defined as  $\sigma^{j}$ . This column vector is seen to represent one particular configuration of the PSG. The product of  $\begin{bmatrix} 1\\0\\0\\0\end{bmatrix}^{T}$   $\hat{M}_{PSA}$  produces a 1×4 vector defined as  $\tilde{\alpha}_{i}$ .

Similarly, this row vector is seen to represent one particular configuration of the PSA. If 16 separate intensity measurements ( $I_{i,j}$ , i, j = 1, 2, 3, 4) are taken from 4 independent combinations of  $\sigma^{j}$  and  $\alpha^{i}$ , then the following matrix equation is produced:

$$I_{ij} = \tilde{\alpha}_i \hat{M}_{SAMPLE} \sigma^j \tag{6.4}$$

In Eq. (6.4), the  $\tilde{\alpha}$  matrix is composed of the row vectors constituting the four independent PSA measurements while the  $\sigma$  matrix is comprised of column vectors representing the four independent PSG measurements.  $\hat{M}_{SAMPLE}$  is recovered through inversion of Eq. (6.4):

$$\hat{M}_{SAMPLE} = \tilde{\alpha}^{-1} I \sigma^{-1} \tag{6.5}$$

Both  $\tilde{\alpha}$  and  $\sigma$  are matrices of rank 4 which emphasizes the independence of their rows and columns. As can be seen from Eq. (6.5), it is critical that both  $\tilde{\alpha}$  and  $\sigma$  can be inverted. That is,  $\tilde{\alpha}$  and  $\sigma$  cannot be singular. In addition, they must be well conditioned in order for the matrix inversion to be stable. This serves to minimize the amplification of any measurement errors [48]. Essentially the condition number of a matrix is the ratio of the largest and smallest eigenvalues. A condition number close to unity is stable. A condition number of infinity implies that the matrix cannot be inverted. Accordingly, it is essential that PSA and PSG configurations be chosen to meet these criterion.



**Figure 6.3** A schematic (a) and (b) a picture of the far-IR ellipsometer at the NSLS U4IR beam line at BNL.

## 6.2.2. Far Infrared Synchrotron Radiation

The light source used for the far-IR ellipsometer in Figure 6.3 is synchrotron radiation at the U4IR beam line at BNL. Far infrared (FIR) is important for the study of materials, which demonstrate various low energy excitations that belong to frequency ranges of  $10 - 100 \text{ cm}^{-1}$  (magnons, ligand-field excitations, and electromagnons) and 100-700 cm<sup>-1</sup>

(optical phonons). Synchrotron radiation is an excellent source for this purpose not only for its ability to generate FIR but also for its brightness. For example, the brightness of synchrotron radiation at NSLS in the FIR spectral range exceeds that of black body radiation by approximately three orders of magnitude [49]. Synchrotron radiation is the electric field emitted from charged particles in circular accelerators at relativistic velocity. As shown in Figure 6.4, a synchrotron light source is composed of three main elements: a particle source (S) with linear accelerator (A), a synchrotron which accelerates the particles and a storage ring.



Figure 6.4 Schematic of synchrotron facility. (Source: [50])

Since a uniform loop of current will not radiate, "bunches' of charged particles are needed for radiation to occur. After being accelerated in the synchrotron, the bunches are stored in the storage ring where they circulate at constant velocity that is very close to the speed of light. Acceleration in the storage ring is by radial forces only. Radiation emitted in the curved parts of the storage ring is allowed to exit through a tube connected to a diamond window. Facilities such as NSLS-BNL have over 30 such windows were experiments using this light source can occur simultaneously. NSLS-BNL has multiple storage rings, which further increase capacity for x-ray, far-IR, and UV parts of the spectrum. Due to radiation losses, the synchrotron must be recharged at regular intervals with additional bunches of charge. Recharge may be required periodically from half a day to few hours [50]. Relativistic speeds change the nature of radiation as seen by an observer in the laboratory frame. As explained in Ref. [51], the radiation pattern of a charged particle moving at relativistic speeds resembles that of a "searchlight" with radiation is elongated in the direction of motion. This is illustrated in Figure 6.5.



Figure 6.5 Searchlight pattern of emitted radiation from synchrotron light source. (Source: [51])

With each revolution, the intense beam momentarily flashes through the exit windows in short pulses. These pulses comprise a broad range of frequencies. Accordingly, the result of synchrotron radiation is an extremely bright source tunable or simultaneously available over a wide range of frequencies [51]. As summarized in Ref. [50], synchrotron radiation provides the following properties: high emission density from a small spot, small beam divergence, large tunable bandwidth, highly polarized radiation (in the plane of motion) and very short light pulses. The brightness of synchrotron radiation allows for compensation for the reflection and absorption losses in the polarization components and in the cryostat windows. The brightness also allows for the study of relatively small single crystals at oblique angles of incidence.

## **6.2.3 Polarization Components**

The polarization components of the FIR spectroscopic ellipsometer consist of polarizers and retarders. A polarizer is an optical element that selects and allows transmission of one particular state of the light polarization through the use of absorption, refraction or reflection techniques. The ellipsometer in Fig. 6.3 uses two sets of wire-grid polarizers, which consist of arrays of parallel Tungsten wires having diameters of 25 microns. The electromagnetic component vibrating parallel to the wires is both reflected and also causes a current to flow in the wire grid. The component which is perpendicular to the wires is allowed to pass through virtually unimpeded. Accordingly, the light passing through the wire grid polarizer is completely polarized in the perpendicular state. Figure 6.6 is an illustration of a wire grid polarizer.



Figure 6.6 Wire Grid Polarizer, schematic of operation and an actual image.

As demonstrated in Figure 6.6, with the wire grid polarizer, completely unpolarized light emerges completely polarized in the vertical direction.

Retarders are very efficient converters of polarization [52]. It can be shown that light emerging from an ideal linear polarizer could be converted into any form of elliptically polarized light by first going through a non-rotated retarder [45]. Retarders introduce a phase shift between the two orthogonal components of light. It is this phase shift that causes the transformation of polarization.

The design of rotating retarders is not straightforward in the far-infrared region. It is imperative that the relative phase shift between the p and s polarizations be very uniform across all wavelengths in the spectral range. The importance of the retarder for the successful performance of the spectroscopic ellipsometer is directly related to the discussion of matrix conditionality in Section 5.2.1. Since the errors in the measured MM are proportional to the condition numbers of  $\tilde{\alpha}$  and  $\sigma$ , it is imperative that the PSG and PSA incorporate maximum flexibility to create linearly independent Stokes vectors. In other words, it is important that the PSG and PSA stages be capable of covering the entire Poincare sphere. However, it is impossible to cover the entire Poincare sphere with linearly-independent Stokes vectors by only changing the linear polarization at the input surface of a stationary retarder [53]. Accordingly, the retarder must be able to rotate. This requirement causes additional challenges for two reasons. First, when the traditional single triangular prism retarder is rotated, there is a shift in beam direction. Second, in the FIR, the performance of the retarder is determined by the spectral range of the measurements. For example, materials such as KRS-5 can only be used above 400 cm<sup>-1</sup> due to optical phonon absorption. In order to eliminate any beam shift, the retarders have been chosen to be of double Fresnel rhomb design manufactured with Si. Ultra pure Silicon is a good choice for the retarder material. It is relatively easy to fabricate and has a relatively flat real part of the refractive index in the far-IR. The retarder is illustrated in Figure 6.7.



Figure 6.7. Design for a silicon double Fresnel rhomb.

As illustrated in Figure 6.7, the retarder uses 4 bounces. For this retarder with index of refraction of 3.42 and angle of 27°, a relative phase shift of 112.5° is obtained. The four bounces result in a total relative phase shift of 90°. As shown in Figure 4.7, a normal incident beam with linear polarization at 45° with respect to the vertical plane will come out of the retarder with circular polarization in the same direction as the incident beam. This retarder design will allow for an average transmission of approximately 30% in the frequency range between 10 and 450 cm<sup>-1</sup>. The importance of the angle and index of refraction combination is critical to retarder design. Figure 6.8 illustrates this dependence.



**Figure 6.8.** Poincare sphere for a retarder with varying indices of refraction. (Source: [53])

In Figure 6.8, three scenarios for different indices of refraction are calculated for a TOPAS Fresnel rhomb with fixed angle of  $52^{\circ}$ : n=1.4 (magenta), n=1.533 (red), and n=1.7 (blue). The red line indicates the performance of a true TOPAS retarder in the far infrared. For purposes of illustration, a lower index material would "undershoot" the poles while a higher index material would "overshoot" the poles preventing a complete coverage of the Poincare sphere [53].

### **6.2.4 Additional Design Features**

Two additional design features important to the proper characterization of materials will now be discussed. These features address (i) the temperature dependence of crystal symmetry, and (ii) the anisotropic characteristics of materials. First, a cryostat is required to produce the low temperature ranges where electric and magnetic order parameters are found in multiferroic materials. The temperature dependence of phase transitions in materials is an important input to their proper characterization. For example, as described in Ref [29], many of the rare-earth manganites  $RMn_2O_5$ , show four sequential temperature dependent magnetic transitions: incommensurate sinusoidal ordering of Mn spins at  $T_1 = 42 - 45K$ , commensurate antiferromagnetic ordering of Mn spins at  $T_2 = 38 - 41K$ , re-entrance back into the incommensurate state at  $T_3 = 20 - 25K$ , and finally an ordering of rare-earth spins below  $T_4 \leq 10K$ . The spectroscopic ellipsometer illustrated in Figure 4.3, uses an ARS optical closed-cycle cryostat that can produce a temperature range between 4.2 K and 450 K. Second, the physical properties of anisotropic material vary with direction. Accordingly, it is important to be able to rotate anisotropic samples in order to produce independent measurements for the proper

characterization of optical constants. The spectroscopic ellipsometer uses a rotatable sample holder and a variable  $\theta - 2\theta$  configuration of the sample positioning system manufactured by Huber.

### 6.3 Fitting Experimental Results to a Model

The output of the optical measurements taken with the spectroscopic ellipsometer consists either of the MM or other optical spectra: reflectivity, transmission or rotating analyzer ellipsometry (RAE), for example. The output data, in and of itself, tell us nothing about the response functions or other materials properties such as film thickness. In order to isolate these properties, the output data must be fitted against an optical model appropriate to the material under consideration. The data fitting process is illustrated in Figure 6.9.



Figure 6.9 Fitting Model Parameters to Experimental Data.

As described in Figure 6.9, the analysis begins with the MM output data. In the next step, optical models are created, which can include formulas for reflection and transmission, for example. These formulas are supplemented with the dispersion relations that are being used to describe the response functions and their resonances. The third step is a non-linear least squares fitting process whereby an initial parameter vector is chosen for input into the model. For the example in Figure 6.9, there are six parameters which represent, in this case, the Lorentzian dispersion models for each of  $\varepsilon$  and  $\mu$  functions. These six parameters constitute an initial parameter vector defined as X. With this initial parameter vector, a calculation of the total least squares error using the model output and experimental data is undertaken. This least squares error is defined as  $\chi^2$ . A non-linear least squares algorithm is then used to calculate a new parameter vector, which may reduce this value of  $\chi^2$ . The algorithm stops when a certain stopping criterion is reached. The stopping criterion could be when a maximum number of iterations is reached or when  $\chi^2$  ceases to change by a certain amount. The result of the non-linear least squares fitting program is a final parameter vector X which minimizes the fit between the model and the experimental data. The algorithm used most often for non-linear least squares fitting is the Levenberg Marquardt algorithm. This algorithm is described in detail in the following Chapter.

#### **CHAPTER 7**

# **OPTIMIZATION METHODS FOR NON-LINEAR LEAST SQUARES FITTING**

# 7.1 Introduction

This chapter explores optimization techniques used to fit experimental data to a userdefined non-linear model. Key references for this chapter are Ref. [54-58]. Non-linear models are based upon an algorithm containing a number of distinct parameters, each designed to represent an actual physical characteristic of the material being investigated. As an example, Figure 7.1 illustrates the reflectivity spectra of non-magnetic material in a semi-infinite configuration at normal incidence.



Figure 7.1 Reflectivity spectra of material in semi-infinite configuration at normal incidence.

In Figure 7.1, the reflectivity spectra is clearly dominated with the shape of a Lorentzian oscillator at 60 wavenumbers. From optics, we know that the complex reflection coefficient for this configuration is given by:

$$r = \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1},$$
(7.1)

and the intensities in Figure 7.1 are calculated as  $R = r \times r^*$ . In Eq. (7.1),  $\varepsilon(\omega)$  is the complex valued dielectric permittivity. As discussed in previous chapters, this function can be modeled as a Lorentzian oscillator consisting of four independent parameters:

$$\mathcal{E}(\omega) = x_1 + \frac{x_2 * x_3^2}{x_3^2 - \omega^2 - i\omega x_4}$$
(7.2)

In Eq. (7.2),  $x_2$  is the oscillator strength,  $S_e$ ;  $x_3$  is the natural frequency of oscillation,  $\omega_0$ ;  $x_4$  is the damping coefficient; and  $x_1$  is the dielectric permittivity measured far away from the resonant frequency. Accordingly, the reflection intensities that are seen in Figure 5.1 are the result of choosing an appropriate  $\vec{x} = [x_1, x_2, x_3, x_4]$  for input in to Eq. (7.2), which can then be inserted into Eq. (7.1) with this result being multiplied its complex conjugate to produce the necessary reflection intensities at each point in the frequency spectrum. This is clearly a non-linear problem. The factor  $\omega$  representing the frequency of incident radiation is the dependent variable in this problem. In optics, the dependent variable could also be angle of incidence (AOI) or the thickness of a thin film, for example. In general terms, a model can consist of N parameters. Since most fitting techniques involve extensive use of matrix and vector algebra, it is useful to think of the parameters as forming a vector in the N dimensional parameter space: Ν  $\vec{x} = (x_1, x_2, x_3, \dots, x_N)$ .  $\vec{x}$  describes the complete set of parameters. Using vector algebra, we can describe the output of a given model for the i<sup>th</sup> experimental data point in the form:

$$y(\omega_{i}, (x_{1}, x_{2}, x_{3}..., x_{N})) = y(\omega_{i}, \vec{x})$$
 (7.3)

The output of this model is then calculated across the range of a given experimental input variable,  $\omega_i$ , where *i* represents the *i*th data point. For each set of modeled physical parameters and for each independent data point, the model can produce an output value  $y(\omega_i, \vec{x})$  which can be compared to the experimentally observed value,  $y_i$ . A function  $f_i$  is introduced to describe the difference, or residual error, between these two values:  $f_i = y_i - y(\omega_i, \vec{x})$ . This error is illustrated in Figure 7.2 where an arbitrary set of initial parameters  $x_0 = [14, 1, 80, 5]$  is chosen as a possible solution to fit the reflectivity spectra in Figure 7.1.



Figure 7.2 Initial solution  $x_0$  (green) compared against experimental data (blue).

In Figure 7.2, it can clearly be seen that  $x_0$  is not a good fit against the experimental data. For example, the resonance appears at 80 cm<sup>-1</sup> for the trial solution, whereas the resonance in the experimental data occurs at 60 cm<sup>-1</sup>. The goal of this non-linear least squares fitting problem is to find consistently better choices for  $\vec{x}$ , which can ultimately minimize the cumulative error of  $f_i$  across all data points. The nomenclature, 'non-linear least squares fitting', originates from that fact that, in order to avoid the difficulties of its sign, the error function is simply squared and then summed. In other words, the goal of this optimization is to find the set of parameters,  $\vec{x}$ , which minimize the following function:

$$F(\vec{x}) = \chi^{2}(\vec{x}) = \frac{1}{2} \sum_{i=1}^{m} \left( \frac{y_{i} - y(t_{i}, (x_{1}, x_{2}, x_{3} \dots x_{M}))}{\sigma_{i}} \right)^{2} = \frac{1}{2} \sum_{i=1}^{m} \left( f_{i}(\vec{x}) \right)^{2}$$
(7.4)

 $F(\vec{x})$  is known as the objective function. It is also known as the  $\chi^2(\vec{x})$  or Chi-Square functional. It calculates the square of the difference between the actual experimental value at a given data point and its modeled value and then sums these up across all data points.  $\sigma_i$  is the standard deviation of the *i*<sup>th</sup> experimental data point.

For non-linear models, the task of finding a minimum value for the objective function can only be done through iterative techniques. The idea is to start with a certain parameter vector and calculate the value of the objective function. A step is taken in parameter space,  $\vec{h}$ , to produce a new parameter vector,  $\vec{x} + \vec{h}$ , which reduces the value of the objective function. The iteration stops when the objective function ceases to change within a certain level of tolerance. Generally speaking, there are four methods to achieve this minimization: (i) the grid search method; (ii) descent methods; (iii) Gauss Newton methods; and (iv) hybrid methods. Each of these methods will be discussed in this chapter.

#### 7.2 Optimization Methods

#### 7.2.1 Grid Search Method

For an objective function whose parameters are not highly correlated, the grid search technique represents a straightforward way of finding a minimum. The procedure starts with the first parameter and its value is adjusted incrementally until a minimum in  $\chi^2$  is found. The first parameter is then set to this value and the process is repeated for each of the other parameters. An important factor in this method is the choice of step in parameter space. Increments need to be small enough to accurately locate the minimum yet large enough to allow for acceptable calculation time. This approach has the advantage of simplicity. Again, for parameters which are not highly correlated, it allows a minimum to be reached with successive iterations. On the other hand, for parameters which are correlated, the procedure requires not just an iteration of a single parameter but of all correlated parameters. This has the result of increasing exponentially the number of calculations. It also requires some user insight into which of the variables are correlated. For a model with many different parameters, such an insight is often difficult *a priori*. The fallback would be to undertake a grid search where every parameter is iterated against every other parameter. While still conceptually a simple approach, it is computationally inefficient. More efficient methods involve the use of derivatives of the objective function in N dimensional parameter space.

## 7.2.2 Derivatives of the Objective Function

Just as in the case of minimization problems involving a single parameter, the use of derivatives of the objective function is critical to optimization techniques involving multi-dimensional parameters. From Eq. (7.4), it follows that:

$$\frac{\partial F}{\partial x_j}(\vec{x}) = \sum_{i=1}^m f_i(\vec{x}) \frac{\partial f_i}{\partial x_j}(\vec{x})$$
(7.5)

The matrix containing the first partial derivatives of the function components is called the

Jacobian: 
$$(J(\vec{x}))_{ij} = \frac{\partial f_i}{\partial x_j}(\vec{x})$$
. With this definition, Eq. (7.5) can be restated as:

$$F'(\vec{x}) = J(\vec{x})^T f(\vec{x})$$
 (7.6)

Similarly, the matrix of second derivatives which is called the Hessian of  $F(\vec{x})$ . From Eq. (7.5), the Hessian is:

$$\frac{\partial^2 F}{\partial x_j \partial x_k} = \sum_{i=1}^m \left[ \frac{\partial f_i}{\partial x_j} (\vec{x}) \frac{\partial f_i}{\partial x_k} (\vec{x}) + f_i (\vec{x}) \frac{\partial^2 f_i}{\partial x_j \partial x_k} (\vec{x}) \right]$$
(7.7)

Again, using the definition of the Jacobian matrix, Eq. (7.7) can be restated as:

$$F''(\vec{x}) = J(\vec{x})^T J(\vec{x}) + \sum_{i=1}^m f_i(\vec{x}) f''_i(\vec{x})$$
(7.8)

Certain numerical methods use a quadratic model for the objective function near a minimum point and, as described below, the Hessian of the objective function is used to calculate the appropriate step in this region. It can be seen from Eq. (7.8) that the Hessian is composed of two parts, namely, the product of the Jacobian matrices and a second term, which contains a more complicated summation of the residual error function with its second derivatives. The second term presents a challenge to the optimization technique when these second derivatives are not available. However, it is argued in Ref. [55], that ignoring this second term is acceptable in many cases. Certainly, when the second derivative terms are small compared to the first term, the second term can be easily dropped from the analysis. It is also argued that, in practice, the second term

should be small because the second derivatives are multiplied by the residual error function,  $f_i$ . Since this represents a random measurement error its sum should cancel out when summed over all of the data points. Finally, it is argued that the inclusion of the second derivative term can, in fact, be destabilizing in the event that there are a number of outlier points which outweigh compensating points of opposite sign. Accordingly, for the techniques discussed in this chapter, the Hessian from Eq. (7.7) will always be approximated as:

$$\frac{\partial^2 F}{\partial x_j \partial x_k} = \sum_{i=1}^m \frac{\partial f_i}{\partial x_j} (\vec{x}) \frac{\partial f_i}{\partial x_k} (\vec{x}) = J(\vec{x})^T J(\vec{x})$$
(7.9)

### 7.2.3 Descent Methods

The descent method is a general minimization technique which seeks to find a perturbation step in the direction of steepest reduction in the objective function. It is one of the most dependable techniques when the parameter vector is far from the minimum point. It is a highly convergent algorithm. It is also an extremely valuable technique when there is a large number of parameters to be modeled. Consider the variation of the objective function starting from an initial position  $\vec{x}$  and proceeding in the direction of  $\vec{h}$  which reduces the value of the objective function. We assume that  $F(\vec{x})$  can be described in terms of a Taylor series expansion:

$$F(\vec{x} + \vec{\alpha}\vec{h}) \cong F(\vec{x}) + \delta h^T F'(\vec{x})$$
(7.10)

Since  $F(\vec{x} + \delta \vec{h}) < F(\vec{x})$ , we see from Eq. (7.10) that  $\vec{h}$  is in a descent direction if  $h^T F'(\vec{x}) < 0$ . In fact, it can be shown that the direction of steepest descent is in a

direction opposite that of the gradient of the objective function, *i.e.*  $-F'(\vec{x})$ . A step in this direction is the basis of steepest descent or gradient methods in minimization problems. From Eq. (7.6), in terms of the Jacobian, the direction of steepest descent is given by  $-J(\vec{x})^T f(\vec{x})$ . A step in this direction of size  $\vec{\alpha}$  is taken. The scalar  $\delta$  can be determined through various line search techniques.

Obtaining the Jacobian involves calculating the partial derivative of the objective function with respect to each of its parameters for every  $\omega_i$ . If analytical formulas for these partial derivatives are not available then a numerical method to approximate the derivative is used:

$$J\left(\vec{x}\right)_{j} = \frac{\partial \chi^{2}}{\partial x_{j}} = \frac{\chi^{2}\left(x_{j} + \Delta x_{j}\right) - \chi^{2}\left(x_{j}\right)}{\Delta x_{j}}$$
(7.11)

In Eq. (7.11), the  $\Delta x_j$  term is usually provided as a user defined input at the beginning of the optimization routine and is applicable to every parameter. The calculation of the Jacobian involves an iterative procedure. After the partial derivative is calculated for one parameter, that parameter is replaced in  $\vec{x}$  by its original value (ie.  $x_j$ , not  $x_j + \Delta x_j$ ) and the routine goes onto the evaluation of the partial derivative of the next parameter. At the end of the calculation  $J(\vec{x})$  will be a matrix of size (*ndata, mx*) where *ndata* is the number of data points and *mx* is the number of variables to be fitted.

This procedure represents a significant improvement as compared to the grid search method for two major reasons. First, a step in the direction of steepest descent guarantees that  $\vec{x}$  is proceeding in a direction which lowers the value of the objective function. Second, the step is a more direct route towards minimization. All of the parameters are

updated simultaneously. After a given step, the gradient is recalculated and another step is taken in the direction of the new steepest descent. Again, the size of the step is a critical decision in this optimization routine. For example, if the step size is too large, then it is possible to 'overshoot' the location of the minimum. One strategy is to continue travelling along the gradient in small steps until  $\chi^2$  begins to increase at which point the gradient is recomputed and a new direction is sought. A major disadvantage of the descent method is that it becomes an inefficient algorithm near the minimum. The reason for this is due to the fact that at a minimum point,  $J(\vec{x})$  should vanish with the result that steps are almost zero. This is particularly true in the case of local minima which correspond to a long flat valleys in parameter space [54].

While the method of steepest descent is robust, near the minimum point, convergence can become much faster when the objective function can be modeled as a quadratic formula. These techniques will be discussed in the next section.

## 7.2.4 The Gauss Newton Method

In the Gauss Newton method, it is assumed that near a minimum point, the residual error function  $f(\vec{x})$  can be based on a linear approximation in the neighborhood of  $\vec{x}$  in the form of:

$$f(\vec{x} + \vec{h}) \cong f(\vec{x}) + J(\vec{x})\vec{h} \tag{7.12}$$

Inserting this expression into Eq. (7.4) provides an expansion for  $F(\vec{x})$  given by:

$$F(\vec{x} + \vec{h}) = \frac{1}{2}f^{T}f + h^{T}J^{T}f + \frac{1}{2}h^{T}J^{T}Jh$$
(7.13)

In Eq. (7.13), it can be seen that the approximation for the objective function now contains as a quadratic term as its third term. At a minimum point, the derivative of Eq. (7.13) with respect to  $\vec{h}$  must be zero and the Gauss Newton step,  $h_{en}$  is given by:

$$(J^T J)h_{gn} = -J^T f (7.14)$$

In Eq. (7.14), the term  $J^T J$  is the approximation for the Hessian of  $\chi^2$  which was discussed in Section 7.2.2.  $h_{gn}$ , the Gauss Newton step, is obtained through matrix inversion methods. This method is also sometimes called the Inverse Hessian method. The advantage of this method is that if  $f(\vec{x})$  does behave in linear fashion, then this method has a quick and accurate convergence to a minimum point. The approximation that  $\chi^2$  behaves in a parabolic manner around the minimum does introduce errors into the calculation but these errors are reduced through successive iterations in the routine. A clear advantage of the Gauss Newton method is that the step size is automatically calculated in the routine.

In summary, when no strong assumptions can be made about the behavior of the objective function, then the descent methods are most appropriate. These methods will guarantee a step in a direction which reduces the value of the objective function. On the other hand, when a quadratic model can be assumed for the objective function, then a step derived from the Gauss Newton formula sets up a quick convergence to a minimum point. Hybrid methods have been developed to utilize the best of both methods. The Levenberg Marquardt method is one of the most powerful of these hybrid methods.

## 7.2.5 Hybrid Methods

As stated above, while the Gauss Newton method provides for rapid convergence near a minimum where a quadratic model represents a good approximation of the objective function, it cannot be relied on to approach this minimum from a point outside the region. Similarly, while the descent method is excellent at approaching a minimum point from far away, it is a poor technique for convergence near the minimum. Hybrid methods combine aspects of both the descent and Gauss Newton methods. The Levenberg Marquardt optimization technique is the best known among the hybrid methods. The Levenberg Marquardt ("LM") method is powerful because it combines both of the above minimization strategies through a self adjusting algorithm described in the following equation:

$$(J^T J + \lambda I)h_{lm} = -J^T f \tag{7.15}$$

In Eq. (7.15), I is the identity matrix. The LM algorithm works as follows. If a step in a given direction does not reduce the value of  $\chi^2$ , then  $\lambda$  is increased. For large values of  $\lambda$ , Eq. (7.15) reduces to:

$$h_{lm} \cong -\frac{1}{\lambda} F'(x), \qquad (7.16)$$

which represents a small step in the steepest descent direction. If a step results in a reduction in the value of  $\chi^2$ , then  $\lambda$  is decreased. For small values of  $\lambda$ , Eq.(7.15) reduces to:

$$(J^T J)h_{bm} \cong -J^T f, \tag{7.17}$$

which is immediately recognizable from Eq. (7.14) as the step calculated in the Gauss Newton method. The LM method proceeds iteratively, updating the step  $\vec{h}$  upon each iteration. The algorithm concludes when user defined stopping criteria are met. These stopping criteria could be a maximum number of iterations or the difference of successive  $\chi^2$  being less than a certain amount.

It is important to note that there is no non-linear least squares fitting algorithm, which guarantees finding a global minimum. Therefore, while the LM technique will converge to a minimum point, this point may not be the global minimum. That is, the LM technique could find a local minimum and conclude at that point when the stopping criteria are met. In this context, the initial choice of the parameter vector is important in finding a global minimum. In addition, given its prominence in all of the above formulas, the calculation of the Jacobian function is critical to the efficient performance of the LM algorithm. It is best if analytical expressions can be found for the Jacobian function. In the absence of such analytical formulas, the Jacobian will need to be calculated from a finite difference method in a user supplied function. With an efficiently designed LM algorithm, a large number of parameters can be fitted in a short time. In addition, the LM algorithm can be easily adapted to fit a number of different data sets against the same model. In this case, Eq. (7.4) becomes:

$$F(\vec{x}) = \chi^{2}(\vec{x}) = \frac{1}{2} \sum_{l=1}^{d} \sum_{i=1}^{m} \left( \frac{y_{il} - y_{l}(t_{i}, (x_{1}, x_{2}, x_{3} \dots x_{M}))}{\sigma_{il}} \right)^{2}$$
(7.18)

In Eq. (7.18), the index l provides for a summation over the number of data sets d.

## 7.3 Simulation Using the Levenberg Marquardt Algorithm

The Levenberg Marquardt technique was used to find the best fit parameters for the reflectivity example given in Section 6.1. The simulation uses 100 data points for frequency between 0 and 100 wavenumbers. The LM technique converged in 22 iterations with an elapsed time of 0.2830 seconds. The results for each iteration in the LM routine are given in Table 7.1.

Iteration	$x_1$	$x_2$	<i>x</i> <sub>3</sub>	$X_4$	λ	$\chi^2$
0	14.00	1.00	80.00	5.00	.001	0.7558
1	17.98	0.37	81.74	6.43	.0001	0.7448
2	18.60	0.18	80.96	9.86	.00001	0.7132
3	18.34	0.53	71.72	3.02	.000001	0.7132
4	18.34	0.53	71.72	3.02	.00001	0.7132
5	18.34	3.85	71.72	3.02	.0001	0.5867
6	16.44	3.85	64.82	3.00	.00001	0.5867
7	17.22	3.35	64.82	3.00	.0001	0.5180
8	17.22	3.35	58.40	1.70	.00001	0.5180
9	17.22	3.35	58.40	1.70	.0001	0.5180
10	16.67	3.61	58.40	1.70	.001	0.5145
11	17.23	3.15	63.12	1.34	.0001	0.4509
12	17.23	3.16	57.69	1.03	.00001	0.4509
13	17.23	3.16	57.69	1.03	.0001	0.4509
14	17.23	3.16	57.69	1.03	.001	0.4509
15	16.84	3.81	59.66	9.86	.01	0.3511
16	16.84	2.38	59.51	3.59	.0001	0.1192
17	17.23	2.38	59.51	3.59	.001	0.1192
18	17.23	1.92	60.50	7.51	.0001	0.1070
19	17.04	2.00	60.10	1.35	.00001	0.0020
20	17.00	2.00	60.00	1.31	.000001	7.45 10-6
21	17.00	2.00	60.00	1.30	.0000001	8.11 10 <sup>-11</sup>
22	17.00	2.00	60.00	1.30	.00000001	$2.45 \ 10^{-19}$

**Table 7.1.** Results of Levenberg Marquardt fitting routine.

The results of Table 7.1 illustrate the convergence process in the LM fitting mechanism. As can be seen from the table, the routine did reach the correct solution for the parameters,  $\vec{x} = [17, 2, 60, 1.3]$ , by the 21<sup>st</sup> iteration. In contrast to the grid search methods, each step in the LM method involves a change in all of the parameters thereby producing a more direct path to a minimum point. For each parameter, the path to convergence usually involves a process of overshooting and undershooting before reaching its final value. Interestingly, this process is not the same for each parameter. For example,  $x_1$  is overshooting in the 3<sup>rd</sup> and 4<sup>th</sup> iterations, while  $x_3$  is undershooting for the same iterations. This is a consequence of the Jacobian calculation at a particular point in parameter space. With each iteration, the value of the objective function either stays the same or is reduced. The 'quarterback' of the entire fitting routine is the parameter  $\lambda$ . This parameter directly influences the type of fitting algorithm that dominates in the hybrid approach.  $\lambda$  is initially seeded with a value of 0.001. Generally speaking, larger values of  $\lambda$  are indicative of the routine pursuing a descent method type of search while the smaller values are indicative of the Gauss Newton approach. As can be seen from the Table, during the last few iterations, the value of  $\lambda$  is continually decreased indicating that the routine is in an area where the objective function is near a minimum which behaves in a parabolic manner.

Figure 7.3 illustrates that the fitted parameters produce reflectivity results which are virtually identical to that of the experimental data.



Figure 7.3 Reflectivity results for fitted parameters. The results are virtually identical to the experimental data in Figure 7.1.  $\chi^2 = 2.54 \times 10^{-19}$ .

The Levenberg Marquardt algorithm can be adjusted to create a descent method approach. Recall that the descent method is characterized with higher values of  $\lambda$  with the results that small steps are made in the descent direction. This approach is recreated in the LM algorithm by setting the intitial value of  $\lambda$  to a higher value such as 0.10 which is two orders of magnitude higher than the same starting parameter in the LM algorithm. The second adjustment is to constrain  $\lambda$  from changing in order that a constant step size can be maintained. When these adjustments were made it took over 1000 iterations and 4.67 seconds for the algorithm to converge. Table 7.2 below illustrates the last iterations of the descent method.

Iteration	<i>x</i> <sub>1</sub>	<i>x</i> <sub>2</sub>	<i>x</i> <sub>3</sub>	<i>x</i> <sub>4</sub>	λ	$\chi^2$
0	14.00	1.00	80.00	5.00	.01	0.9693
990	16.9997	1.9999	60.0000	1.3000	.01	0.9678
991	16.9997	1.9999	60.0000	1.3000	.01	0.7812
992	16.9997	1.9999	60.0000	1.3000	.01	0.6306
993	16.9998	1.9999	60.0000	1.3000	.01	0.5090
994	16.9998	1.9999	60.0000	1.3000	.01	0.4109
995	16.9998	1.9999	60.0000	1.3000	.01	0.3316
996	16.9999	1.9999	60.0000	1.3000	.01	0.2677
997	16.9999	1.9999	60.0000	1.3000	.01	0.2161
998	16.9999	1.9999	60.0000	1.3000	.01	0.1744
999	16.9999	1.9999	60.0000	1.3000	.01	0.1408
1000	16.9999	1.9999	60.0000	1.3000	.01	0.1137
1001	16.9999	1.9999	60.0000	1.3000	.01	9.173 10 <sup>-11</sup>
1002	16.9999	1.9999	60.0000	1.3000	.01	7.405 10 <sup>-11</sup>
1003	16.9999	1.9999	60.0000	1.3000	.01	5.977 10-11
1004	16.9999	1.9999	60.0000	1.3000	.01	4.824 10-11
1005	16.9999	1.9999	60.0000	1.3000	.01	3.894 10 <sup>-11</sup>

 Table 7.2 Simulation of the Descent method.

In Table 7.2, note that the value of  $\lambda$  is constant for all of the iterations. This accounts for the much longer convergence compared to the LM method.

# 7.4 Error Analysis

As explained in Ref. [59], a way to visualize the subject of error analysis is illustrated in

Figure 7.4.



Figure 7.4 Error analysis for a two dimensional fit. (Source: [59]).

For the purposes of illustration, we consider an optical experiment such as the measurement of the reflectivity spectra as discussed previously. Assume that only two parameters, A and d (instead of the four in the previous section) are modeled. For example, A could represent  $x_2$ , the oscillator strength and d could represent  $x_3$ , the natural frequency. Consider each of the other two parameters as being set to a constant. If the experiment is repeated many times, the fitting of the two parameters would result in some distribution of the fitted parameters. Each experiment would also result in its own value of  $\chi^2$ . Figure 6.4 presents a plot of these results. Each dot represents the  $\chi^2$  result of an individual experiment. After many experiments, an ellipse could be drawn around all of the data points that would enclose 95% of the data for the case of a  $2\sigma$  distribution. In Figure 7.4, the height and width of the ellipse correspond to the correlated error for the two parameters. The uncorrelated error is given by the height and width of the ellipse at A<sub>f</sub> and d<sub>f</sub>. The degree of correlation between the two parameters is indicated by the tilt of the ellipse [54]. In fact, if the two parameters were not correlated at all, the axes of the ellipse would be parallel to the coordinate axes and the ellipse would be symmetric about the two axes. In the extreme case where the two parameters were very highly correlated the ellipse would be long and narrow and would follow the relation d = tA, where t is a constant [59].

The values for standard error of the parameter,  $\sigma_j$ , are obtained directly from the results of the Levenberg Marquardt fitting algorithm:  $\sigma_j = (\sqrt{\breve{\alpha}_{jj}})^{-1}$  where  $\breve{\alpha}$  is the Hessian matrix as defined in Eq. (7.9).  $\ddot{\alpha}$  is also known at the curvature matrix and its inverse is also known as C, the covariance matrix [55].

To illustrate the error analysis in the reflection example, we again use LM to fit the four Lorentzian parameters. We begin with a set of experimental data as illustrated in Figure 7.5.



Figure 7.5 Simulated experimental data used in LM error analysis.

The simulated data in Figure 7.5 were calculated by taking the data in Figure 7.1 and applying up to a random  $\pm 20\%$  change to each of the 100 data points. The LM fitting algorithm was then used to fit the four parameters using the following objective function [59]:

$$F(\vec{x}) = \chi^{2}(\vec{x}) = \frac{1}{N - m - 1} \sum_{i=1}^{m} \left( \frac{y_{i} - y(t_{i}, (x_{1}, x_{2}, x_{3} \dots x_{M}))}{\sigma_{i}} \right)^{2},$$
(7.19)

Where *N* is the number of data points, *m* is the number of fitted variables and  $\sigma_i$  is assumed to equal .005 for each data point. The same initial starting vector was used as in the previous cases. The algorithm converged in 0.8917 seconds using 58 iterations. The final parameter vector was calculated to be  $\vec{x} = [16.5016, 2.2914, 59.6532, 1.6723]$ . Figure 7.6 is a plot of the fitted results versus the simulated experimental data.



Figure 7.6 Fitted results (green) versus simulated experimental data (blue).

The final covariance matrix was calculated to be:

0.1983	0.0083	0.0243	-0.0057
0.0083	0.0275	-0.0307	0.0243
0.0243	-0.0307	0.0548	-0.0185
-0.0057	0.0243	-0.0185	0.0723

The square root of the diagonal terms in the covariance matrix gives the standard error of the estimate for each parameter. The error bars for two standard deviations (95%)

probability) are then:  $x_1 = 16.501 \pm 0.891$ ,  $x_2 = 2.201 \pm 0.331$ ,  $x_3 = 59.653 \pm 0.468$  and  $x_4 = 1.672 \pm 0.538$ . Note that the solution for the unadjusted data  $\vec{x} = [17, 2, 60, 1.3]$  is contained within the error estimates for each parameter.

#### CHAPTER 8

# MUELLER MATRICES OF ANISOTROPIC METAMATERIALS GENERATED USING 4×4 MATRIX FORMALISM

#### **8.1 Introduction**

The original results presented in this Chapter are published in P. D. Rogers, T. D. Kang, T. Zhou, M. Kotelyanskii, and A. A. Sirenko, "*Mueller matrices for anisotropic metamaterials generated using 4×4 matrix formalism*", Thin Solid Films, **519**, 2668 (2011) doi: 10.1016/j.tsf.2010.12.066 [1] and have been presented at the ICSE-V Conference in May 2010.

Magnetically active materials in general and metamaterials in particular comprise important classes of materials both from a theoretical perspective as well as for possible device applications. The study of metamaterials has been of interest since the late 1960's when Veselago first explored the properties of *isotropic* materials having simultaneous negative values of  $\varepsilon$  and  $\mu$  [36]. In this Chapter, we have used the Mueller Matrix (MM) formalism for theoretical study of the optical properties of *anisotropic* metamaterials in the frequency range close to the magnetic resonances, where  $\mu(\omega) \neq 1$ . Forward MM models that match the symmetry of planar metamaterials are calculated by treating their behavior as a continuous anisotropic thin film. Our results focus on recently published studies pertaining to artificially created planar metamaterials [6], which use oscillator models for the diagonal components of the  $\varepsilon$  and  $\mu$  tensors [38, 60]. It will be shown that the MM formalism is useful in the analysis of the separation of the dielectric and magnetic contributions to the optical properties of a material including the important case of the negative index of refraction.

The calculation of a forward model for the MM components of a dielectric-magnetic material is critical to the analysis of experimental data obtained from full MM spectroscopic ellipsometry. Through an iterative numerical comparison of the forward model against experimental data, the optical properties of a dielectric-magnetic material can be analyzed. Specifically, dispersion models for the relative dielectric permittivity tensor  $\varepsilon$  and the relative magnetic permeability tensor  $\mu$  can be developed. 4×4 matrix formalism [16] provides a powerful and systematic method to calculate the complex reflection coefficients and the MMs of dielectric-magnetic materials having both arbitrary crystal symmetry and magnetic permeability tensor  $\mu \neq 1$ . For a sample whose principal axes are coincident with the laboratory system, that has simultaneously diagonalizable  $\varepsilon$ and  $\mu$  tensors (with coincident principal axes), and is characterized by orthorhombic crystal symmetry or higher, exact analytical solutions for allowed electromagnetic wave propagation in a dielectric-magnetic medium are produced. For a non-depolarizing medium, forward MM models are determined directly from the complex reflection coefficients. Although the optical properties of a non-depolarizing medium can be also analyzed using the Jones Matrices (JM), the MM approach has an advantage for experimental systems with imperfect, and hence, depolarizing optical elements. In addition, the investigated sample itself may introduce depolarization, as in the case of surface plasmon propagation in metal hole arrays [61]. In this paper, we demonstrate how the angle of incidence dependence of the off-diagonal elements  $M_{\rm 12}$  and  $M_{\rm 34}$  of the MM exhibit asymmetric results when materials having negative index of refraction are simulated. The MM approach can be used to determine these effects experimentally. Alternatively, measurements at variable angles of incidence of the ellipsometry

parameters  $\Psi$  and  $\Delta$  (in which the sign of  $\Delta$  is resolved) [17, 62] may be applicable to non-depolarizing anisotropic metamaterials.

## 8.2 4×4 Matrix Formalism

The procedures for using Berreman's  $4 \times 4$  matrix formalism were outlined for the *isotropic* case in Chapter 3. In this Chapter, we use the technique to calculate the complex reflection coefficients for an *anisotropic* magnetic material in both the semiinfinite and thin film configurations. For a crystal with orthorhombic symmetry having principal axes parallel to the *x*, *y* and *z* coordinate axes,  $\tilde{\Delta}$  in Eq. (4.1) is a 4×4 matrix [16]:

$$\tilde{\Delta} = \begin{pmatrix} 0 & \mu_{yy} - \frac{N_0^2 \sin(\theta_0)^2}{\varepsilon_{zz}} & 0 & 0\\ \varepsilon_{xx} & 0 & 0 & 0\\ 0 & 0 & 0 & \mu_{xx}\\ 0 & 0 & \varepsilon_{yy} - \frac{N_0^2 \sin(\theta_0)^2}{\mu_{zz}} & 0 \end{pmatrix}$$
(8.1)

 $q_{zp}$  and  $q_{zs}$  are the eigenvalues associated with *p* and *s* polarizations, respectively and constitute the *z* components of the wave vectors in the medium. These are:

$$q_{zp} = \frac{\omega}{c} \sqrt{\varepsilon_{xx}} \sqrt{\mu_{yy} - \frac{N_0^2 \sin^2(\theta_0)}{\varepsilon_{zz}}}$$
(8.2)

$$q_{zs} = \frac{\omega}{c} \sqrt{\mu_{xx}} \sqrt{\varepsilon_{yy} - \frac{N_0^2 \sin^2(\theta_0)}{\mu_{zz}}}$$
(8.3)

The *x* component of the wave vector is constant for all of the incident and refracted waves. It is through these equations (eigenvalues of the Berreman equation) that information about the anisotropic optical properties of the medium [17] enters into the calculation of the complex reflection coefficients and, in turn, MM elements. For example, the anisotropic  $\varepsilon$  or  $\mu$  tensors and the consequent differences between  $q_{zp}$  and  $q_{zy}$  are responsible for the two refracted waves shown in Figure 3.1.

#### 8.3 Analytic Formulas

One of the key benefits of using  $4\times4$  matrix formalism to calculate complex reflection and transmission coefficients is that procedures for matching electromagnetic boundary conditions are automatically built in to the method when both incident and, in the case of thin films, substrate media are isotropic and non-magnetic. For each polarization state there are two eigenvectors representing forward and backward propagating waves. In  $4\times4$  matrix formalism, the complex reflection coefficients  $r_{pp}(\omega)$  and  $r_{ss}(\omega)$  and the complex transmission coefficients  $t_{pp}(\omega)$  and  $t_{ss}(\omega)$  are calculated from the eigenvectors of Eq. (4.1) via the solution of simultaneous boundary value equations relating to the continuity of the electric and magnetic fields at the media interface(s). For semi-infinite samples, backward propagating waves are not considered. For thin film samples, retention of the two backward propagating waves is essential to the proper calculation of the complex reflection and transmission coefficients as well as the MM elements. In this section, the cross polarization terms  $r_{ps}(\omega)$ ,  $r_{sp}(\omega)$ ,  $t_{ps}(\omega)$  and  $t_{sp}(\omega)$  vanish because the principal axes of the crystal correspond to the laboratory coordinate axes.

#### 8.3.1 Semi-Infinite Sample

For a semi-infinite material, the two eigenvectors representing the forward propagating waves are used to calculate the complex reflection coefficients for *p* and *s* polarized radiation. The procedure for calculating the complex reflection coefficients involves matching the tangential components of the incident and reflected E and H fields to a linear combination of the two eigenvectors calculated at the common interface located at z = 0 [16, 17]. The complex reflection coefficients are:

$$r_{pp} = \frac{\varepsilon_{xx}k_{z0} - N_0^2 q_{zp}}{\varepsilon_{xx}k_{z0} + N_0^2 q_{zp}}$$
(8.4)

$$r_{ss} = \frac{\mu_{xx}k_{z0} - q_{zs}}{\mu_{xx}k_{z0} + q_{zs}}.$$
(8.5)

In Eq. (8.4) and Eq. (8.5), the complex reflection coefficients are expressed as functions of the *z* components of the incident and refracted wave vectors which themselves take into account the anisotropic characteristics of the medium. Complex reflection coefficients stated in this formalism have been used in the study of media with indefinite permittivity and permeability tensors [44].
# 8.3.2 Thin Film Sample

For a single layer thin film material, all four eigenvectors and eigenvalues are used in the calculation of both the complex reflection and transmission coefficients. Both incident and substrate media are assumed to be isotropic, non-magnetic materials. The z components of the incident and substrate wave vectors are  $k_{z0} = \frac{\omega}{c} N_0 \cos(\theta_0)$  and

$$k_{z2} = \frac{\omega}{c} N_2 \cos(\theta_2)$$
, respectively. The thin film has thickness *d* and is described by  $\varepsilon$   
and  $\mu$  tensors each having orthorhombic symmetry. We assume that the  $\varepsilon$  and  $\mu$   
tensors can be simultaneously diagonalized and have coincident principal axes. Higher  
symmetries can easily be derived from the orthorhombic case. The crystal is aligned such  
that its principal axes are coincident with the laboratory axes. Light is again incident in  
the  $x-z$  plane (see Fig. 6.1).  $4 \times 4$  matrix formalism matches the tangential components  
of the electric and magnetic field vectors at  $z=0$  and  $z=d$  to produce two generalized  
field vectors  $\psi(0)$  and  $\psi(d)$ , respectively. A thin film layer matrix *L* is utilized to relate  
the fields inside the anisotropic film of thickness *d* at its two boundaries [17].

$$\psi(d) = L\psi(0) \tag{8.6}$$

L is a  $4 \times 4$  matrix calculated from the eigenvalues and eigenvectors of the  $\tilde{\Delta}$  matrix according to:

$$L(d) = \tilde{\Psi}^* K(d)^* \tilde{\Psi}^{-1}$$
(8.7)

In Eq. (8.7),  $\tilde{\Psi}$  is composed of the four  $\tilde{\Delta}$  eigenvectors as columns while *K* is a diagonal matrix given by  $K_{ll} = e^{iq_l d}$  with  $q_l$  representing the four eigenvalues of  $\tilde{\Delta}$ . After some algebra relating the incident and reflected waves, the complex reflection coefficients for a thin film can be calculated. A similar process allows for the calculation of the complex transmission coefficients [16, 17]. Using these procedures, we derived analytic expressions for both *p* and *s* polarizations.

The complex reflection and transmission coefficients for p polarized radiation are:

$$r_{pp} = \frac{q_{zp} \cos(q_{zp}d) \left(\frac{N_2}{N_0} k_{z0} - \frac{N_0}{N_2} k_{z2}\right) + i \left(\frac{N_0 N_2 q_{zp}^2}{\varepsilon_{xx}} - \frac{\varepsilon_{xx} k_{z0} k_{z2}}{N_0 N_2}\right) \sin(q_{zp}d)}{q_{zp} \cos(q_{zp}d) \left(\frac{N_2}{N_0} k_{z0} + \frac{N_0}{N_2} k_{z2}\right) - i \left(\frac{N_0 N_2 q_{zp}^2}{\varepsilon_{xx}} + \frac{\varepsilon_{xx} k_{z0} k_{z2}}{N_0 N_2}\right) \sin(q_{zp}d)}$$

$$t_{pp} = \frac{2k_{z0} q_{zp}}{q_{zp} \cos(q_{zp}d) \left(\frac{N_2}{N_0} k_{z0} + \frac{N_0}{N_2} k_{z2}\right) - i \left(\frac{N_0 N_2 q_{zp}^2}{\varepsilon_{xx}} + \frac{\varepsilon_{xx} k_{z0} k_{z2}}{N_0 N_2}\right) \sin(q_{zp}d)}$$

$$(8.8)$$

The complex reflection and transmission coefficients for *s* polarized radiation are:

$$r_{ss} = \frac{q_{zs}\cos(q_{zs}d)(k_{z0} - k_{z2}) + i\left(\frac{q_{zs}^2}{\mu_{xx}} - k_{z0}k_{z2}\mu_{xx}\right)\sin(q_{zs}d)}{q_{zs}\cos(q_{zs}d)(k_{z0} + k_{z2}) - i\left(\frac{q_{zs}^2}{\mu_{xx}} + k_{z0}k_{z2}\mu_{xx}\right)\sin(q_{zs}d)}$$
(8.9)

$$t_{ss} = \frac{2k_{z0}q_{zs}}{q_{zs}\cos(q_{zs}d)(k_{z0} + k_{z2}) - i\left(\frac{q_{zs}^2}{\mu_{xx}} + k_{z0}k_{z2}\mu_{xx}\right)\sin(q_{zs}d)}$$

The formulas are functions of the optical properties of the film material as well as the characteristics of both incident and substrate media. For example, in a vacuum-thin film-vacuum configuration, the first terms in the numerator of each of the complex reflection coefficients become zero. This simpler form is applicable to many experimental configurations and will be used in the analysis of planar metamaterials below.

In order to verify the accuracy of our analytical expressions, we have calculated the complex reflection and transmission coefficients for the cases of the semi-infinite sample, and a single layer film on a semi-infinite substrate using both our numerical implementation of the  $4 \times 4$  matrix algorithm and the analytical expressions in Eq. (4.9), Eq. (8.5), Eq. (8.8) and Eq. (8.9). We found that the results coincide within the rounding errors of the  $4 \times 4$  matrix algorithm. This analysis was performed for a variety of conditions including negative permittivity and permeability values, which are expected to be observed in metamaterials.

## 8.4. Mueller matrices of a planar metamaterial

For the sample symmetry and the experimental configurations assumed in this paper, the off diagonal elements of the  $2\times2$  Jones matrix are zero. For non-depolarizing materials, there are well established formulas to transform the Jones matrix to a full MM [17] and Eq. (8.10) is the transformation formula applicable when the off diagonal Jones matrix elements are both zero.

$$\begin{pmatrix} \frac{1}{2} (|r_{pp}|^{2} + |r_{ss}|^{2}) & \frac{1}{2} (|r_{pp}|^{2} - |r_{ss}|^{2}) & 0 & 0 \\ \frac{1}{2} (|r_{pp}|^{2} - |r_{ss}|^{2}) & \frac{1}{2} (|r_{pp}|^{2} + |r_{ss}|^{2}) & 0 & 0 \\ 0 & 0 & \Re(r_{pp}r_{ss}^{*}) & \Im(r_{pp}r_{ss}^{*}) \\ 0 & 0 & -\Im(r_{pp}r_{ss}^{*}) & \Re(r_{pp}r_{ss}^{*}) \end{pmatrix}$$

$$(8.10)$$

The MM of a dielectric-magnetic material is produced from its complex reflection coefficients which are, in turn, calculated from its frequency dependent  $\varepsilon$  and  $\mu$  tensors. Accordingly, to produce a MM, accurate complex reflection formulas appropriate to the orientation of the crystal must be available. In addition, models for the dielectric and magnetic functions of the material are required for input into these reflection formulas. Eq. (8.10) illustrates that, for our configuration, there will be eight non-zero MM elements. However, only four of these terms are independent. Procedures for calculating the forward model of a MM for a planar metamaterial will now be discussed.

To date, there have been relatively few spectroscopic studies of metamaterials which analyze their reflection properties using oblique angles of incidence. Driscoll *et al.* have done one such study using a planar array of split-ring resonators (SRRs) [6]. Reflection and transmission intensities were recorded for the single *s* polarization at varying angles of incidence. These results were fitted using the Fresnel equations to model the optical properties of the metamaterial as though it behaved as a continuous anisotropic thin film crystal.

These results are important to our study of MMs because the frequency dependent models of the material's  $\varepsilon$  and  $\mu$  tensors together with our Eq. (8.8) and Eq. (8.9) enable the calculation of predictive MMs of this planar metamaterial. In the Driscoll

experimental configuration, the  $\varepsilon$  and  $\mu$  tensors have the following anisotropic symmetry:

$$\mathcal{E}(\omega) = \begin{pmatrix} \mathcal{E}_{xx}(\omega) & 0 & 0 \\ 0 & \mathcal{E}_{yy}(\omega) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
$$\mu(\omega) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \mu_{zz}(\omega) \end{pmatrix}$$
(8.11)

The tensors are described by the SHO oscillator model for  $\varepsilon$  and Pendry's model for  $\mu$  shown in Eq. (8.12).

$$\varepsilon_{xx}(\omega) = \varepsilon_s - \frac{A_e \omega_p^2}{\omega^2 - \omega_{e0}^2 + i\omega\gamma_e}$$

$$\mu_{zz}(\omega) = 1 - \frac{A_m \omega^2}{\omega^2 - \omega_{m0}^2 + i\omega\gamma_m}$$
(8.12)

In the formula for the  $\varepsilon$  tensor,  $\varepsilon_s$  is the static dielectric constant and  $\omega_p$  is the plasma frequency.  $A_e$  and  $A_m$  are oscillator amplitudes. The formula for the  $\mu$  tensor is modified from the traditional Lorentzian model in that the square of the frequency of incident radiation ( $\omega$ ) enters the numerator and  $\mu$  (0) is forced to be equal to 1 [6, 38, 60]. The  $\varepsilon_{yy}(\omega)$  response was not analyzed in the Driscoll paper.

The general formulas for thin films derived using  $4 \times 4$  matrix formalism are used to calculate the complex reflection and transmission coefficients for this fabricated material. The experiment performed by Driscoll *et al.* is set up such that both incident and substrate medium are vacuum with x axis parallel to s polarized radiation. In this

$$r_{pp} = \frac{\frac{i}{2} \left( \frac{q_{zp}}{k_{z0} \varepsilon_{yy}} - \frac{k_{z0} \varepsilon_{yy}}{q_{zp}} \right) \sin(q_{zp} d)}{\cos(q_{zp} d) - \frac{i}{2} \left( \frac{q_{zp}}{k_{z0} \varepsilon_{yy}} + \frac{k_{z0} \varepsilon_{yy}}{q_{zp}} \right) \sin(q_{zp} d)}$$

$$r_{ss} = \frac{\frac{i}{2} \left( \frac{q_{zs}}{k_{z0} \mu_{yy}} - \frac{k_{z0} \mu_{yy}}{q_{zs}} \right) \sin(q_{zs} d)}{\cos(q_{zs} d) - \frac{i}{2} \left( \frac{q_{zs}}{k_{z0} \mu_{yy}} + \frac{k_{z0} \mu_{yy}}{q_{zs}} \right) \sin(q_{zs} d)}$$
(8.13)

In Eq. (8.13),  $q_{zp}(\omega)$  and  $q_{zs}(\omega)$  have the same definitions as in Eq.(8.2) and Eq. (8.3) except for the interchange of the x and y axes to accommodate the experimental setup.  $k_{z0}$  is the z component of the free space wave vector.

Due to the complexity of the analysis using the Fresnel approach, Driscoll *et al.* [6] constrained themselves to study only the *s* polarization incident at the sample.  $4\times4$  matrix formalism and full MM measurement should allow more complete analysis of the sample properties using incident light of linear and elliptical polarizations. In order to develop a forward model and analyze the measurements of MMs at oblique angles of incidence, assumptions about the permittivity and permeability along other directions are required. Specifically, assumptions about the  $\varepsilon_{yy}(\omega)$  response are necessary in order to illustrate how  $4\times4$  matrix formalism could have been used to predict the MM for this

metamaterial. Asymmetries in the SRR fabrication between the *x* and *y* axis suggest that  $\varepsilon_{yy}(\omega) \neq \varepsilon_{xx}(\omega)$ . For purposes of illustration only, we assume that the natural resonance of the  $\varepsilon_{yy}(\omega)$  oscillation is 15 GHz as compared to 19.9 GHz for the  $\varepsilon_{xx}(\omega)$  oscillation. We assume all other fitted parameters are identical. Using these parameters, the frequency dependent  $\varepsilon_{xx}(\omega)$ ,  $\varepsilon_{yy}(\omega)$  and  $\mu_{zz}(\omega)$  values are calculated and are then input into Eq. (8.13) to produce the complex reflection coefficients. Eq. (8.10) is then used to transform the complex reflection coefficients into MM elements. Given the coincidence of the principal axes of the metamaterial with the laboratory system, the off diagonal Jones matrix elements will vanish and there will be only 8 non-zero elements of the predicted MM. These elements are illustrated in Fig. 8.1.



**Figure 8.1** The Mueller Matrix components of a planar metamaterial in the proximity of the resonant feature at 14 GHz for two AOI. Dotted line  $\theta_0 = 0^\circ$ . Solid line  $\theta_0 = 40^\circ$ .

4×4 matrix formalism was used for the systematic calculation of the complex reflection coefficients. Driscoll *et al.* found that the  $r_{ss}$  coefficient, when calculated in conjunction with the fitted oscillator models, produced a good qualitative fit with *s* polarized experimental reflectivity data [6]. The simulated MM components, generated from the  $\varepsilon$ and  $\mu$  tensors, contain additional critical information about the anisotropic dielectric and magnetic properties of the metamaterial. Actual experimental MM data should allow for the extraction of the anisotropic oscillator parameters through non-linear fitting procedures.

#### 8.5. Separation of Dielectric and Magnetic Contributions

For proper characterization of materials whose magnetic effects have non-negligible influence on their optical properties, it is important to be able to separate dielectric and magnetic contributions. Spectroscopic experiments usually provide values for the complex refractive index  $n = \sqrt{\epsilon \mu}$  at different frequencies, which do not contain any direct information as to whether it is  $\epsilon$  or  $\mu$  which is responsible for a particular feature observed in the spectrum. The difference in the change of the various MM components in response to whether  $\epsilon$  or  $\mu$  is changing can separate dielectric and magnetic contributions. For metamaterials, this information is crucial for their design.

This discrimination is indeed possible by performing MM measurements made at varying angles of incidence. To illustrate this point, we model conditions where the index of refraction of a dielectric-magnetic material remains constant but its inputs ( $\varepsilon$  and  $\mu$ ) are varied. Specifically, we model a hypothetical case of isotropic  $\varepsilon$  and  $\mu$  where each are

allowed to vary between 1 and 6, but their product,  $n^2 = \varepsilon \mu$ , is held constant at 6. We simulate a given material composition ( $\varepsilon$ ,  $\mu$ ) and compare it to another material whose values for  $\varepsilon$  and  $\mu$  are interchanged. For example, Fig. 8.2 shows that the values of the diagonal MM elements are identical for both materials characterized by (3, 2) and (2, 3), respectively. However, this degeneracy is removed when the off-diagonal MM elements are analyzed over varying angles of incidence (AOI).



**Figure 8.2** Dielectric and magnetic contributions in the diagonal and off-diagonal MM components as functions of AOI. Different  $(\varepsilon, \mu)$  combinations illustrate the difference in response of M<sub>12</sub> and M<sub>34</sub> compared to M<sub>11</sub> and M<sub>33</sub>. For example, the (2, 3) combination (black dotted line, online dotted green) and the (3, 2) combination (black squares, online solid yellow line) are degenerate for M<sub>11</sub> and M<sub>33</sub> but have opposite signs for M<sub>12</sub> and M<sub>34</sub>.

It is evident in Fig. 8.3 that the MM response of the off-diagonal elements is the same in magnitude, but is either positive or negative depending on whether it is  $\varepsilon$  or  $\mu$  that is changing. The (2,3) material has positive off-diagonal elements while the (3,2) material has negative off-diagonal elements. Moreover, as seen in Fig. 8.3, when we introduce the "left handed" [36] material with negative permittivity and permeability, but keeping  $\varepsilon\mu = 6$ , the  $M_{12}$  and  $M_{34}$  components respond in opposite directions.



**Figure 8.3** Dielectric and magnetic contributions in the diagonal and off-diagonal MM components as functions of AOI. Different  $(\varepsilon, \mu)$  combinations illustrate the difference in response of M<sub>12</sub> compared to M<sub>34</sub> when "left handedness" is introduced via negative values for  $\varepsilon$  and  $\mu$ . The (-2,-3) combination (black "x", online red "x") and the (2, 3) combination (black dotted line, online solid green line) are degenerate for M<sub>11</sub> and M<sub>33</sub> but have opposite signs for M<sub>34</sub>. In addition, the (-2, -3) combination and the (-3, -2) combination (black "o", online blue "o") are degenerate for M<sub>11</sub> and M<sub>33</sub> but have opposite signs for both M<sub>12</sub> and M<sub>34</sub>.

For example, while the (-2,-3) material has diagonal and off-diagonal MM elements identical in magnitude to the (+2, +3) material, the sign of  $M_{34}$  becomes negative. It is also interesting to note that the off-diagonal MM responses for two left handed materials can be distinguished. For example, the signs of the  $M_{12}$  and  $M_{34}$  components respond in opposite directions for the (-2,-3) material as compared to the (-3,-2) material. The difference in the angular response between  $M_{12}$  and  $M_{34}$  is an indication of the material being "left handed". This observation is extremely important as it is happening in the thin film sample where the study of such MM measurements at varying AOI may be the only way to identify the anomalous properties of the metamaterial comprising the film. In the above cases for both right handed and left handed materials, the ability to distinguish  $\varepsilon$ and  $\mu$  vanishes at normal incidence. However, the contrast between the magnetic and electric contributions is at maximum for AOIs that are close or even exceed the Brewster angle of ~68° that corresponds to  $n = \sqrt{6}$ . Given that there are only 4 independent MM elements to measure, varying the AOI contributes a critical degree of freedom to the proper characterization of  $\varepsilon$  and  $\mu$  tensors. Fig. 8.3 also shows the interesting impedance matching condition discussed in Section 3. When  $\varepsilon = \mu$ , there is zero reflection at normal incidence.

The simple examples considered above can, of course, be analyzed using the alternative approach of the Jones Matrices. Switching between dielectric and magnetic contributions as well as between the positive and negative values of these contributions does naturally cause changes in  $\Psi$  and  $\Delta$  dependencies. However, the behavior of these ellipsometric

parameters is more complex, and not as illustrative, as compared to switching signs in the off-diagonal Mueller Matrix components.

Since real metamaterial samples are usually anisotropic, one should not always expect to see such well pronounced and easily understandable effects in real experimental data. However, the fact that the angular dependencies of the MM elements respond differently to dielectric and magnetic contributions, as well as to the positive and negative values of  $\varepsilon$  and  $\mu$ , should allow for the ability to distinguish these different situations while extracting  $\varepsilon$  and  $\mu$  by non-linear fitting of the experimental data.

## 8.6. Summary

We have presented an analytical approach for the study of dielectric-magnetic materials using 4×4 matrix formalism. Wave vectors in a dielectric-magnetic medium are derived directly from the eigenvalue solutions of the Berreman equation. We utilized the wave vector approach to derive analytic formulas for the complex reflection and transmission coefficients of thin films whose  $\boldsymbol{\varepsilon}$  and  $\boldsymbol{\mu}$  tensors both have an orthorhombic symmetry. Any other system that has simultaneously diagonalizable  $\boldsymbol{\varepsilon}$  and  $\boldsymbol{\mu}$  tensors (with coincident principal axes) can be reduced to this case by rotations of the reference frame. We have demonstrated how these calculations can produce the full MM of a nondepolarizing material. Forward models for the active MM elements of a planar metamaterial were calculated. The separation of the magnetic and dielectric contributions to the optical properties of an anisotropic material, as well as identification of negative refractive index in a thin film, are possible using the MM approach at varying AOI. The following original results have been presented in this Chapter:

- formulae for the complex reflection and transmission coefficients have been derived for materials with µ≠1 in the thin film configuration having orthorhombic symmetry or higher. These formulae incorporate the case of nonvacuum incident and substrate media.
- the behavior of Mueller matrix components for a planar metamaterial in proximity to resonance have been illustrated at varying AOI.
- for the first time, the separation of dielectric and magnetic contributions in the optical spectra of a magnetic material has been demonstrated by performing MM simulations at varying AOI
- for the first time, the identification of the Negative Index of Refraction condition in the optical spectra of a magnetic material is illustrated by performing MM simulations at varying AOI.

# **CHAPTER 9**

# ADJUSTED OSCILLATOR STRENGTH MATCHING FOR HYBRID MAGNETIC AND ELECTRIC EXCITATIONS IN DY<sub>3</sub>FE<sub>5</sub>O<sub>12</sub> GARNET

The original results presented in this Chapter are published in:

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# 9.1 Introduction

Far-infrared (IR) spectra of the optical modes in magnetic materials have recently attracted a lot of attention, especially with respect to the multiferroic effect and electromagnons [63-65]. However, no universal mechanisms have been proposed to explain the occurrence of electromagnons and the accompanying magneto-dielectric effect [30, 66]. One challenge to theoretical modeling is its dependence on empirical data obtained with a single optical technique, such as transmittance, which, as we will see in this paper, cannot always unambiguously distinguish between electric and magnetic excitations. As we show in this Chapter, a combination of several complementary techniques, such as transmittance and reflectivity, for the measurements of both the complex dielectric function  $\varepsilon(\omega)$  and the magnetic permeability  $\mu(\omega)$  spectra can improve understanding of the coupling between magnetic and electric excitations [67]. The quantitative interpretation of the optical spectra requires an adequate modeling approach for light propagation in magneto-dielectric crystals with  $\mu(\omega) \neq 1$ . We applied Berreman's 4×4 matrix formalism [16] for the numerical and analytic analysis of

experimental data for transmittance, reflectivity, and rotating analyzer ellipsometry (RAE) in  $Dy_3Fe_5O_{12}$  garnet (Dy-IG). Through the combination of these optical techniques, we determined whether an IR-active mode was (i) entirely of dielectric origin, (ii) entirely of magnetic origin, or (iii) a hybrid with a mixed electric- and magnetic dipole activity. In this paper, we show that the magnetic components of the hybrid modes are not negligibly weak and can result in a complete cancellation of the mode in reflectivity. The observed vanishing of certain hybrid modes is explained in terms of the adjusted oscillator strength matching (AOSM) condition, which has some similarities to the impedance matching phenomenon in metamaterials [42]. We also show that the RAE data, in addition to being consistent with the results of normal incidence reflectivity, illustrate that the AOSM condition is applicable for varying angles of incidence.

## 9.2 Material Preparation

The high-temperature flux growth technique was utilized to produce bulk crystals of Dy-IG (Dy<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>). A sample with a (0 0 1) surface, a cross section area of  $5\times5$  mm<sup>2</sup>, thickness of 0.55 mm, and a 3° offset between opposite sides was used for the optical experiments. Transmittance spectra with resolution of 0.3 cm<sup>-1</sup> were measured between 13 and 100 cm<sup>-1</sup> at the National Synchrotron Light Source, Brookhaven National Laboratory, at the U4IR beamline equipped with a Bruker IR spectrometer, and a LHe-pumped bolometer. The RAE and reflectivity measurements were carried out at Fribourg University using a Hg lamp in the spectral range between 45 and 100 cm<sup>-1</sup> with resolution of 0.7 cm<sup>-1</sup>. The RAE experimental setup is similar to that described in Ref. [68]. Temperature and magnetic field dependencies for static values of  $\varepsilon(0, H, T)$  and  $\chi(0, H, T)$  were measured using an LCR meter at 44 kHz and a SQUID magnetometer.

## 9.3 Results and Analysis

Dy-IG, as well as other RE-IG (RE=Ho, Tb), is a ferrimagnetic material with a huge magnetostriction, which is related to the combination of a strong anisotropy of the crystal field of the  $RE^{3+}$  ions and a strong and anisotropic superexchange interaction between RE and iron [69-72]. Although there are no literature reports that Dy-IG is multiferroic, recently two related compounds, antiferromagnetic orthoferrite DyFeO<sub>3</sub> and Tb-IG, were shown to be multiferroic and magneto-dielectric [73, 74]. We found a magneto-dielectric effect in a weak external magnetic field H of about 2 kOe. We also observed two indications of the ferromagnetic ordering of Dy spins at  $T_C = 16$  K: (i) the sharp minimum in the temperature derivative of magnetic susceptibility  $\partial \chi / \partial T$  at  $T_C$  [Fig. 9.1(a)] and (ii) the temperature dependence of the exchange resonance IR mode frequencies, which will be discussed below. The quasi-static value of the dielectric constant  $\varepsilon(0)$  of Dy-IG has anomalies in the temperature and external magnetic field dependencies [Fig. 9.1(b,c)].  $\varepsilon(0,T)$  has a peak at  $T_C = 16$  K that can be explained by the local electric polarization due to anti-ferroelectric lattice ordering. The latter occurs in the same temperature range as the ferromagnetic ordering of the Dy spins below 16 K. The anti-ferroelectric lattice ordering does not create a global electric polarization, but affects the spin and lattice dynamics at the microscopic scale. Using RAE we found that the soft optical modes at  $\Omega \approx 146 \text{ cm}^{-1}$  and 595 cm<sup>-1</sup>, which are associated primarily with Dy and oxygen displacements, contribute to the changes in  $\mathcal{E}(0,T)$  through the Lyddane-Sachs-Teller relationship:  $\varepsilon(0,T) \sim \Omega^{-2}(T)$  [see Figure 9.1(b)]. The magneto-dielectric effect in Dy-IG reveals itself in the variation of  $\varepsilon(0,H)$  for H < 10 kOe [Fig. 9.1(c)].



**Figure 9.1** (a) Temperature dependence of the static magnetic susceptibility (red curve, left scale) and its derivative (blue curve, right scale) for a Dy<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> single crystal. Ferromagnetic ordering of Dy<sup>3+</sup> occurs at  $T_C = 16$  K. (b) Temperature dependence of the static dielectric constant at H=0 (solid red line) and H=10 kOe (blue dashed line). Black squares represent the temperature dependence of the soft optical phonon frequency at 146 cm<sup>-1</sup> measured with RAE. (c) Magnetic field dependence of the static dielectric constant at T= 5 K. In all graphs  $E \parallel [1 \ 0 \ 0]$  and  $H \parallel [0 \ 1 \ 1]$ .

The appearance of anti-ferroelectric ordering and a Dy–Dy ferromagnetic interaction motivates us to re-visit the far-IR optical spectra of Dy-IG. *RE*-IGs have been studied in Refs. [14, 75-77]. It was shown that below 80 cm<sup>-1</sup>, transmission spectra in

polycrystalline *RE*-IGs are dominated by both *RE*<sup>3+</sup> single ion electronic transitions and Kaplan-Kittel (KK) modes, which were attributed to magnetic dipoles [14, 78]. Figure 9.2(a,b) shows a transmittance spectrum of Dy<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> at T = 5 K, and the transmittance intensity map. In addition to the optical phonon at 81 cm<sup>-1</sup> [see Ref. [79]], a number of crystal field (CF) lines of Dy<sup>3+</sup> at 20, 52, 72, and 87 cm<sup>-1</sup> are observed for T > 16 K. At low temperatures T<16 K, however, the number of absorption lines increases. The ligand field (LF) and KK modes appear at 13, 22, 29, 43, 51, 59.5, 73, 78, 87, 91, and 98 cm<sup>-1</sup> for T=5 K. In a simplified model for two-spin ferrimagnetic systems, like *RE*-Fe, a single exchange-type KK mode is expected with the frequency of  $\omega_M$ . The LF mode  $\omega_{LF}$ corresponds to precession of the Dy<sup>3+</sup> moments in the effective field imposed by the iron magnetization due to the superexchange interaction between Fe and *RE*. The latter is modified by the ferromagnetic interaction between Dy<sup>3+</sup> spins at low temperature. The zone-center frequencies of these collective excitations of Dy<sup>3+</sup> and Fe<sup>3+</sup> spins are: [75, 76, 78]

$$\omega_{M}(T) = \lambda_{Fe-Dy} \mu_{B} \Big[ g_{Dy} M_{Fe} - g_{Fe} M_{Dy}(T) \Big]$$
  
$$\omega_{LF}(T) = g_{Dy} \mu_{B} \Big[ \lambda_{Fe-Dy} M_{Fe} + \lambda_{Dy-Dy} M_{Dy}(T) \Big],$$
  
(9.1)

where  $\mu_B$  is the Bohr magneton,  $\lambda_{Fe-Dy}$  is the exchange constant between Fe and Dy ions,  $\lambda_{Dy-Dy}$  is the ferromagnetic exchange constant,  $g_{Fe} = 2$  and  $g_{Dy}$  are the corresponding *g*-factors,  $M_{Dy}(T)$  is the Dy-sublattice magnetization, and  $M_{Fe}$  is the combined Fe magnetization. The LF and KK modes can be distinguished based on the temperature dependence of their frequencies [see Eq. (9.1)]. For T< 16 K, the KK modes  $\omega_M(T)$ exhibit softening due to increase of  $M_{Dy}(T)$ . Figure 9.2(a,b) shows three KK modes at 43, 51, and 59.5 cm<sup>-1</sup>, that can be explained by the double umbrella structure for Dy<sup>3+</sup> spins and by the strongly anisotropic and temperature-dependent superexchange interaction between Dy<sup>3+</sup> and Fe<sup>3+</sup> ions. The temperature-induced variation of the LF mode frequencies below 16 K is also proportional to  $M_{Dy}(T)$  [see Eq. (9.1)], but it has an opposite sign compared to that for KK modes. Fig. 2(b) indicates a phase transition at  $T_C$ =16 K with appearance of the long range ordering of Dy spins.

According to the simplified model for collinear Dy<sup>3+</sup> and Fe<sup>3+</sup> spins, the KK and LF modes were viewed as pure magnons [75, 76]. However, their spectral proximity to the phonon at 81 cm<sup>-1</sup> and modification of the LF due to local electric polarization should result in a hybrid electric- and magnetic-dipole activity. In the following, we will prove this suggestion using a combination of several optical techniques: transmittance and reflectivity at normal incidence, and RAE. The terms "LF" and "hybrid" will be applied interchangeably to the same modes. The first term refers to the origin of the IR-active excitation as described above, while the latter corresponds to the mixed dipole activity of the mode in the optical spectra.



**Figure 9.2** (a) Far-IR transmission spectrum for a Dy<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> single crystal measured at T=5 K. The light propagation is along the [0 0 1] direction. Arrows indicate the frequencies of the IR modes. (b) Transmission map *vs.* temperature and light frequency. The blue (dark) color corresponds to stronger absorption and red (light) color indicates high transmission. The horizontal green line represents the ferromagnetic transition temperature  $T_C = 16$  K. The white dots represent the phonon at 81 cm<sup>-1</sup>. The black dots show the KK and LF excitations.

Figure 9.3(a,b) compares the transmittance  $T_s(\omega)$  and reflectivity  $R_s(\omega)$  spectra of the same Dy-IG sample as in Figure 9.2.  $T_s(\omega)$  and  $R_s(\omega)$  have been measured at T=8 K and 9 K, respectively, at near-normal incidence, *i. e.*, the angle of incidence (AOI) is close to zero. RAE measurements were taken for the same sample at T=8 K and AOI=75 deg. The results of the RAE measurements are shown in terms of the real part of the pseudodielectric function  $\langle \varepsilon_1(\omega) \rangle$ , [Fig. 9.3(c)]. Modes of three kinds can be identified in Fig. 9.3(a,b,c): (i) The phonon at 81 cm<sup>-1</sup>, which is obviously an electric dipole, has a

conventional Lorentz shape in the  $R_s(\omega)$  and RAE spectra. The phonon is also strong in  $T_s(\omega)$ ; (ii) The KK mode at 59.5 cm<sup>-1</sup> has an inverted Lorentz shape in both the  $R_s(\omega)$  and RAE spectra. As shown below, this shape is typical for magnetic dipoles. (iii) The LF modes at 73, 78, and 91 cm<sup>-1</sup> are as strong as the phonon in  $T_s(\omega)$ , but practically invisible in both the  $R_s(\omega)$  and RAE spectra. The  $T_s(\omega)$  and  $R_s(\omega)$  spectra, both measured for the same sample and at the same AOI, can be reconciled by suggesting that the LF modes in Dy-IG possess a hybrid, *i.e.*, magnetic- and electric-dipole activity. This suggestion can be qualitatively understood based on Veselago's approach for light propagation in an isotropic, semi-infinite medium with  $\mu(\omega) \neq 1$ . Here a simple replacement of the refractive index is used: for Fresnel's reflection coefficient,  $n(\omega) \to \sqrt{\varepsilon(\omega) / \mu(\omega)}$ ; while in transmittance,  $n(\omega) \to \sqrt{\varepsilon(\omega) \cdot \mu(\omega)}$  [36]. These formulas explain that a magnetic mode has an inverted shape in the reflectivity spectrum since  $n(\omega) \sim \sqrt{1/\mu(\omega)}$  in the vicinity of the mode where  $\varepsilon(\omega) \approx const$ . They also naturally account for the suppression of the mode feature in the reflectivity spectrum for a hybrid, *i.e.*, magnetic-dielectric mode, where the magnetic and dielectric components tend to cancel each other (see Appendix C for further details).



**Figure 9.3** Optical spectra of a Dy<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> single crystal. (a) Transmission spectrum at AOI=0, *T*=8 K. (b) Absolute far-IR reflectivity at AOI=0, *T*=9 K. (c) Rotating analyzer ellipsometry (RAE) data for pseudo dielectric function  $\langle \varepsilon_1(\omega) \rangle$  at AOI=75 deg, *T*=8 K. In (a,b,c), the blue diamonds are experimental data and the red solid curves represent results of the fit. Electric (d) and magnetic (e) susceptibilities as determined from the fit results. Magnetic, electric, and hybrid modes are marked with *m*, *e*, and *h*, respectively.

In order to properly analyze the experimental data in Fig. 9.3(a,b,c), we developed an exact numeric method (see Ref. [1] for details), which is based on Berreman's  $4\times4$  matrix formalism.[1, 16] Our method incorporates the exact geometry of the measured Dy-IG sample with average thickness d=0.55 mm, multiple reflections, variable AOI's, and

possible magnetic and electric anisotropies. The response functions of Dy-IG,  $\varepsilon(\omega)$  and  $\mu(\omega)$ , were modeled using a set of Lorentz oscillators:

$$\varepsilon(\omega) = \varepsilon_{\infty} + \sum_{j=1}^{N} \frac{S_{j,e} \omega_{j,e0}^{2}}{\omega_{j,e0}^{2} - \omega^{2} - i\gamma_{j,e}} \omega$$

$$\mu(\omega) = \mu_{\infty} + \sum_{j=1}^{M} \frac{S_{j,m} \omega_{j,m0}^{2}}{\omega_{j,m0}^{2} - \omega^{2} - i\gamma_{j,m}} \omega$$
(9.2)

Here  $\mathcal{E}_{\infty}$  is the infinite-frequency value of the dielectric function,  $\mu_{\infty} \cong 1$ ,  $S_{e(m)}$  is the oscillator strength,  $\gamma_{e(m)}$  is the damping constant, and  $\omega_{e(m)0}$  is the resonance frequency. Although the response functions of Dy-IG can be in principle anisotropic, the comparison of the reflectivity and ellipsometric data taken at different AOI do not reveal any anisotropy within the accuracy of the data. The hybrid modes in this model have nonzero electric and magnetic oscillator strengths  $S_e$  and  $S_m$  at the same resonant frequency  $\omega_h = \omega_{e(m)0}$ , thus creating a contribution to both  $\mathcal{E}(\omega)$  and  $\mu(\omega)$ . The electric and magnetic damping constants for the hybrid modes are assumed to be the same:  $\gamma_e = \gamma_m$ . The results of the fit using 4×4 matrix formalism for  $R_s(\omega)$ ,  $T_s(\omega)$ , and  $\langle \mathcal{E}_1(\omega) \rangle$  are shown in Figs. 9.3(a,b,c) with solid curves. The corresponding values of  $S_e$  and  $S_m$  are summarized in Table 9.1 and the real parts of the dielectric function and the magnetic permeability are shown in Figure 9.3(d,e). Note that for Dy-IG,  $S_e$  and  $S_m$  are not large enough to modify significantly the background values of  $\varepsilon_{\infty} \cong 17$  and  $\mu_{\infty} \cong 1$ . Hence, both  $\mathcal{E}(\omega)$  and  $\mu(\omega)$  are positive everywhere in the vicinity of the hybrid mode frequencies [see Fig. 9.3(d,e)]. Thus, the natural occurrence of a negative index of refraction does not take place at the spectral range dominated by the hybrid modes that might otherwise occur if their damping were sufficiently low.

**TABLE 9.1.** The values of parameters of optical phonon at 81 cm<sup>-1</sup> (*e*), magnetic KK mode at 59.5 cm<sup>-1</sup> (*m*), and three hybrid modes (*h*) at 73 cm<sup>-1</sup>, 78 cm<sup>-1</sup> and 91 cm<sup>-1</sup> obtained from the analysis of the combination of the transmission, RAE and reflectivity measurements.

$\omega_0, \text{ cm}^{-1}$	$S_e$	$S_m$	Type
59.5	_	0.0019	т
73	0.036	0.0021	h
78	0.035	0.0022	h
81	0.077	_	е
91	0.032	0.0010	h

Certain analytical formulas can be obtained which assist in describing the measured  $T_s(\omega)$ ,  $R_s(\omega)$ , and RAE spectra. Consider two electric and magnetic oscillators that are separated on the energy scale and have comparable values of  $\gamma_e \approx \gamma_m$ . If the backside reflection is not strong, the ratio of the amplitudes of the modes in the reflectivity spectra at their respective resonances are related to  $\partial R_{ss}(\omega)/\partial \omega|_{\omega e(m)0}$  as follows:

$$\frac{\partial R_{ss}/\partial \omega|_{\omega e0}}{\partial R_{ss}/\partial \omega|_{\omega m0}} \approx -\frac{\mu_{\infty}}{\varepsilon_{\infty}} \frac{S_e}{S_m} \frac{\omega_{e0}}{\omega_{m0}}, \qquad (9.3)$$

where  $S_e \ll \varepsilon_{\infty}$ .  $\mu_{\infty}$  and  $\varepsilon_{\infty}$  are determined at the frequencies shifted from  $\omega_{e(m)0}$  by at least  $3\gamma_{e(m)}$ . Note that the negative sign corresponds to the inverted Lorentzian shape at the magnetic resonance. If the thickness of the sample *d* is optimized to prevent saturation of the transmitted intensity at the resonance, then the following relationship for transmission amplitudes of the magnetic- and electric modes can be obtained:

$$\frac{\Delta T_e}{\Delta T_m} \approx \frac{\mu_{\infty}}{\varepsilon_{\infty}} \frac{S_e}{S_m} \frac{\omega_{e0}^2}{\omega_{m0}^2}$$
(9.4)

where  $\Delta T_{e(m)} \approx T(\omega_{e(m)0}) - T(\omega_{e(m)0} \pm 3\gamma_{e(m)})$ . In the case of hybrid modes with a mixed electric- and magnetic dipole activity, Eq. (9.3) and Eq. (9.4) indicate that the

contribution of the dielectric and magnetic oscillators to the transmission spectra is additive with an adjusted oscillator strength (AOS)  $S_T \approx \mu_{\infty} \cdot S_e + \epsilon_{\infty} \cdot S_m$ , while their total contribution to reflectivity is subtractive with AOS of  $S_R = (\mu_m \cdot S_e - \epsilon_m \cdot S_m)/\mu_m^2$ . Here, the relevant magnetic or dielectric oscillator strength is multiplied by its constitutive response function complement. For the general case of a spectrum with several hybrid modes, a complete cancellation in reflectivity measurements is possible for each mode if the adjusted oscillator strength matching condition (AOSM) occurs:  $\mu(\omega_h) \cdot S_e = \epsilon(\omega_h) \cdot S_m$ . These results are consistent with the aforementioned Veselago approach (see Appendix C). In our experiment, the AOSM condition is realized for the hybrid modes at 73 and 78 cm<sup>-1</sup> that are not visible in either normal-incidence reflectivity or RAE experiments. The hybrid mode contribution to  $dR_{ss}(\omega_h)/d\omega$  is negligible and the  $R_s(\omega)$  spectrum looks essentially featureless around the resonance frequencies. Analysis of RAE spectra taken at AOI=75° shows that the AOSM condition  $\mu(\omega_h) \cdot S_e = \epsilon(\omega_h) \cdot S_m$  is valid across a wide range of AOIs, even close to the Brewster angle (76.4° for  $\epsilon_m = 17$  and  $\mu_m = 1$ ).

#### **9.4 Conclusions**

In conclusion, the rare occurrence of the AOSM condition for hybrid modes was studied in Dy-IG. The proximity of the  $Dy^{3+}$  LF exchange resonances (73 and 78 cm<sup>-1</sup>) to the frequency of the lowest optical phonon (81 cm<sup>-1</sup>), local electric polarization, and the noncollinear spin structure for the Dy-Fe magnetic system are responsible for the mode hybridization. The AOSM condition is used to explain the almost complete cancellation of the hybrid modes in the reflectivity spectra while remaining strong in the transmission spectra. One of the possible applications of the AOSM condition is for the design of antireflective coatings in the far-IR spectral range using magnetic- and metamaterials.

# 9.5 Chapter Summary

The following original results were presented in this Chapter:

- for the first time, Adjusted Oscillator Strength (AOS) formulas for a magnetoelectric material have been derived for reflection in the semi-infinite configuration and reflection and transmission in the thin film configuration.
- using the AOS formulas, the proper ratio of the size of dielectric and magnetic excitations in the optical spectra can be calculated
- for the first time, hybrid magnetic and dielectric modes in the optical spectra of a multiferroic material have been identified
- for the first time, the Adjusted Oscillator Strength Matching (AOSM) condition has been derived which completely explains the behavior of the hybrid modes in the optical spectra of Dy-IG.

### Chapter 10

# MODELING OF ELECTROMAGNETIC WAVE PROPAGATION AND SPECTRA OF OPTICAL EXCITATIONS IN COMPLEX MEDIA USING 4×4 MATRIX FORMALISM

#### **10.1 Introduction**

### **10.1.1 Motivation**

Optical spectra of complex materials, such as magneto-electric (ME) and multiferroic crystals, materials with intrinsic or artificial chirality, and metamaterials, are in the focus of modern experimental and theoretical studies. The common feature of these complex materials is that their optical properties cannot be described only with a  $3\times3$  dielectric susceptibility tensor  $\hat{\varepsilon}(\omega)$ . By analogy with *bi-axial* dielectrics, the complex materials can reveal a so-called *bi-anisotropic* optical behavior in a form of the fascinating effects, such as nonreciprocal light propagation, negative index of refraction (NIR), and polarization plane rotation. These exotic optical phenomena usually occur in a relatively narrow part of the optical spectrum. For example, the NIR effect could occur in metamaterials or multiferroics only in the GHz or THz spectral ranges, but above a certain frequency such materials behave as normal metals or dielectrics and, hence, a simple  $\varepsilon(\omega)$  function could perfectly describe their optical properties in, for example, the visible part of the spectrum. Note also that the bi-anisotropic optical phenomena, such as magneto-electric and chirality effects, are not mutually exclusive and can coexist in the same or different parts of the optical spectrum. The proper description of the bianisotropic optical effects in complex materials requires an adequate theoretical description and advanced experimental spectroscopic approaches. Calculations of the

optical *spectra* and *polarization* for complex anisotropic materials are particularly important at the resonance with the related elementary excitations, such as, i. g., electromagnons in magneto-electric materials.

Recently, spectra of electromagnons in TbMnO<sub>3</sub> multiferroic crystals have been discovered by Pimenov et al. [63]. Similar electromagnon excitations have been also observed in other related multiferroic oxides, including  $REMnO_3$  and  $REMn_2O_5$  (RE =rare earths) [64, 80-82]. The polarization selection-rules analysis for the transmission optical configuration suggested that this electromagnon mode is excited by an electric field of light, in contrast to antiferromagnetic resonance (AFMR) that can be excited by the magnetic field only. However, the polarization analysis of the electromagnon spectra has been always restricted by the experimental geometry with the normal light incidence on the sample surface. The limitations of this approach revealed themselves recently by failing to explain the experimentally-observed suppression of electromagnons in reflectivity measurements of  $GdMnO_3$  [83]. As we will see in the following, electromagnons in uniaxial crystals are not optically active in a back-reflection configuration, while transmission technique applied alone is not capable to differentiate between pure magnetic- and electric dipoles and, of course, cannot distinguish them from electromagnon-type of excitations. As we demonstrate in this Chapter, the most suitable theoretical representation of bi-anisotropic phenomena can be done with the help of the Jones and/or Mueller Matrices. Correspondingly, the most efficient experimental technique for the experimental studies of complex materials is Mueller Matrix Spectroscopic Ellipsometry (MMSE) that can be realized in both reflection and transmission configurations with variable azimuthal angle and variable angle of incidence (AOI).

The primary goal of this Chapter is to apply  $4 \times 4$  Berreman's matrix formalism to calculate polarization of the optical spectra in complex materials. We illustrate our results with examples of Mueller Matrix calculations for the far-infrared spectral range, which is mostly interesting for spectra of electromagnons in multiferroic materials. Nevertheless, these calculations are also easily applicable to a diverse group of bi-anisotropic materials, such as metamaterials and chiral structures. Our results should provide a foundation for building the adequate forward models that can be used in the experimental data analysis obtained with MMSE and other spectroscopic techniques, such as Rotating Analyzer Ellipsometry, Generalized Ellipsometry, and Transmission Polarimetry.

### **10.1.2. Modeling Approach**

Models for electromagnetic wave propagation in a medium require solutions to Maxwell's equations. These solutions, in turn, depend upon the proper characterization of the electromagnetic properties of the medium. As Weiglhofer explains in a theatrical analogy, if Maxwell's equations are a play with intricate plots, then the medium is the stage in which the electromagnetic processes take place [34]. The stage is described by a set of equations which are known as the medium's constitutive relations:

$$\vec{D} = \hat{\varepsilon}\vec{E} + \hat{\rho}\vec{H}$$

$$\vec{B} = \hat{\rho}'\vec{E} + \hat{\mu}\vec{H}$$
(10.1)

In Eq. (10.1),  $\vec{D}$  is the dielectric displacement,  $\vec{B}$  is the magnetic induction,  $\vec{E}$  is the primary electric field vector,  $\vec{H}$  is the primary magnetic field vector,  $\hat{\varepsilon}$  is the dielectric permittivity tensor,  $\hat{\mu}$  is the magnetic permeability tensor, and  $\hat{\rho}$  and  $\hat{\rho}'$  are the bi-

anisotropic tensors. Each tensor is associated with a unique physical property of the medium and can be described by a  $3\times3$  matrix [33]. Further, the physical properties of the medium, which the tensors represent, are often frequency-dependent and must be described by a set of dispersion equations. Various mathematical models including the simple harmonic oscillator (SHO) and coupled harmonic oscillator (CHO) models are usually used for these dispersion relationships. Some of these models will be considered below. In this paper, a *simple medium* is defined to have isotropic  $\hat{\varepsilon}$  and  $\hat{\mu}$  tensors but no bi-anisotropic activity. A *complex medium* will refer to all other possible tensor symmetries and allowed tensor combinations [34]. We do not consider the effects of non-linearity nor spatial dispersion in this paper. The combination of Maxwell's equations, boundary conditions, the constitutive relations, and the dispersion relations are required to derive a proper solution for electromagnetic wave propagation and to model excitations in the optical spectra.

In contrast to  $\hat{\varepsilon}$  and  $\hat{\mu}$  tensors, the bi-anisotropic tensors  $\hat{\rho}$  and  $\hat{\rho}'$  are less known and their properties require clarification. In this paper we will consider two major additive contributions to  $\hat{\rho}$  and  $\hat{\rho}'$ : the magneto-electric effect and chirality, so that:

$$\hat{\rho} = \hat{\alpha} + j \cdot \hat{\xi}$$

$$\hat{\rho}' = \hat{\alpha}' - j \cdot \hat{\xi}^{T}$$
(10.2)

One can see that the ME contribution is described by the complex tensor  $\hat{\alpha}$ , and chirality is represented by tensor  $\hat{\xi}$ . Both tensors,  $\hat{\xi}$  and  $\hat{\alpha}$ , are complex and can have both real and imaginary parts. Accordingly,  $\hat{\rho}$  and  $\hat{\rho}'$  are not expected to be the complexconjugate-transpose for each other [43]. According to Dzyaloshinskii, the corresponding ME contribution to  $\hat{\rho}'$  should be a "transpose" tensor:  $\hat{\alpha}' = \hat{\alpha}^T$ . This requirement follows from the Dzyaloshinsky's definition of  $\hat{\alpha}$  in the static case:

$$\alpha_{ij} = \frac{\partial^2 F}{\partial E_i \partial H_i} \tag{10.3}$$

At present, however, this requirement of  $\hat{\alpha}' = \hat{\alpha}^T$  for optical frequencies is under debate in the literature [32]. In the following theoretical analysis we won't implement Dzyaloshinskii's restriction and keep a general notation for the  $\hat{\rho}$  and  $\hat{\rho}'$  tensors. In any case, both  $\hat{\alpha}$  and  $\hat{\alpha}'$  have the same sign of their complex parts, so that the oscillators in both  $\hat{\alpha}$  and  $\hat{\alpha}'$  should absorb light in the transmission experiments. Tensors  $\hat{\alpha}$  and  $\hat{\alpha}'$ change sign under space inversion and time inversion operation, remaining unchanged if both operations are applied simultaneously. This property results in the requirement that  $\hat{\alpha} = \hat{\alpha}' \equiv 0$  in materials with the center of inversion or with time-reversal symmetry (see Refs. [18, 25] for more detail). In contrast to  $\hat{\alpha}$ , the chirality term  $j \cdot \hat{\xi}$  has its transposecomplex conjugate counterpart  $-i \cdot \hat{\xi}^T$  that contributes to  $\hat{\rho}'$ . For isotropic materials, Georgieva [41] showed that the chirality parameter  $\xi$ , which originates from the  $\partial \vec{H}/\partial t$ and  $\partial \vec{E}/\partial t$  terms in the Maxwell equations, scales proportionally to  $\omega$  which requires its disappearance at zero frequency:  $\xi(0) \rightarrow 0$ . In the case of a crystal, we assume that the chirality effect can also have a resonant behavior and should diminish at high frequencies:  $\xi(\infty) \rightarrow 0$ .

The main challenge to the analysis of bi-anisotropic materials is a vast number of possible tensor symmetries in the bulk crystals and thin films. The task of obtaining

analytical solutions for all possible configurations appears daunting. Fortunately,  $4 \times 4$  matrix formalism, as developed by Berreman [16], provides for an accurate and systematic method of obtaining numerical, and in some cases, analytic solutions for electromagnetic wave propagation in both simple and complex media. A complete description of electromagnetic wave propagation in a complex medium is made possible using Berreman's matrix equation [16]:

$$\begin{pmatrix} 0 & -curl \\ curl & 0 \end{pmatrix} \begin{pmatrix} \vec{E} \\ \vec{H} \end{pmatrix} = i \frac{\omega}{c} \begin{pmatrix} \hat{\varepsilon} & \hat{\rho} \\ \hat{\rho}' & \hat{\mu} \end{pmatrix} \begin{pmatrix} \vec{E} \\ \vec{H} \end{pmatrix}$$
(10.4)

In Eq. (2.52), *curl* represents the  $3\times3$  matrix operator. The first matrix on the right hand side is a  $6\times6$  matrix called the optical matrix **M**. This matrix contains all information about the constitutive relations and completely describes the anisotropic properties of the material [17]. Eq. (2.52) can be reduced to the Berreman equation which describes electromagnetic wave propagation in a crystal:

$$\frac{d\Psi}{dz} = i\frac{\omega}{c}\tilde{\Delta}\Psi \tag{10.5}$$

In Eq. (10.5),  $\Psi$  is an array of the transverse components of the electromagnetic wave  $[E_x, H_y, E_y, -H_x]^T$  in the medium and is an eigenvector of  $\tilde{\Delta}$ , where  $\tilde{\Delta}$  is a 4×4 matrix constructed from the components of the  $\hat{\varepsilon}$ ,  $\hat{\mu}$ ,  $\hat{\rho}$  and  $\hat{\rho}'$  tensors. Eq. (10.5) is at the heart of 4×4 matrix formalism. The eigenvalue and eigenvector solutions to Eq. (10.5) represent wave vectors and the transverse components of the propagating electromagnetic waves, respectively. These solutions are unique to the crystal symmetries and constitutive relations incorporated into the  $\tilde{\Delta}$  matrix.

In this paper, five different configurations of crystal symmetry and constitutive tensors will be examined. They are presented in increasing order of complexity. The five cases have been selected to illustrate both the application of  $4 \times 4$  matrix formalism as well as aspects of electromagnetic wave propagation.

Case 1 examines a medium with anisotropic  $\hat{\varepsilon}$  and  $\hat{\mu}$  tensors only  $(\hat{\rho} = \hat{\rho}' = 0)$ . This case is applicable, for example, to a system with a center of inversion or with time-reverse invariance. We consider this as the base case of our analysis because it illustrates how the eigenvalues of the  $\tilde{\Delta}$  matrix are evident not only in the eigenvectors describing the electromagnetic waves but also in the complex reflection coefficients,  $\vec{k}$  vectors and Poynting vectors associated with each polarization. Case 1 illustrates how birefringence is contained in the non-degenerate eigenvalue solutions of the  $\tilde{\Delta}$  matrix.

Case 2 examines isotropic  $\hat{\varepsilon}$  and  $\hat{\mu}$  tensors. We have presented this simple medium case second because it is an immediate consequence of Case 1. We use Case 2 to compare results obtained using 4×4 matrix formalism to the Veselago approach for materials having magnetic permeability  $\mu \neq 1$ [36].

Case 3 introduces magneto-electric tensors into the analysis by examining the case of a multiferroic material with uniaxial  $\hat{\varepsilon}$  and  $\hat{\mu}$  tensors and magneto-electric tensors having only one off-diagonal element. The results of this analysis permit the interesting observation of irreversibility in electro-magnetic wave propagation in magneto-electric crystals [25].

In Case 4, the analysis of isotropic  $\hat{\varepsilon}$ ,  $\hat{\mu}$ ,  $\hat{\rho}$  and  $\hat{\rho}'$  tensors is presented. Solutions for this symmetry are more mathematically complicated compared to the first three cases yet

still permit analytic solutions. Case 4 illustrates how anisotropy can be introduced into an isotropic crystal through the magneto-electric effect.

Finally, Case 5 analyzes anisotropic  $\hat{\varepsilon}$ ,  $\hat{\mu}$ ,  $\hat{\rho}$  and  $\hat{\rho}'$  tensors, all in orthorhombic symmetry. Case 5 illustrates how the  $\tilde{\Delta}$  matrix can be constructed for such a set of complicated constitutive relations. Case 5 will be illustrated using results of our numerical analysis. A simulation tool that covers reflectivity geometry for semi-infinite bi-anisotropic material is available in Ref. [84].

In Section 10.2, each of the five cases is analyzed in the semi-infinite configuration. The analysis follows the flowchart for  $4 \times 4$  matrix formalism outlined in Fig. 1. This procedure begins with the **M** matrix which enables the  $\tilde{\Delta}$  matrix to be calculated along with its eigenvalues and eigenvectors. From the eigenvalues, the  $\vec{k}$  vectors can be immediately determined which, in turn, allow for the analysis of possible birefringence in the medium. The eigenvectors, together with the tangential boundary conditions on  $\vec{E}$  and  $\vec{H}$  for non-magnetic incident media, provide for the solution of the complex reflection coefficients. Finally, when the *z* components of  $\vec{E}$  and  $\vec{H}$  are recovered, the Poynting Vector is returned, which can then be compared to the wave vector for analysis of possible divergence between the direction of the wave fronts and energy flow.



Fig. 10.1. Flowchart for steps in  $4 \times 4$  matrix formalism.

In Section 10.3, the procedure is applied to the thin film configuration for Cases 1 and 3, where the method takes into account interference from the multiply reflected waves at the surface boundaries. The analysis of bi-anisotropic materials in thin film configuration also allows for the calculation of the complex transmission coefficients assuming a non-magnetic substrate. In Section 10.4, the need for dispersion models for proper modeling of the response functions is examined. For Case 3, which incorporates the magneto-electric effect, the implications of dispersion for wave propagation and Negative Index of Refraction (NIR) are discussed. In Section 10.5, the interesting case of hybrid modes, *i.e.*,

electric and magnetic excitations at the same resonant frequency, is examined for variable angle of light incidence. Using the complex reflection and transmission formulas derived in previous Sections, together with the dispersion models, the condition called the Adjusted Oscillator Strength Matching is discussed. Under this condition, we show that the hybrid modes can disappear in the Reflectivity spectra but still remain strong in the transmission spectra [2]. Finally, in Section 10.6, we simulate electric, magnetic, hybrid and electromagnon modes in the Reflectivity spectra. Mueller Matrices (MM) are used to illustrate these simulations in both the frequency and AOI domains. Full MM analysis allows for the possibility of distinguishing between many of the electric, magnetic and magneto-electric effects. Simulations such as these should assist in the proper characterization of material constitutive relations through fitting of experimental data.

In recent literature, both Berreman's  $4\times4$  matrix formalism as calculation tool and Mueller Matrices as an analytical tool for optical spectra have been employed. Konstantinova *et al.* have used  $4\times4$  matrix formalism to analyze a number of crystal characteristics including optical activity [85, 86]. Mayerhofer *et al.* have recently used this approach to calculate the reflection coefficients of non-magnetic crystals with monoclinic symmetry [87]. Georgieva et al. have used the Berreman method in the analysis of chirality including the calculation of the Poynting vector [41] for optically active materials. Bahar *et al.* [88-92] and Arteaga *et al.* [93-97] have both employed Mueller Matrices extensively in the study of chiral materials. The work in this Chapter is unique because it considers the most general case of crystals comprised of the various constitutive tensors in anisotropic symmetries. This analysis is made possible through the combination of  $4\times4$  matrix formalism and the use of Mueller Matrices.
## **10.2 Semi-Infinite Configuration**

# **10.2.1** Case 1 - Orthorhombic $\hat{\varepsilon}$ and $\hat{\mu}$ Tensors; $(\rho = \rho' = 0)$

The case of a material having orthorhombic  $\hat{\varepsilon}$  and  $\hat{\mu}$  tensors will now be examined. It is assumed that this crystal has principal axes parallel to the x, y and z coordinate axes which form a right hand system with the z axis pointing downwards and the x axis pointing to the right. Radiation is incident in the x-z plane. This configuration is illustrated in Fig. 2 [1].



**Fig. 10.2.** Wave vector diagram for incident and refracted waves propagating in a complex medium.

We further assume that the  $\hat{\varepsilon}$  and  $\hat{\mu}$  tensors can be simultaneously diagonalized in the same x - y - z coordinate system. In crystals, the principal axes for  $\hat{\varepsilon}$  and  $\hat{\mu}$  tensors

rarely coincide. Accordingly, this symmetry realization is mostly applicable to metamaterials. With no magneto-electric activity, the optical matrix **M** becomes:

$$\begin{pmatrix} \boldsymbol{\varepsilon}_{xx} & 0 & 0 & 0 & 0 & 0 \\ 0 & \boldsymbol{\varepsilon}_{yy} & 0 & 0 & 0 & 0 \\ 0 & 0 & \boldsymbol{\varepsilon}_{zz} & 0 & 0 & 0 \\ 0 & 0 & 0 & \boldsymbol{\mu}_{xx} & 0 & 0 \\ 0 & 0 & 0 & 0 & \boldsymbol{\mu}_{yy} & 0 \\ 0 & 0 & 0 & 0 & 0 & \boldsymbol{\mu}_{zz} \end{pmatrix},$$
(10.6)

and the  $\tilde{\Delta}$  is a 4×4 matrix calculated to be [16]:

$$\tilde{\Delta} = \begin{pmatrix} 0 & \mu_{yy} - \frac{N_0^2 \sin(\theta_0)^2}{\varepsilon_{zz}} & 0 & 0\\ \varepsilon_{xx} & 0 & 0 & 0\\ 0 & 0 & 0 & \mu_{xx}\\ 0 & 0 & \varepsilon_{yy} - \frac{N_0^2 \sin(\theta_0)^2}{\mu_{zz}} & 0 \end{pmatrix} (10.7)$$

Inserting Eq. (10.6) and Eq. (10.7) into Eq. (3) returns four exact solutions of the form  $\psi_l(z) = \psi_l(0)e^{iq_l z}$  with l = 1, 2, 3 or 4, two for each of the *p* and *s* polarization states.  $\theta_0$  is the angle of incidence (AOI) while p(s) refers to radiation parallel (perpendicular) to the plane of incidence.  $q_{zp}$  and  $q_{zs}$  are the eigenvalues associated with *p* and *s* polarizations, respectively and constitute the *z* components of the wave vectors in the medium. These are:

$$q_{zp} = \pm \frac{\omega}{c} \sqrt{\varepsilon_{xx}} \sqrt{\mu_{yy} - \frac{N_0^2 \sin^2(\theta_0)}{\varepsilon_{zz}}}$$

$$q_{zs} = \pm \frac{\omega}{c} \sqrt{\mu_{xx}} \sqrt{\varepsilon_{yy} - \frac{N_0^2 \sin^2(\theta_0)}{\mu_{zz}}}$$
(10.8)

Given the *z* components of the wave vector in Eq. (D.1), the complete wave vectors for each of the p and s polarization states can be written as:

$$\vec{k}_{p} = \left( \left( \frac{\omega}{c} \right) N_{0} \sin\left(\theta_{0}\right), 0, \frac{\omega}{c} \sqrt{\varepsilon_{xx}} \sqrt{\mu_{yy} - \frac{N_{0}^{2} \sin^{2}\left(\theta_{0}\right)}{\varepsilon_{zz}}} \right)$$

$$\vec{k}_{s} = \left( \left( \frac{\omega}{c} \right) N_{0} \sin\left(\theta_{0}\right), 0, \frac{\omega}{c} \sqrt{\mu_{xx}} \sqrt{\varepsilon_{yy} - \frac{N_{0}^{2} \sin^{2}\left(\theta_{0}\right)}{\mu_{zz}}} \right)$$

$$(10.9)$$

The two k vectors in Eq. (10.9) identify the direction of propagation of the waves associated with each polarization. It is clear that for non normal AOI, the two k vectors will not be identical and will therefore diverge as they propagate forward (downward) into the medium. This phenomenon is known as birefringence and is evidenced by two separate forward propagating electromagnetic waves.

The eigenvector solutions (in columns) are:

$$\begin{pmatrix} 1 & 0 & 1 & 0 \\ \frac{\sqrt{\varepsilon_{xx}}}{\sqrt{\varepsilon_{xx}}} & 0 & -\frac{\sqrt{\varepsilon_{xx}}}{\sqrt{\varepsilon_{xx}}} & 0 \\ \sqrt{\mu_{yy}} - \frac{N_0^2 \sin(\theta_0)^2}{\varepsilon_{zz}} & 0 & \sqrt{\mu_{yy}} - \frac{N_0^2 \sin(\theta_0)^2}{\varepsilon_{zz}} & 0 \\ 0 & 1 & 0 & 1 \\ 0 & \sqrt{\varepsilon_{yy}} - \frac{N_0^2 \sin(\theta_0)^2}{\mu_{zz}} & 0 & -\frac{\sqrt{\varepsilon_{yy}} - \frac{N_0^2 \sin(\theta_0)^2}{\mu_{zz}}}{\sqrt{\mu_{xx}}} \end{pmatrix}$$
(10.10)

In Eq. (10.10), the eigenvectors in columns 1 and 2 represent forward propagating waves while those in columns three and four represent backward propagating waves. The eigenvectors in columns one and three are associated with the  $q_{zp}$  eigenvalue and represent p polarized radiation. A complete description of this wave involves multiplication by  $e^{\pm iq_{zp}z}$ . Similarly, the eigenvectors in columns two and four are associated with the  $q_{zs}$  eigenvalue and represent s polarized radiation. A complete description of this wave also involves multiplication by  $e^{\pm iq_{zp}z}$ . For a semi-infinite material, the two eigenvectors representing the forward propagating waves are used to calculate the complex reflection coefficients for p and s polarized radiation. The procedure for calculating the complex reflection coefficients involves matching the tangential components of the incident and reflected  $\vec{E}$  and  $\vec{H}$  fields to a linear combination of the two eigenvectors calculated at the common interface located at z = 0[16, 17]. The complex reflection coefficients are:

$$r_{pp} = \frac{\varepsilon_{xx}k_{z0} - N_0^2 q_{zp}}{\varepsilon_{xx}k_{z0} + N_0^2 q_{zp}}$$
(10.11)

$$r_{ss} = \frac{\mu_{xx}k_{z0} - q_{zs}}{\mu_{xx}k_{z0} + q_{zs}}.$$
 (10.12)

In Eq. (4.9) and Eq. (8.5),  $k_{z0} = \frac{\omega}{c} N_0 \cos(\theta_0)$  is the *z* component of the wave vector and  $N_0$  is the index of refraction in the incident medium. The eigenvectors in Eq. (10.10) can also be used to calculate the Poynting vector for each of the *p* and *s* polarized radiation states. This procedure first requires recapture of the *z* components of the  $\vec{E}$  and  $\vec{H}$  fields which were originally suppressed in the Berreman equations in order to reduce from a  $6 \times 6$  to a  $4 \times 4$  formalism. By solving the two algebraic equations associated with the initial Berreman matrices, for orthorhombic symmetry, the solutions for the *z* components are:

$$E_{z} = -\frac{H_{y}N_{0}\sin(\theta_{0})}{\varepsilon_{zz}}$$

$$H_{z} = \frac{E_{y}N_{0}\sin(\theta_{0})}{\mu_{zz}}$$
(10.13)

Eq. (10.13) can be applied to each of the *p* and *s* polarization states. Since the terms in Eq. (10.10) recur frequently in this analysis, we define  $\zeta = \sqrt{\varepsilon_{yy} - \frac{N_0^2 \sin(\theta_0)^2}{\mu_{zz}}}$  and  $\eta = \sqrt{\mu_{yy} - \frac{N_0^2 \sin(\theta_0)^2}{\varepsilon_{zz}}}$ . First consider *p* polarization. Here,  $H_z$  becomes zero and the vector fields are:

$$\vec{E} = E_x \left( 1, 0, \frac{-\sqrt{\varepsilon_{xx}} N_0 \sin(\theta_0)}{\varepsilon_{zz} \eta} \right) e^{iq_{zp}z}$$

$$\vec{H} = E_x \left( 0, \frac{\sqrt{\varepsilon_{xx}}}{\eta}, 0 \right) e^{iq_{zp}z}$$
(10.14)

The fields in Eq. (10.14) now permit the calculation of the Poynting vector,  $\vec{S} = \frac{1}{2} (\vec{E} \times \vec{H}^*)$  applicable to *p* polarization:

$$\vec{S}_{p} = \frac{1}{2} \left| E_{x} \right|^{2} \left( \left| \frac{\sqrt{\varepsilon_{xx}}}{\eta} \right|^{2} \frac{N_{0} \sin(\theta_{0})}{\varepsilon_{zz}}, 0, \left( \frac{\sqrt{\varepsilon_{xx}}}{\eta} \right)^{*} \right)$$
(10.15)

where the asterisks, \*, represents the complex conjugate operation. From Eq. (10.15), the tangent of the Poynting vector angle in the medium is:

$$\tan\left(\theta_{\bar{s}}\right)_{p} = \frac{\sqrt{\varepsilon_{xx}}N_{0}\sin\left(\theta_{0}\right)}{\varepsilon_{zz}\eta}$$
(10.16)

From Eq. (10.9), the tangent of the *k* vector angle in the medium is:

$$\tan\left(\theta_{\vec{k}}\right)_{p} = \frac{N_{0}\sin\left(\theta_{0}\right)}{\sqrt{\varepsilon_{xx}}\eta}$$
(10.17)

While the expressions in Eq. (10.16) and Eq. (10.17) are similar, a comparison shows that if  $\varepsilon_{xx} \neq \varepsilon_{zz}$  they are not identical. This analysis points out the well known observation that for a crystal with orthorhombic symmetry, the direction of the wave vector is not identical to that of the energy flow as given by the Poynting vector. For *s* polarization,  $E_z$  is zero and the fields become:

$$\vec{E} = E_{y} (0,1,0) e^{iq_{zz}z} , \qquad (10.18)$$
$$\vec{H} = E_{y} \left( -\frac{\varsigma}{\sqrt{\mu_{xx}}}, 0, \frac{N_{0} \sin(\theta_{0})}{\mu_{zz}} \right) e^{iq_{zz}z}$$

and the Poynting vector for *s* polarization is found to be:

$$\vec{S} = \frac{1}{2} \left| E_{y} \right|^{2} \left( \left| \frac{N_{0} \sin(\theta_{0})}{\mu_{zz}} \right|^{*}, 0, \left| \frac{\varsigma}{\sqrt{\mu_{xx}}} \right|^{*} \right).$$
(10.19)

From Eq. (10.19), the tangent of the Poynting vector angle for s polarization is:

$$\tan\left(\theta_{\vec{s}}\right)_{s} = \frac{\sqrt{\mu_{xx}}N_{0}\sin\left(\theta_{0}\right)}{\mu_{zz}\varsigma},$$
(10.20)

and from Eq. (10.9), the tangent of the k vector angle for s polarization is calculated to be:

$$\tan\left(\theta_{\bar{k}}\right)_{s} = \frac{N_{0}\sin\left(\theta_{0}\right)}{\sqrt{\mu_{xx}}\varsigma}.$$
(10.21)

Again, while the expressions in Eq. (10.21) and Eq. (10.20) are similar, a comparison shows that if  $\mu_{xx} \neq \mu_{zz}$  they are not identical. Accordingly, the *s* polarized state will also experience a divergence between the direction of wave propagation in the crystal and the direction of energy flow. In summary, a crystal with orthorhombic  $\hat{\varepsilon}$  and  $\hat{\mu}$  tensors will give rise to four unique vectors: one unique  $\vec{k}$  vector for each polarization and one unique  $\vec{S}$  vector for each polarization, neither of which is coincident with its corresponding wave vector. These four vectors are simulated in Fig. 10.3(b) for an imaginary material with diagonal tensor components:  $\varepsilon = (4, 6, 8)$  and  $\mu = (1, 2, 3)$ .

## **10.2.2** Case 2-Isotropic $\mathcal{E}$ and $\mu$ Tensors $(\rho = \rho' = 0)$

Case 2 deals with a simple medium described by isotropic  $\hat{\varepsilon}$  and  $\hat{\mu}$  tensors. The **M** matrix for isotropic symmetry is given by:

$$\begin{pmatrix} \varepsilon & 0 & 0 & 0 & 0 & 0 \\ 0 & \varepsilon & 0 & 0 & 0 & 0 \\ 0 & 0 & \varepsilon & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu \end{pmatrix}$$
 (10.22)

Conclusions regarding this symmetry are immediately available from the previous case by setting  $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = \varepsilon$  and  $\mu_{xx} = \mu_{yy} = \mu_{zz} = \mu$ . A key result is the degeneracy of the eigenvalues:

$$q_{zp} = \frac{\omega}{c} \sqrt{\varepsilon \mu - N_0^2 \sin^2(\theta_0)}$$
(10.23)  
$$q_{zs} = \frac{\omega}{c} \sqrt{\varepsilon \mu - N_0^2 \sin^2(\theta_0)}$$

According to Eq. (10.23), for an isotropic crystal, there will be no birefringence that existed for the orthorhombic symmetry of Case 1. Both electromagnetic waves will, of course, follow identical paths. In addition, from Eqs. (10.16), (10.17), (10.20) and (10.21) it is clear that the direction of energy flow is also identical to the direction of wave propagation. This configuration is simulated in Fig. 10.3(a) for a material with diagonal tensor components:  $\varepsilon = (4, 4, 4)$  and  $\mu = (2, 2, 2)$ , where all four vectors are coincident.



**Fig. 10.3** Wave vector  $\vec{k}$  and Poynting vector  $\vec{S}$  in for various symmetries and tensor combinations given in the table below. Unless otherwise indicated, diagonal tensor components are given.  $\vec{k}$  for *p* and *s* polarizations are solid green and solid red lines, respectively.  $\vec{S}$  for *p* and *s* polarizations are dotted green and dotted red lines, respectively.

Plot	Symmetry	$\hat{oldsymbol{arepsilon}}$	û	$\hat{ ho}$	$\hat{ ho}$ '
(a)	Case 2	(4,4,4)	(2,2,2)	-	-
(b)	Case 1	(4,6,8)	(1,2,3)	-	-
(c)	Case 3	(4,4,5)	(2,2,3)	$\rho_{xy} = 3$	$\rho'_{xy} = 3$
(d)	Case 3	(4,4,4)	(2,2,2)	$\rho_{xy} = 3$	$\rho'_{xy} = 3$

This case also illustrates how Veselago's approach for materials with  $\mu \neq 1$  is automatically incorporated into the results using 4×4 matrix formalism via the solution

of Maxwell's equations. For radiation normally incident from vacuum, Eq. (8.5) reduces to:

$$r_{ss} = \frac{\sqrt{\frac{\mu}{\varepsilon}} - 1}{\sqrt{\frac{\mu}{\varepsilon}} + 1}$$
(10.24)

For a non-magnetic material, Fresnel's reflection coefficient is given by:  $r_{ss} = \frac{n_1 - n_2}{n_1 + n_2}$ 

where  $n = \sqrt{\varepsilon}$  [51]. However, for a semi-infinite isotropic magnetic material, Veselago explained that *n* should not be replaced by  $\sqrt{\varepsilon \mu}$  but rather by  $\sqrt{\varepsilon \mu} = 1/z$  where *z* is the wave impedance [36, 37]. The formula for the reflection coefficient then becomes:  $r_{ss} = \frac{z_2 - z_1}{z_2 + z_1}$ . This expression is identical to Eq. (10.24) which is derived using 4×4

matrix formalism.

## **10.2.3 Case 3-Anisotropic** $\hat{\varepsilon}$ and $\hat{\mu}$ **Tensors; Off-diagonal Magneto-Electric Tensors**.

In Case 3, we introduce the magneto-electric effect in which a polarization  $\vec{P}$  may be induced by the application of magnetic field  $\vec{H}$ , and a magnetization  $\vec{M}$  may be induced from the application of electric field  $\vec{E}$  [18]. There is much debate surrounding the theoretical explanation of these coupling mechanisms. The effect is modeled through the magneto-electric tensors,  $\hat{\rho}$  and  $\hat{\rho}'$ , which couple the response functions of a magnetoelectric material. In the case of zero chirality ( $\xi = 0$ ),  $\hat{\rho} = \hat{\alpha}$  and  $\hat{\rho}' = \hat{\alpha}'$ . As we mentioned in Introduction, in the static case,  $\alpha'$  is the transpose of  $\alpha$ . For the dynamic case, this relationship does not necessarily hold [32]. We note that other variables can be used to describe magneto-electric tensors in the  $(\vec{E}, \vec{B})$  basis [18, 32]. In this paper we use the  $(\vec{E}, \vec{H})$  basis because is the most convenient for the 4×4 formalism. Crystal symmetry plays a critical role in correctly defining the **M** matrix for magneto-electric and multiferroic materials. For example, the requirement that  $\hat{\rho} = \hat{\alpha} \neq 0$  infers a simultaneous absence of both center of inversion and the time-reverse invariance. In symmetry terms, these constraints limit the number of possible magnetic point groups to 58 where the magneto-electric effect is possible [25].

Recent theoretical studies have included derivations of magneto-electric symmetries for spiral magnetic ordering. It has been shown that the magneto-electric tensor for a cycloidal distribution, such as found in *R*MnO<sub>3</sub> compounds (*R*=rare earth), has only one non-zero element,  $\rho_{xy}$  [32]. For hexagonal crystals of HoMnO<sub>3</sub> [11], the  $\hat{\varepsilon}$  and  $\hat{\mu}$  tensors are uniaxial [33]. For the  $\hat{\varepsilon}$  tensor we use:  $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{\perp}$  and  $\varepsilon_{zz} = \varepsilon_p$ ; for the  $\hat{\mu}$  tensor we use  $\mu_{xx} = \mu_{yy} = \mu_{\perp}$  and  $\mu_{zz} = \mu_p$ . For this configuration, the **M** matrix for cycloidal magnetic ordering becomes:

$$\begin{pmatrix} \varepsilon_{\perp} & 0 & 0 & 0 & \rho & 0 \\ 0 & \varepsilon_{\perp} & 0 & 0 & 0 & 0 \\ 0 & 0 & \varepsilon_{p} & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu_{\perp} & 0 & 0 \\ \rho' & 0 & 0 & 0 & \mu_{\perp} & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu_{p} \end{pmatrix},$$
(10.25)

and its associated  $\tilde{\Delta}$  matrix is calculated to be:

$$\begin{pmatrix} \rho' & \mu_{\perp} - \frac{N_0^2 \sin(\theta_0)^2}{\varepsilon_p} & 0 & 0\\ \varepsilon_{\perp} & \rho & 0 & 0\\ 0 & 0 & 0 & \mu_{\perp} \\ 0 & 0 & \varepsilon_{\perp} - \frac{N_0^2 \sin(\theta_0)^2}{\mu_p} & 0 \end{pmatrix}.$$
(10.26)

Inserting the  $\tilde{\Delta}$  matrix in Eq. (10.26) into the Berreman equation (see Eq. (10.5)) returns the following four eigenvalue solutions:

$$q_{1} = \frac{\omega}{2c} \left( \rho + \rho' + \sqrt{\left(\rho - \rho'\right)^{2} + 4\varepsilon_{\perp}\mu_{\perp} - \frac{4\varepsilon_{\perp}N_{0}^{2}\sin\left(\theta_{0}\right)^{2}}{\varepsilon_{p}}} \right)$$

$$q_{2} = \frac{\omega}{c} \sqrt{\mu_{\perp} \left(\varepsilon_{\perp} - \frac{N_{0}^{2}\sin\left(\theta_{0}\right)^{2}}{\mu_{p}}\right)}$$

$$q_{3} = \frac{\omega}{2c} \left(\rho + \rho' - \sqrt{\left(\rho - \rho'\right)^{2} + 4\varepsilon_{\perp}\mu_{\perp} - \frac{4\varepsilon_{\perp}N_{0}^{2}\sin\left(\theta_{0}\right)^{2}}{\varepsilon_{p}}} \right)$$

$$q_{4} = -\frac{\omega}{c} \sqrt{\mu_{\perp} \left(\varepsilon_{\perp} - \frac{N_{0}^{2}\sin\left(\theta_{0}\right)^{2}}{\mu_{p}}\right)}$$
(10.27)

In Eq. (10.27),  $q_1$  and  $q_3$  are associated with p polarized radiation and at normal incidence ( $\theta_0 = 0$ ), these wave vectors reduce to exactly those derived in Ref. [32].  $q_1$  and  $q_3$  represent forward and backward propagating waves, respectively. The wave vectors  $q_2$  and  $q_4$  are associated with s polarized radiation and are similar in form to those derived for s polarization in Case 1. Here  $\varepsilon_{yy} = \varepsilon_{xx}$  as required to model uniaxial

symmetry. With these derivations for the z components, the complete description of the wave vectors for both polarization states is:

$$\vec{k}_{p} = \left( \left( \frac{\omega}{c} \right) N_{0} \sin\left(\theta_{0}\right), 0, \frac{\omega}{2c} \left( \rho + \rho' + \sqrt{\varepsilon_{\perp}} \sqrt{\frac{\left(\rho - \rho'\right)^{2}}{\varepsilon_{\perp}}} + 4\mu_{\perp} - \frac{4N_{0}^{2} \sin\left(\theta_{0}\right)^{2}}{\varepsilon_{p}} \right) \right)$$

$$(10.28)$$

$$\vec{k}_{s} = \left( \left( \frac{\omega}{c} \right) N_{0} \sin\left(\theta_{0}\right), 0, \frac{\omega}{c} \sqrt{\mu_{\perp}} \sqrt{\left( \varepsilon_{\perp} - \frac{N_{0}^{2} \sin\left(\theta_{0}\right)^{2}}{\mu_{p}} \right)} \right)$$

As is evident in Eq. (10.28), this magneto-electric crystal will display birefringence as the two wave vectors will diverge in the direction of propagation (see Fig. 10.3(c)). Of course, this result is expected for a uniaxial crystal. However, even if we had assumed isotropic  $\hat{\varepsilon}$  and  $\hat{\mu}$  tensors (which were not birefringent in Case 2), as can be seen from Eq. (10.28), the birefringence would still have been in effect due to the presence of the magneto-electric tensors (see Fig. 10.3(d)). With the definition  $\frac{4\varepsilon N^2 \sin(\theta)^2}{2}$ 

 $q_{a} = \sqrt{\left(\rho - \rho'\right)^{2} + 4\varepsilon_{\perp}\mu_{\perp} - \frac{4\varepsilon_{\perp}N_{0}^{2}\sin\left(\theta_{0}\right)^{2}}{\varepsilon_{p}}}, \text{ the associated eigenvectors (in columns) are:}$ 

$$\begin{pmatrix} 1 & 0 & 1 & 0 \\ \frac{2\varepsilon_{\perp}}{\rho' - \rho + q_a} & 0 & \frac{2\varepsilon_{\perp}}{\rho' - \rho - q_a} & 0 \\ 0 & 1 & 0 & 1 \\ & & \sqrt{\varepsilon_{\perp} - \frac{N_0^2 \sin(\theta_0)^2}{\mu_p}} & & \sqrt{\varepsilon_{\perp} - \frac{N_0^2 \sin(\theta_0)^2}{\mu_p}} \\ 0 & \frac{\sqrt{\varepsilon_{\perp} - \frac{N_0^2 \sin(\theta_0)^2}{\mu_p}}}{\sqrt{\mu_{\perp}}} & 0 & - \frac{\sqrt{\varepsilon_{\perp} - \frac{N_0^2 \sin(\theta_0)^2}{\mu_p}}}{\sqrt{\mu_{\perp}}} \end{pmatrix}$$
(10.29)

In Eq. (10.29), the first column is the eigenvector associated with  $q_1$  while the second and fourth columns are associated with  $q_2$ . Their complete descriptions require multiplication by  $e^{iq_1z}$  and  $e^{\pm iq_2z}$ , respectively. The third column is associated with  $q_3$  and its complete description requires multiplication by  $e^{-iq_3z}$ . As stated earlier,  $q_{1,2}$  are the z components of the wave vectors of the forward propagating waves while  $q_{3,4}$  are the z components of the wave vectors of the backward propagating waves. The eigenvectors in columns one and three are influenced by the magneto-electric effect. The forward propagating eigenvectors when combined with the tangential boundary conditions for  $\vec{E}$ and  $\vec{H}$  return the complex reflection coefficients which make up the Jones matrix:

$$\begin{pmatrix} \frac{2\varepsilon_{\perp}\cos(\theta_{0}) - N_{0}(\rho' - \rho + q_{a})}{2\varepsilon_{\perp}\cos(\theta_{0}) + N_{0}(\rho' - \rho + q_{a})} & 0 \\ 0 & \frac{N_{0}\sqrt{\mu_{\perp}}\cos(\theta_{0}) - \sqrt{\varepsilon_{\perp} - \frac{N_{0}^{2}\sin(\theta_{0})^{2}}{\mu_{p}}}}{N_{0}\sqrt{\mu_{\perp}}\cos(\theta_{0}) + \sqrt{\varepsilon_{\perp} - \frac{N_{0}^{2}\sin(\theta_{0})^{2}}{\mu_{p}}}} \end{pmatrix}$$
(10.30)

As will be discussed later, with proper dispersion relations for the  $\hat{\varepsilon}$ ,  $\hat{\mu}$  and  $\hat{\rho}$  tensors, the reflectivity spectra for this crystal can be simulated using Eq. (10.30).

The presence of three distinct eigenvalues for  $\tilde{\Delta}$  matrix gives rise to the interesting phenomenon of the irreversibility of the *p* polarized wave propagation. The wave propagation associated with wave vectors  $q_1$  and  $q_3$  is irreversible because they represent different phase velocities [32]. The same path will not be followed for each the forward and backward propagating waves. On the other hand,  $q_2$  and  $q_4$  are clearly reversible because the electro-magnetic effect is not picked up for *s* polarized incident radiation. It also shows that optical reflectivity spectra measured for *s* polarized radiation not sensitive to magneto-electric excitations. As previously explained, the *s* polarized eigenvalues are entirely consistent with those of Case 1 for after adjusting for uniaxial symmetry.

As in the previous two cases, through  $4 \times 4$  matrix formalism, comparisons can be made between the direction of propagation and the direction of energy flow. For this crystal symmetry, the formulas for the recapture of the *z* components of  $\vec{E}$  and  $\vec{H}$  vectors are identical to those in Eq. (10.13) derived in Case 1. We restrict our analysis to the wave influenced by the magneto-electric effect. For the  $q_1$  eigenvalue, the complete expressions for  $\vec{E}$  and  $\vec{H}$  are:

$$\vec{E} = E_x \left( 1, 0, \frac{-2\varepsilon_{\perp} N_0 \sin(\theta_0)}{\varepsilon_p \left(\rho' - \rho + q_a\right)} \right) e^{iq_1 z}$$

$$\vec{H} = E_x \left( 0, \frac{2\varepsilon_{\perp}}{\rho' - \rho + q_a}, 0 \right) e^{iq_1 z}$$
(10.31)

and the associated Poynting vector is calculated to be :

$$\vec{S}_{q1} = \left( \left| \frac{\varepsilon_{\perp}}{(\rho - \rho' + q_a)} \right|^2 \frac{2N_0 \sin(\theta_0)}{\varepsilon_p}, 0, \left( \frac{\varepsilon_{\perp}}{\rho' - \rho + q_a} \right)^* \right)$$
(10.32)

From Eq. (10.32), the tangent of the S vector angle in the medium is:

$$\tan\left(\theta_{s}\right) = \frac{2\varepsilon_{\perp}N_{0}\sin\left(\theta_{0}\right)}{\varepsilon_{p}\left(\rho' - \rho + q_{a}\right)}$$
(10.33)

Similarly, from Eq. (10.28), the tangent of the k vector angle in the medium is:

$$\tan\left(\theta_{k}\right) = \frac{2N_{0}\sin\left(\theta_{0}\right)}{\left(\rho + \rho' + q_{a}\right)}$$
(10.34)

Again, while Eq. (10.33) and Eq. (10.34) are similar in form, they are not identical. As a result, there will be a divergence between the direction of wave propagation  $\vec{k}$  and the direction of energy flow  $\vec{S}$ . As was shown in Case 1, for the *s* polarization state, the  $\vec{k}$  and  $\vec{S}$  vectors are also not coincident. This configuration is simulated in Fig. 10.3(c) for a material with diagonal tensors:  $\varepsilon = (4,4,5)$  and  $\mu = (2,2,3)$  and  $\rho_{xy} = 3$ . Again, all four vectors are distinct.

Finally, in addition to deriving the properties of birefringence and irreversibility, 4×4 matrix formalism allows for the derivation of certain energy constraints pertaining to the magneto-electric crystal. From Eq. (10.27), it can be shown that the backward propagating wave,  $q_3$ , becomes zero at normal incidence when  $\rho \rho' = \varepsilon_{\perp} \mu_{\perp}$ . Under this constraint, this wave will not propagate inside the crystal as the only remaining non-zero component of this wave vector is in the *x* direction.

### **10.2.4.** Case 4-Isotropic $\hat{\varepsilon}$ and $\hat{\mu}$ Tensors; Isotropic Magneto-Electric Tensors

In Case 4, the constitutive relationships are described by simultaneously diagonalized isotropic tensors. While this configuration is not strictly allowed given symmetry constraints, for certain multiferroic crystals and polycrystalline materials, the anisotropy is small and the crystal can be effectively modeled using the isotropic assumption. The corresponding optical matrix **M** is:

$$\begin{pmatrix} \varepsilon & 0 & 0 & \rho & 0 & 0 \\ 0 & \varepsilon & 0 & 0 & \rho & 0 \\ 0 & 0 & \varepsilon & 0 & 0 & \rho \\ \rho' & 0 & 0 & \mu & 0 & 0 \\ 0 & \rho' & 0 & 0 & \mu & 0 \\ 0 & 0 & \rho' & 0 & 0 & \mu \end{pmatrix}$$
(10.35)

The associated  $\tilde{\Delta}$  matrix is:

$$\tilde{\Delta} = \begin{pmatrix} 0 & \mu - \frac{\mu N_0^2 \sin(\theta_0)^2}{\epsilon \mu - \rho \rho'} & \rho' - \frac{\rho N_0^2 \sin(\theta_0)^2}{\epsilon \mu - \rho \rho'} & 0 \\ \varepsilon & 0 & 0 & -\rho \\ \rho' & 0 & 0 & \mu \\ 0 & \rho - \frac{\rho' N_0^2 \sin(\theta_0)^2}{\epsilon \mu - \rho \rho'} & \varepsilon - \frac{\epsilon N_0^2 \sin(\theta_0)^2}{\epsilon \mu - \rho \rho'} & 0 \end{pmatrix}$$
(10.36)

which has the following four eigenvalue solutions:

$$q_{z1,z3} = \pm \frac{\omega}{c} \sqrt{\frac{2\varepsilon\mu - (\rho^2 + {\rho'}^2) + (\rho - \rho')K - 2N_0^2 \sin^2(\theta_0)}{2}}$$
$$q_{z2,z4} = \pm \frac{\omega}{c} \sqrt{\frac{2\varepsilon\mu - (\rho^2 + {\rho'}^2) - (\rho - \rho')K - 2N_0^2 \sin^2(\theta_0)}{2}}$$
(10.37)

Using Eq. (10.37),  $K = \sqrt{(\rho + \rho')^2 - 4\epsilon\mu}$ . The two  $\vec{k}$  vectors in the medium are  $\left(\frac{\omega}{c}N_0\sin(\theta_0), 0, q_{z1}\right)$  and  $\left(\frac{\omega}{c}N_0\sin(\theta_0), 0, q_{z2}\right)$ . For  $\rho = \rho'$  the wave vectors are

identical and there will be no birefringence. However, for  $\rho \neq \rho'$ , which is possible in the dynamic case and/or in the medium with chirality,  $q_{z1} \neq q_{z2}$  and there will be two refracted waves with the direction of each wave being influenced by the combination of the  $\varepsilon$ ,  $\mu$ ,  $\rho$  and  $\rho'$  parameters. This material is bi-anisotropic and behaves similar to a

birefringent one. For  $\rho \neq \rho'$ , the magneto-electric tensors introduce birefringence even in the presence of isotropic  $\hat{\varepsilon}$  and  $\hat{\mu}$ . In Eq. (10.37), the positive signs indicate forward propagating waves while the negative signs indicate backward propagating waves. Note that the phase is identical for both forward and backward propagating waves. Reversibility for this configuration is expected, of course, given that all tensors are isotropic. For  $\rho \neq \rho'$ , the eigenvector solutions  $([E_x, H_y, E_y, -H_x]^T)$ , in columns, for the

 $\tilde{\Delta}$  matrix are:

$$\begin{pmatrix} 1 & 1 & 1 & 1 \\ \frac{-c\Xi Lq_{z1}}{\omega\mu\left[\Xi M + QN_0^2\sin^2(\theta_0)\right]} & \frac{c\Xi Lq_{z1}}{\omega\mu\left[\Xi M + QN_0^2\sin^2(\theta_0)\right]} & \frac{c\Xi Uq_{z2}}{\omega\mu\left[\Xi Q + MN_0^2\sin^2(\theta_0)\right]} & \frac{-c\Xi Uq_{z2}}{\omega\mu\left[\Xi Q + MN_0^2\sin^2(\theta_0)\right]} \\ \frac{2c\Xi q_{z1}}{\omega\left[\Xi M + QN_0^2\sin^2(\theta_0)\right]} & \frac{-2c\Xi q_{z1}}{\omega\left[\Xi M + QN_0^2\sin^2(\theta_0)\right]} & \frac{-2c\Xi q_{z2}}{\omega\left[\Xi Q + MN_0^2\sin^2(\theta_0)\right]} & \frac{2c\Xi q_{z2}}{\omega\left[\Xi Q + MN_0^2\sin^2(\theta_0)\right]} \\ \frac{L}{2\mu} & \frac{L}{2\mu} & \frac{U}{2\mu} & \frac{U}{2\mu} \end{pmatrix}$$

$$(10.38)$$

where

$$\Xi = \rho \rho' - \varepsilon \mu$$

$$K = \sqrt{(\rho + \rho')^2 - 4\varepsilon \mu}$$

$$L = \rho + \rho' - K$$

$$M = -\rho + \rho' + K$$

$$Q = \rho - \rho' + K$$

$$U = \rho + \rho' + K$$
(10.39)

As can be seen in Eq. (10.38), there are four distinct eigenvector solutions. The first two columns of Eq. (10.38) are associated with the  $q_{z1}$  eigenvalue and their complete description requires multiplication by  $e^{\pm iq_{z1}z}$ . The last two columns are associated with the  $q_{z2}$  eigenvalue and their complete description requires multiplication by  $e^{\pm iq_{z2}z}$ .

Completing the reflection calculation using  $4 \times 4$  matrix formalism returns four complex reflection coefficients:

$$r_{pp} = -\frac{2q_{z1}q_{z2}K + 2k_{0}^{2}K(\rho\rho' - \varepsilon\mu) - k_{0}(\varepsilon - \mu)[q_{z1}(\rho - \rho' + K) + q_{z2}(-\rho + \rho' + K)]}{2q_{z1}q_{z2}K + 2k_{0}^{2}K(-\rho\rho' + \varepsilon\mu) + k_{0}(\varepsilon + \mu)[q_{z1}(\rho - \rho' + K) + q_{z2}(-\rho + \rho' + K)]}$$

$$r_{ps} = \frac{2k_{0}\{-q_{z1}\rho K - q_{z2}\rho K - (q_{z1} - q_{z2})[\rho(\rho + \rho') - 2\varepsilon\mu]\}}{2q_{z1}q_{z2}K + 2k_{0}^{2}K(-\rho\rho' + \varepsilon\mu) + k_{0}(\varepsilon + \mu)[q_{z1}(\rho - \rho' + K) + q_{z2}(-\rho + \rho' + K)]}$$

$$r_{sp} = \frac{2k_{0}\{-q_{z1}\rho' K - q_{z2}\rho' K + (q_{z1} - q_{z2})[\rho'(\rho + \rho') - 2\varepsilon\mu]\}}{2q_{z1}q_{z2}K + 2k_{0}^{2}K(-\rho\rho' + \varepsilon\mu) + k_{0}(\varepsilon + \mu)[q_{z1}(\rho - \rho' + K) + q_{z2}(-\rho + \rho' + K)]}$$

$$r_{ss} = -\frac{2q_{z1}q_{z2}K + 2k_0^2K(\rho\rho' - \varepsilon\mu) + k_0(\varepsilon - \mu)[q_{z1}(\rho - \rho' + K) + q_{z2}(-\rho + \rho' + K)]}{2q_{z1}q_{z2}K + 2k_0^2K(-\rho\rho' + \varepsilon\mu) + k_0(\varepsilon + \mu)(q_{z1}(\rho - \rho' + K) + q_{z2}(-\rho + \rho' + K))}$$
(10.40)

Compared to the previous cases, we see that the off-diagonal Jones matrix elements are occupied. As expected, if  $\rho$  and  $\rho'$  are identically zero, the off-diagonal elements vanish and  $r_{pp}$  and  $r_{ss}$  reduce to previously calculated results for the p and s polarized reflection coefficients for a non magneto-electric semi-infinite medium [1]. For this symmetry, the formulas for recapture of the z components of  $\vec{E}$  and  $\vec{H}$  vectors are more complicated than for the previous cases and are given by:

$$E_{z} = N_{0} \sin\left(\theta_{0}\right) \left(\frac{E_{y}\rho + H_{y}\mu}{\rho\rho' - \varepsilon\mu}\right)$$

$$H_{z} = -N_{0} \sin\left(\theta_{0}\right) \left(\frac{H_{y}\rho' + E_{y}\varepsilon}{\rho\rho' - \varepsilon\mu}\right)$$
(10.41)

We again note that the solutions in Eq. (10.41) can be applied to both eigenvectors. For purposes of illustration, we will analyze propagation associated with the  $q_{z1}$  eigenvalue only. For  $q_{z1}$ , the electromagnetic fields in the medium are:

$$\vec{E} = \left(1, \frac{2c(\rho\rho - \varepsilon\mu)q_{z1}}{\omega\left[(\rho\rho - \varepsilon\mu\right)M + QN_0^2\sin^2(\theta_0)\right]}, N_0\sin(\theta_0)\frac{c}{\omega\left[(\rho\rho - \varepsilon\mu)M + QN_0^2\sin^2(\theta_0)\right]}\right)e^{iq_{z1}z}$$

$$\vec{H} = \left(-\frac{L}{2\mu}, \frac{-c\left(\rho\rho' - \varepsilon\mu\right)Lq_{z1}}{\omega\mu\left[\left(\rho\rho' - \varepsilon\mu\right)M + QN_0^2\sin^2\left(\theta_0\right)\right]}, N_0\sin\left(\theta_0\right)\frac{c}{\omega}\frac{+q_{z1}\left(L\rho' - 2\varepsilon\mu\right)}{\mu\left[\left(\rho\rho' - \varepsilon\mu\right)M + QN_0^2\sin^2\left(\theta_0\right)\right]}\right)}e^{iq_{z1}z}$$
(10.42)

The *y* and *z* component terms in Eq. (10.42) are dependent upon the angle of incidence  $\theta_0$ . Therefore, it is interesting to note that even at normal incidence, the eigenvector solutions will have both *x* and *y* components for each of  $\vec{E}$  and  $\vec{H}$ . Accordingly, while still vibrating in the x-y plane, the magneto-electric effect causes the eigenvector to be rotated off the principal axes as it propagates into the material. This suggests that modeling of bi-anisotropic activity can be implemented using planar thin film layers each having different values for the response function tensors. This is different from orthorhombic  $\hat{\varepsilon}$  and  $\hat{\mu}$  (Case 1), for example, where the eigenvectors remain on the principal axes only (see Eq. (10.10). For general AOI, the calculation of the Poynting vector,  $\vec{S} = \frac{1}{2}\vec{E} \times \vec{H}^*$ , is a complicated algebraic expression and proper modeling requires a numerical approach. Analytically, it can be shown that at normal incidence ( $\theta_0 = 0$ ), both the  $\vec{k}$  and  $\vec{S}$  vectors are parallel with propagation along the *z* axis only, as expected

for this trivial case. Numerical simulations show that for variable AOI, the two Poynting vectors are coincident with the two  $\vec{k}$  vectors. We ascribe this to the isotropic symmetry assumption for the  $\rho$  tensor. We simulate this material having diagonal tensors:  $\varepsilon = (4, 4, 4)$  and  $\mu = (2, 2, 2)$  and  $\rho = (2.5, 2.5, 2.5)$ . Fig. 10.4(a) illustrates that all four vectors are coincident. However, if the medium is chiral, it can be shown that birefringence will result.

Finally, it should be noted that at normal incidence,  $q_{z1}$  and  $q_{z3}$  vanish when  $\rho \rho' = \epsilon \mu$ . This condition results in the fascinating outcome whereby the wave vector will not penetrate the medium and will continue along the *x* axis only. This condition, derived using 4×4 matrix formalism, is consistent with the thermodynamically derived limitation that the square of the magneto-electric susceptibility must be less than the geometric mean of the diagonalized  $\hat{\epsilon}$  and  $\hat{\mu}$  tensors [21, 98]. We note further that the condition  $\rho \rho' = \epsilon \mu$  is identical to the condition in Case 3 which was derived using a completely different symmetry for the  $\hat{\rho}$  tensor. This configuration is modeled in Fig. 10.4(b) for a material with diagonal tensors:  $\epsilon = (4, 4, 4)$  and  $\mu = (2, 2, 2)$  and  $\rho = (\sqrt{8}, \sqrt{8}, \sqrt{8})$ .



**Figure. 10.4** Wave vector  $\vec{k}$  and Poynting vector  $\vec{S}$  in for various symmetries and tensor combinations given in the table below. Unless otherwise indicated, diagonal tensor components are given.  $\vec{k}$  for *p* and *s* polarizations are solid green and solid red lines, respectively.  $\vec{S}$  for *p* and *s* polarizations are dotted green and dotted red lines, respectively.

Plot	Symmetry	$\hat{\mathcal{E}}$	û	ρ	$\hat{ ho}$ '
(a)	Case 4	(4,4,4)	(2,2,2)	(2.5,2.5,2.5)	(2.5,2.5,2.5)
(b)	Case 4	(4,4,4)	(2,2,2)	$\left(\sqrt{8},\sqrt{8},\sqrt{8}\right)$	$\left(\sqrt{8},\sqrt{8},\sqrt{8}\right)$
(c)	Case5	(4,6,8)	(3,4,5)	(1,2,3)	(1,2,3)
(d)	Case 1	(-4,-6,-8)	(-1,-2,-3)	-	-

## **10.2.5** Case 5-Anisotropic $\hat{\varepsilon}$ and $\hat{\mu}$ Tensors; Anisotropic Magneto-Electric Tensors

In Case 5, the configuration of anisotropic  $\hat{\varepsilon}$ ,  $\hat{\mu}$  and magneto-electric tensors is examined. Orthorhombic symmetry, which is appropriate for crystals belonging to the 222 point group, is chosen for each tensor [25, 33]. The **M** matrix for this configuration is:

$$\begin{pmatrix} \varepsilon_{xx} & 0 & 0 & \rho_{xx} & 0 & 0 \\ 0 & \varepsilon_{yy} & 0 & 0 & \rho_{yy} & 0 \\ 0 & 0 & \varepsilon_{zz} & 0 & 0 & \rho_{zz} \\ \rho'_{xx} & 0 & 0 & \mu_{xx} & 0 & 0 \\ 0 & \rho'_{yy} & 0 & 0 & \mu_{yy} & 0 \\ 0 & 0 & \rho'_{zz} & 0 & 0 & \mu_{zz} \end{pmatrix},$$
(10.43)

and its associated  $\tilde{\Delta}$  matrix is calculated as:

$$\tilde{\Delta} = \begin{pmatrix} 0 & \mu_{yy} - \frac{\mu_{zz} N_0^2 \sin(\theta_0)^2}{\varepsilon_{zz} \mu_{zz} - \rho_{zz} \rho'_{zz}} & \rho'_{yy} - \frac{\rho_{zz} N_0^2 \sin(\theta_0)^2}{\varepsilon_{zz} \mu_{zz} - \rho_{zz} \rho'_{zz}} & 0 \\ \varepsilon_{xx} & 0 & 0 & -\rho_{xx} \\ \rho'_{xx} & 0 & 0 & \mu_{xx} \\ 0 & \rho_{yy} - \frac{\rho'_{zz} N_0^2 \sin(\theta_0)^2}{\varepsilon_{zz} \mu_{zz} - \rho_{zz} \rho'_{zz}} & \varepsilon_{yy} - \frac{\varepsilon_{zz} N_0^2 \sin(\theta_0)^2}{\varepsilon_{zz} \mu_{zz} - \rho_{zz} \rho'_{zz}} & 0 \end{pmatrix}$$
(10.44)

In Eq. (10.44), it can be seen that all direction components of each tensor enter into the  $\tilde{\Delta}$  matrix. With 12 different variables entering into the calculation, the analytic solution for the wave vectors is quite complicated. Accordingly, this is an example of a configuration which requires numerical analysis for proper modeling. This configuration is simulated in Fig. 10.4(c) for a material with diagonal tensors:  $\varepsilon = (4, 6, 8)$  and  $\mu = (3, 4, 5)$  and  $\rho = (1, 2, 3)$ . As expected, all four vectors are distinct.

We again note that the condition  $\varepsilon_{zz}\mu_{zz} = \rho_{zz}\rho'_{zz}$  causes the solutions for this symmetry to diverge. In this case, singularities will occur in the denominators in the first and fourth rows of Eq. (10.44) and no solutions for the Del matrix are possible.

#### **10.3 Thin Film Configuration**

The analytical procedures for thin films using  $4 \times 4$  matrix formalism are identical to those of the semi-infinite configuration up to the calculation of the complex reflection and transmission coefficients. In the following analysis, we restrict our work to a single layer thin film structure with the thickness *d*. For this configuration, both forward and backward propagating waves (*i.e.*, all four eigenvectors) are needed to satisfy the electromagnetic boundary conditions at both top and bottom interfaces. The tangential components of the electric and magnetic field vectors are matched at z=0 and z=d to produce two generalized field vectors  $\psi(0)$  and  $\psi(d)$ , respectively. A thin film layer matrix *L* is utilized to relate the fields inside the film of thickness *d* at its two boundaries [16, 17]:

$$\psi(d) = L\psi(0) \tag{10.45}$$

L is a 4×4 matrix calculated from the eigenvalues and eigenvectors of the  $\tilde{\Delta}$  matrix according to:

$$L(d) = \tilde{\Psi}^* K(d)^* \tilde{\Psi}^{-1}$$
(10.46)

In Eq. (8.7),  $\tilde{\Psi}$  is composed of the four  $\tilde{\Delta}$  eigenvectors as columns while *K* is a diagonal matrix given by  $K_{ll} = e^{iq_l d}$  with  $q_l$  representing the four eigenvalues of  $\tilde{\Delta}$ . After

some algebra relating the incident and reflected waves, the complex reflection and transmission coefficients for a thin film can be calculated.

## **10.3.1 Case 1- Anisotropic** $\hat{\varepsilon}$ and $\hat{\mu}$ **Tensors; No Magneto-Electric Activity**

Analytic expressions for the case of orthorhombic  $\hat{\varepsilon}$  and  $\hat{\mu}$  for both *p* and *s* polarizations have been given in Ref. [1]. For purposes of comparison to other material symmetries, the equations are reproduced here. The complex reflection and transmission coefficients for *p* polarized radiation are:

$$r_{pp} = \frac{q_{zp} \cos(q_{zp}d) \left(\frac{N_2}{N_0} k_{z0} - \frac{N_0}{N_2} k_{z2}\right) + i \left(\frac{N_0 N_2 q_{zp}^2}{\varepsilon_{xx}} - \frac{\varepsilon_{xx} k_{z0} k_{z2}}{N_0 N_2}\right) \sin(q_{zp}d)}{q_{zp} \cos(q_{zp}d) \left(\frac{N_2}{N_0} k_{z0} + \frac{N_0}{N_2} k_{z2}\right) - i \left(\frac{N_0 N_2 q_{zp}^2}{\varepsilon_{xx}} + \frac{\varepsilon_{xx} k_{z0} k_{z2}}{N_0 N_2}\right) \sin(q_{zp}d)}$$

$$t_{pp} = \frac{2k_{z0} q_{zp}}{q_{zp} \cos(q_{zp}d) \left(\frac{N_2}{N_0} k_{z0} + \frac{N_0}{N_2} k_{z2}\right) - i \left(\frac{N_0 N_2 q_{zp}^2}{\varepsilon_{xx}} + \frac{\varepsilon_{xx} k_{z0} k_{z2}}{N_0 N_2}\right) \sin(q_{zp}d)}$$

$$(10.47)$$

The complex reflection and transmission coefficients for *s* polarized radiation are:

$$r_{ss} = \frac{q_{zs} \cos(q_{zs}d) (k_{z0} - k_{z2}) + i \left(\frac{q_{zs}^2}{\mu_{xx}} - k_{z0} k_{z2} \mu_{xx}\right) \sin(q_{zs}d)}{q_{zs} \cos(q_{zs}d) (k_{z0} + k_{z2}) - i \left(\frac{q_{zs}^2}{\mu_{xx}} + k_{z0} k_{z2} \mu_{xx}\right) \sin(q_{zs}d)}$$
(10.48)

$$t_{ss} = \frac{2k_{z0}q_{zs}}{q_{zs}\cos(q_{zs}d)(k_{z0}+k_{z2}) - i\left(\frac{q_{zs}^{2}}{\mu_{xx}} + k_{z0}k_{z2}\mu_{xx}\right)\sin(q_{zs}d)}$$

In Eq. (8.8) and Eq. (8.9),  $q_{zp}$  and  $q_{zs}$  have the same definitions as derived in Case 1 for

the semi-infinite configuration (see Eq. (10.9)).  $k_{z0} = \frac{\omega}{c} N_0 \cos(\theta_0)$  and

 $k_{z2} = \frac{\omega}{c} N_2 \cos(\theta_2)$  are the *z* components of the incident and substrate wave vectors, respectively.

#### **10.3.2** Case 3-Anisotropic $\varepsilon$ and $\mu$ Tensors; Off-Diagonal Magneto-Electric Tensors

In this section, we will analyze the thin film complex reflection and transmission coefficients of the crystal discussed in Case 3 of Section 10.2. This work permits the interesting analysis of the impact of the magneto-electric tensor on reflection and transmission. *A priori*, we would expect that the magneto-electric tensor would affect only the *p* polarization terms since it is only this wave vector which has been influenced by the magneto-electric effect for this symmetry (see Eq. (10.27)). Using the above procedures for  $4 \times 4$  matrix formalism, the complex reflection coefficients are calculated to be:

$$r_{pp} = \frac{\frac{\omega}{c}q_{a}\cos\left(\frac{\omega}{2c}q_{a}d\right)\left(\frac{N_{2}}{N_{0}}k_{z0}-\frac{N_{0}}{N_{2}}k_{z2}\right) - i\frac{\omega}{c}(\rho-\rho')\left(\frac{N_{2}}{N_{0}}k_{z0}+\frac{N_{0}}{N_{2}}k_{z2}\right)\sin\left(\frac{\omega}{2c}q_{a}d\right) + 2i\left(\frac{N_{0}N_{2}q_{w}^{2}}{\varepsilon_{xx}}-\frac{\varepsilon_{xx}k_{z0}k_{z2}}{N_{0}N_{2}}\right)\sin\left(\frac{\omega}{2c}q_{a}d\right)}{\frac{\omega}{c}q_{a}\cos\left(\frac{\omega}{2c}q_{a}d\right)\left(\frac{N_{2}}{N_{0}}k_{z0}+\frac{N_{0}}{N_{2}}k_{z2}\right) + i\frac{\omega}{c}(\rho-\rho')\left(\frac{N_{0}}{N_{2}}k_{z2}-\frac{N_{2}}{N_{0}}k_{z0}\right)\sin\left(\frac{\omega}{2c}q_{a}d\right) - 2i\left(\frac{N_{0}N_{2}q_{w}^{2}}{\varepsilon_{xx}}+\frac{\varepsilon_{xx}k_{z0}k_{z2}}{N_{0}N_{2}}\right)\sin\left(\frac{\omega}{2c}q_{a}d\right)}{r_{ss}}$$

$$r_{ss} = \frac{q_{zs}\cos(q_{zs}d)(k_{z0}-k_{z2}) + i\left(\frac{q_{w}^{2}}{\mu_{xx}}-k_{z0}k_{z2}\mu_{xx}\right)\sin(q_{zs}d)}{q_{zs}\cos(q_{zs}d)(k_{z0}+k_{z2}) - i\left(\frac{q_{w}^{2}}{\mu_{xx}}+k_{z0}k_{z2}\mu_{xx}\right)\sin(q_{zs}d)}$$

$$(10.49)$$

The formulas for the complex transmission coefficients are:

$$t_{pp} = \frac{2e^{i\frac{\omega}{c}\left(\frac{\rho+\rho'}{2}\right)}\frac{\omega}{c}q_{a}k_{z0}}{\frac{\omega}{c}q_{a}\cos\left(\frac{\omega}{2c}q_{a}d\right)\left(\frac{N_{2}}{N_{0}}k_{z0}+\frac{N_{0}}{N_{2}}k_{z2}\right)+i\frac{\omega}{c}(\rho-\rho')\left(\frac{N_{0}}{N_{2}}k_{z2}-\frac{N_{2}}{N_{0}}k_{z0}\right)\sin\left(\frac{\omega}{2c}q_{a}d\right)-2i\left(\frac{N_{0}N_{2}q_{zp}^{2}}{\varepsilon_{xx}}+\frac{\varepsilon_{xx}k_{z0}k_{z2}}{N_{0}N_{2}}\right)\sin\left(\frac{\omega}{2c}q_{a}d\right)}{t_{ss}} = \frac{2k_{z0}q_{zs}}{q_{zs}\cos(q_{zs}d)(k_{z0}+k_{z2})-i\left(\frac{q_{zs}^{2}}{\mu_{xx}}+k_{z0}k_{z2}\mu_{xx}\right)\sin(q_{zs}d)}{(10.50)}$$

As expected, the magneto-electric tensors affect only the *p* polarization terms. The equations for  $r_{ss}$  and  $t_{ss}$  are the same as for Case 1 since the *s* polarization is not affected.

In Eq. (10.49) and Eq. (10.50), 
$$q_a = \sqrt{\left(\rho - \rho'\right)^2 + 4\varepsilon_{\perp}\mu_{\perp} - \frac{4\varepsilon_{\perp}N_0^2\sin(\theta_0)^2}{\varepsilon_p}}$$
. It is

interesting to note that it is only  $q_a$  and not the entire eigenvalue expression for  $q_1$  (see Eq. (10.27), that enters into the argument for the trigonometric functions in both the thin film reflection and transmission coefficients. In  $r_{pp}$ , the magneto-electric terms enter as the middle terms of each of the numerator and denominator in Eq. (10.49) and for transmission they enter in the middle term of the denominator in  $t_{pp}$ . If  $\rho = \rho'$ , it can be

seen that  $\frac{\omega}{c}q_a = 2q_{zp}$ , where  $q_{zp}$  is as defined in Case 1 for the semi-infinite configuration. Under this condition, the magneto-electric terms vanish and  $r_{pp}$  and  $t_{pp}$ reduce to the identical expressions derived in Case 1 for thin films (see Eq. (8.8) and Eq. (8.9)). We note further that this scenario is also consistent with the fact that the magnetoelectric effect for hexagonal manganites is forbidden for symmetry reasons for the static case [35]. Eq. (10.49) and Eq. (10.50), which accommodate variable AOI, should be of significant use to experimentalists in the analysis of the reflectivity spectra of magnetoelectric thin film materials and should also assist in the proper characterization of the magneto-electric tensor and in the study of electromagnons. We note that if the experiment is designed as a vacuum-thin film-vacuum configuration, then the first term in the numerators for both reflection polarizations vanish and the formulas are further simplified:

$$r_{pp} = \frac{i\left(\frac{q_{w}^{2}}{k_{z0}\varepsilon_{xx}} - \varepsilon_{xx}k_{z0}\right)\sin\left(\frac{\omega}{2c}q_{a}d\right) - i\frac{\omega}{c}\left(\rho - \rho'\right)\sin\left(\frac{\omega}{2c}q_{a}d\right)}{\frac{\omega}{c}q_{a}\cos\left(\frac{\omega}{2c}q_{a}d\right) - i\left(\frac{q_{w}^{2}}{k_{z0}\varepsilon_{xx}} + \varepsilon_{xx}k_{z0}\right)\sin\left(\frac{\omega}{2c}q_{a}d\right)}$$

$$r_{ss} = \frac{\frac{i}{2}\left(\frac{q_{zs}}{k_{z0}\mu_{xx}} - \frac{k_{z0}\mu_{xx}}{q_{zs}}\right)\sin(q_{zs}d)}{\cos(q_{zs}d) - \frac{i}{2}\left(\frac{q_{zs}}{k_{z0}\mu_{xx}} + \frac{k_{z0}\mu_{xx}}{q_{zs}}\right)\sin(q_{zs}d)}$$

$$(10.51)$$

### **10.4 Dispersion Models for** $\varepsilon$ and $\mu$

In order to simulate the response functions in the optical spectra (for example,  $R_s(\omega)$  and  $T_s(\omega)$ ), assumptions must be made about the models that can describe their frequency dependent excitations. A common approach is to model the excitations using a combination of Lorentzian oscillators. We first consider models for  $\hat{\varepsilon}$  and  $\hat{\mu}$ :

$$\mathcal{E}(\omega) = \mathcal{E}_{\infty} + \sum_{j=1}^{N} \frac{S_{j,e} \omega_{j,e0}^{2}}{(\omega_{j,e0}^{2} - \omega^{2} - i\gamma_{j,e}\omega)}$$
$$\mu(\omega) = 1 + \sum_{j=1}^{M} \frac{S_{j,m} \omega_{j,m0}^{2}}{(\omega_{j,m0}^{2} - \omega^{2} - i\gamma_{j,m}\omega)}, \qquad (10.52)$$

where  $\varepsilon_{\infty}$  is the infinite-frequency of the dielectric function,  $S_{e,m}$  is the corresponding mode oscillator strength,  $\gamma_{e,m}$  is the damping constant, and  $\omega_{e0,m0}$  is the resonance frequency. Poles in the Lorentzian formulas are also known as modes for the response functions. We note in Eq. (10.52) that for metamaterials, the model for magnetic permeability is adjusted from the Lorentzian model via the replacement of  $\omega_{m0}^2$  with  $\omega^2$ in the numerator. This is known as the Pendry model and it ensures that the static value for the magnetic permeability is unity. For multiferroics, this condition is not applicable and we use the SHO model. Other dispersion models including the Coupled Harmonic Oscillator (CHO) model [5] can be used to describe the response functions.

With the above dispersion formulas, expressions for reflected and transmitted intensities can be obtained by multiplying the complex formulas by their complex conjugate. For example, for thin film *s* polarization:

$$R_{s}(\omega) = r_{ss} \times r_{ss}$$

$$T_{s}(\omega) = t_{ss} \times t_{ss}^{*}$$
(10.53)

It is clear from the foregoing analysis that the intensities in Eq. (10.53) are functions of  $\hat{\varepsilon}$ ,  $\hat{\mu}$ ,  $\hat{\rho}$  and  $\hat{\rho}'$ .

However, even before the simulation step, from the dispersion formulas alone, it is possible to make conclusions about two interesting optical effects possible for complex media: (i) the inverted Lorentzian shape in reflectivity for a pure magnetic dipole excitation; and (ii) the phenomenon of negative index of refraction (NIR).

As explained in Ref. [2], the shape of the response function of a pure magnetic dipole is best understood by using the Veselago approach presented in Section 10.2.2, where  $n \rightarrow \sqrt{\varepsilon/\mu}$ . It is assumed that the natural frequency of the magnetic dipole is far from dielectric resonance so that the dielectric function can be treated as a constant,  $\varepsilon_{\infty}$ . That is, we assume  $S_e = 0$ . The expression for reflection using the Veselago approach becomes [2]:

$$R_{ss}(\omega) = f\left(\sqrt{\varepsilon_{\infty} - \frac{\varepsilon_{\infty}S_m\omega_m^2}{(\omega_m^2(1+S_m) - \omega^2 - i\gamma\omega)}}\right) \approx f\left(\sqrt{\varepsilon_{\infty} - \frac{\varepsilon_{\infty}S_m\omega_m^2}{(\omega_m^2 - \omega^2 - i\gamma\omega)}}\right), (10.54)$$

where  $f(x) = |(1-x)/(1+x)|^2$ . The negative sign in Eq. (10.54) corresponds to the inverted Lorentzian shape of a pure magnetic dipole with an adjusted oscillator strength (AOS)  $S_R = S_m \cdot \varepsilon_\infty$ . As is evident from the equation, a pole in the effective dielectric function measured, for example, in RAE experiments, is shifted from  $\omega_m$ , appearing at the longitudinal frequency  $\omega_{LO} = \omega_m \cdot \sqrt{1+S_m}$ . Note that this frequency shift is small due to  $S_m \ll \mu_\infty$  for magnetic modes. As will be discussed later, the inverted shape of the magnetic dipole response is responsible for the partial or complete cancellation of an electric mode in reflectivity when both excitations occur at the same frequency.

If the background dielectric function is not too large, it is possible for both  $\varepsilon$  and  $\mu$  to become simultaneously negative in the frequency spectra. This is the condition for NIR which causes materials to become 'left handed' [36]. The NIR phenomenon has been observed experimentally [39]. The consequence of this condition to the direction of wave propagation and the direction of energy flow can be analyzed qualitatively using  $4 \times 4$ matrix formalism. In Case 1, the vector components for the  $\vec{k}$  vector (see Eq. (10.9)) and the Poynting vector,  $\vec{S}$  (see Eq. (10.15) and Eq. (10.19)) were derived. For each of these vectors, both the x and z components are positive indicating that the wave direction and the direction of energy flow are downward and to the right in the medium (recall that the positive z axis is downward). However, both of these equations change when  $\mathcal{E} \rightarrow -\mathcal{E}$ and  $\mu \rightarrow -\mu$ . For the wave vectors, while the *x* component remains positive, the *z* component becomes negative. This indicates that the direction of the wave fronts is upward and to the right in the material. For the Poynting vectors, the x component becomes negative while the z component remains positive. This indicates the direction of energy flow is downward to the left in the material. The opposite directions for  $\vec{k}$  and  $\vec{S}$ as well as their propagation in the third quadrant of the material is now a common understanding for NIR [44]. The qualitative results using  $4 \times 4$  matrix formalism further suggest that under conditions of NIR, for crystals with orthorhombic symmetry, the kand  $\vec{S}$  vectors should diverge as they propagate in the medium in the left handed configuration. Fig. 10.4(d) simulates this configuration for a material with the negative value of the response functions to those of Section II A:  $\varepsilon = (-4, -6, -8)$  and  $\mu = (-1, -2, -3).$ 

The implications of the dispersion relations to the magneto-electric case studied in Section II. C will now be explored. As explained in that section, a complete description of the *p* polarized eigenvector required multiplication by  $e^{iq_1z}$ . This expression can be rewritten in terms of  $k_x$ , the x component of the incident wave vector:

 $e^{\frac{i\omega}{2c}(\rho+\rho)z}e^{\frac{i\omega}{2c}(\sqrt{(\rho-\rho')^2+4\varepsilon_x,\mu_x}-\frac{c^2}{\rho^2}\frac{4\varepsilon_x,k_x^2}{\varepsilon_z})z}$ . The square root term can be recognized as  $q_a$  as defined in Case 3. Consider the case where  $\varepsilon$  and  $\mu$  are real and  $\rho$  and  $\rho'$  are modeled as chiral complex conjugates. The sign of  $q_a^2$  will determine the nature of wave propagation in the magneto-electric crystal. For  $q_a^2 > 0$ , the wave will propagate into the material with sinusoidal amplitude; for  $q_a^2 < 0$  the wave will decay exponentially and form an evanescent solution. Following a similar analysis to that for indefinite media outlined in Ref. [44], there will be a value for  $k_x$  that makes  $q_a = 0$  which is denoted as  $k_c$ , the cut-off wave vector. This cut off wave vector, which separates propagating waves

from decaying waves, can be calculated as: 
$$k_x = \frac{\omega}{2c} \sqrt{\frac{\varepsilon_{zz}}{\varepsilon_{xx}}} \sqrt{(\rho - \rho')^2 + 4\varepsilon_{xx}\mu_{xx}}$$
. Since

anisotropic dispersion relations permit the combinations of  $\varepsilon$  and/or  $\mu$  to have differing signs, various cases for propagation need to be examined. For example, if  $\varepsilon_{xx}\mu_{xx} > 0$  and  $\varepsilon_{xx} / \varepsilon_{zz} > 0$ , then propagation will occur only if  $k_x < k_c$ . On the other had, if  $\varepsilon_{xx}\mu_{xx} > 0$ and  $\varepsilon_{xx} / \varepsilon_{zz} < 0$ , there will always be propagation. For *s* polarized radiation, the cut off conditions will be identical to those in Ref. [44] upon adjustment for uniaxial symmetry.

The cut-off analysis can assist in the derivation of the condition for NIR in the magnetoelectric crystal examined in Case 3. Recent studies have suggested that this type of magnetic ordering may result in NIR [32]. We consider the case where the damping constants for the response functions are sufficiently small such that all four responses become negative in the same frequency range. From Eq. (10.28), it can be seen that if  $\varepsilon \rightarrow -\varepsilon$ ,  $\mu \rightarrow -\mu$ ,  $\rho \rightarrow -\rho$  and  $\rho' \rightarrow -\rho'$ , the *z* component of the wave vector will become negative if  $k_x < k_c$ . From Eq. (10.32), it can be seen that this same condition causes the sign of the *x* component of the Poynting vector to become negative. These changes cause the wave vector to propagate upward and to the right in the material while the direction of energy flow will be downward and to the left. Accordingly, when  $k_x < k_c$ , we expect that NIR can be produced in the magneto-electric crystal.

As explained in Eq. (10.2),  $\rho$  and  $\rho'$  may have contributions from both magneto-electric and chiral effects. As explained by Cano, the magneto-electric tensor takes on a chiral character for Case 3 [32]. In order to illustrate the influence of the chirality on NIR, a material with diagonal tensors  $\varepsilon = (-4, -4, -5)$  and  $\mu = (-3, -3, -4)$  and  $\xi = 3i$  is examined. For these inputs,  $q_a^2 = 10.4$  indicating that the wave should propagate without decay in the material. As simulated in Fig. 10.5(a), the magneto-electric material displays NIR. However, if  $\rho$  is changed by only one unit to -4i,  $q_a^2 = -17.6$  and the cut-off condition is met. As illustrated in Fig. 10.5(b), the *p* polarized wave no longer enters the medium while the *s* polarized wave remains unaffected by the magneto-electric effect. In summary, for proper study of NIR in chiral magneto-electric materials, the interaction of all four response functions must be examined.

The effects of chirality can also be examined for the isotropic symmetry in Case 4. Fig. 10.5(c) shows the expected results for the wave vectors and Poynting vectors for isotropic  $\hat{\varepsilon}$  and  $\hat{\mu}$  tensors. When a sufficiently large chiral parameter is introduced, the *s* polarized wave demonstrates NIR while the *p* polarized wave remain propagating downward and to the right.



**Figure. 10.5** Wave vector  $\vec{k}$  and Poynting vector  $\vec{S}$  in for various symmetries and tensor combinations given in the table below. Unless otherwise indicated, diagonal tensor components are given.  $\vec{k}$  for *p* and *s* polarizations are solid green and solid red lines, respectively.  $\vec{S}$  for *p* and *s* polarizations are dotted green and dotted red lines, respectively.

Plot	Symmetry	$\hat{\mathcal{E}}$	ĥ	$\hat{ ho}$	$\hat{ ho}$ '
(a)	Case 3	(-4,-4,-5)	(-3,-3,-4)	$\rho_{xy} = 3i$	$\rho'_{yx} = -3i$
(b)	Case 3	(-4,-4,-5)	(-3,-3,-4)	$\rho_{xy} = 4i$	$\rho'_{yx}$ = -4i
(c)	Case 4	(2,2,2)	(1.1, 1.1, 1.1)	-	-
(d)	Case 4	(2,2,2)	(1.1, 1.1, 1.1)	(4i,4i,4i)	(-4i,-4i,-4i)

#### 10.5 Hybrid Modes and Adjusted Oscillator Strength Matching (AOSM)

A rare occurrence of coincident electric and magnetic resonances is possible in, for example, magneto-electric materials, where ligand-field excitations occur in RE-IG [10]. We recently observed this effect and have explained it using the concept of the AOSM condition [2]. The condition for the matching has been derived for the case of isotropic  $\hat{\varepsilon}$ and  $\hat{\mu}$  tensors at AOI=0. Below, we expand the theoretical treatment of the AOSM effect for AOI  $\neq$  0 and for the case of anisotropic  $\hat{\varepsilon}$  and  $\hat{\mu}$  tensors.

As discussed in the previous section, the Lorentzian profiles of magnetic and electric dipole excitations have opposing shapes in the reflectivity spectra. A hybrid mode is produced if these modes appear at the same frequency,  $\omega_h$ . We do not consider the magneto-electric effect in the analysis of hybrid modes:  $\rho = \rho' = 0$ . For hybrid modes, there is the interesting possibility for partial or complete cancelation of the excitation in the  $R_s(\omega)$  and RAE spectra. This motivates the analysis of the derivative  $\frac{\partial R_s(\omega_h)}{\partial \omega}$  for each mode. Conceptually, for electric and magnetic modes with the same damping coefficient, if their derivatives are identical but of opposite sign, then cancellation should result. This analysis will be undertaken for both semi-infinite and thin film configurations at normal incidence.

## 10.5.1 Semi-infinite Configuration and Hybrid Modes

From Eq. (10.53), the following partial derivative expansion is used for  $\frac{\partial R_s(\omega_h)}{\partial \omega}$ :

$$\frac{dR_{ss}}{d\omega} = r_{ss}^{*} \left( \frac{\partial r_{ss}}{\partial \varepsilon} \frac{\partial \varepsilon}{d\omega} + \frac{\partial r_{ss}}{\partial \mu} \frac{\partial \mu}{d\omega} \right) + r_{ss} \left( \frac{\partial r_{ss}}{\partial \varepsilon} \frac{\partial \varepsilon}{d\omega} + \frac{\partial r_{ss}}{\partial \mu} \frac{\partial \mu}{d\omega} \right)^{*}$$
(10.55)

Eq. (8.5) provides the formula for  $r_{ss}$  and the Lorentzian oscillator models found in Eq. (10.52) are used for the response functions,  $\varepsilon$  and  $\mu$ . The same  $\gamma_h$  apply to both response functions. When these expressions are inserted into Eq. (10.55), the following exact derivative can be calculated:

$$\frac{dR_{ss}}{d\omega} = r_{ss} \left(\omega_{h}\right)^{*} \left(\frac{-1}{\sqrt{\varepsilon(\omega_{h})\mu(\omega_{h})}}\right) \left(\frac{2\omega_{h}}{\gamma_{h}} + i\gamma_{h}\right) \left(\alpha_{e}^{SI}(\omega_{h})\right) \left[\mu(\omega_{h})S_{e} + \varepsilon(\omega_{h})S_{m}\frac{\alpha_{m}^{SI}(\omega_{h})}{\alpha_{e}^{SI}(\omega_{h})}\right] + r_{ss} \left(\omega_{h}\right) \left(\left(\frac{-1}{\sqrt{\varepsilon(\omega_{h})\mu(\omega_{h})}}\right) \left(\frac{2\omega_{h}}{\gamma_{h}} + i\gamma_{h}\right) \left(\alpha_{e}^{SI}(\omega_{h})\right) \left[\mu(\omega_{h})S_{e} + \varepsilon(\omega_{h})S_{m}\frac{\alpha_{m}^{SI}(\omega_{h})}{\alpha_{e}^{SI}(\omega_{h})}\right]\right)^{*}$$
(10.56)

In Eq. (10.56), the  $\alpha_{e,m}^{SI}$  terms are part of the expressions for  $\frac{dr_{ss}}{d\varepsilon}$  and  $\frac{dr_{ss}}{d\mu}$ , respectively.

The superscript SI refers to the semi-infinite configuration. In Eq. (10.56), we define the bracketed terms,  $\mu(\omega_h)S_e + \varepsilon(\omega_h)S_m \frac{\alpha_m^{SI}(\omega_h)}{\alpha_e^{SI}(\omega_h)}$ , as the Adjusted Oscillator Strength

(AOS) for reflection,  $S_R$ . At normal incidence,  $\alpha_e^{SI}(\omega_h) = -\alpha_m^{SI}(\omega_h)$  and  $S_R$  is:

$$S_{R}(\omega_{h}) = (\mu(\omega_{h})S_{e} - \varepsilon(\omega_{h})S_{m}).$$
(10.57)

Eq. (10.57) suggests that the two modes should cancel in reflection. The condition for complete cancellation is:

$$S_m \mathcal{E}(\omega_h) = S_e \mu(\omega_h) \tag{10.58}$$
We define Eq. (10.58) as the Adjusted Oscillator Strength Matching (AOSM) condition. More detail about AOSM and its application to the optical spectra of DY-IG are available in Ref. [2]. When the AOSM condition is satisfied, the electric and magnetic modes interact in such a way as to have no net impact on the background Reflectivity at that point in the spectrum. In other words, the Reflectivity spectra should appear essentially featureless at  $\omega_h$ . This outcome is also consistent with the opposite slope of each mode in the Reflectivity spectra. Note that we have made no assumptions in deriving Eq. (10.56) and the AOSM condition is therefore exact. Furthermore, to establish the AOSM condition perfectly, both the real and imaginary components in Eq. (10.58) must be identical. It is quite improbable to find a magneto-electric sample where the real and imaginary parts of  $\varepsilon(\omega)$  and  $\mu(\omega)$  will satisfy simultaneously Eq. (10.58). However, the AOSM calculation using only real components will suffice to result in significant damping of the hybrid modes in Reflectivity even for  $S_m \varepsilon(\omega_h) \approx S_e \mu(\omega_h)$ . Note that the AOSM condition has three major similarities to the phenomenon of impedance matching in metamaterials [42]. First, both effects require the presence of a magnetic response. Second, in both effects, reflection due to the mode is eliminated. For impedance matching, all reflection is eliminated. For AOSM, the contribution to reflection from the hybrid mode is eliminated although there will still be a background reflection from the presence of other higher-frequency excitations that contribute to  $\varepsilon_{_{\infty}}$  and  $\mu_{_{\infty}}$ . Third, both effects are described by an exact matching of the real and imaginary parts in their equations. For impedance matching, the complex valued impedances of the incident and material media must match exactly. For AOSM, the complex valued adjusted oscillator strengths must match exactly.

$$\frac{\partial r_{ss}}{\partial \omega} \approx \frac{2\omega_{h}}{\gamma_{h}^{2}} \frac{\cos(\theta_{0})}{\mu(\omega_{h})\sqrt{\varepsilon(\omega_{h}) - \frac{\sin^{2}(\theta_{0})}{\mu(\omega_{h})}}} \left(\cos(\theta_{0}) + \sqrt{\varepsilon(\omega_{h}) - \frac{\sin^{2}(\theta_{0})}{\mu(\omega_{h})}}\right)^{2} \left\{\mu(\omega_{h})S_{e} - \left(\varepsilon(\omega_{h}) - \frac{2\sin^{2}(\theta_{0})}{\mu(\omega_{h})}\right)S_{m}\right\}$$

$$(10.59)$$

From Eq. (10.59), it can easily be seen that the AOSM condition for variable AOI will be:

$$\mu(\omega_h)S_e = \left(\varepsilon(\omega_h) - \frac{2\sin^2(\theta_0)}{\mu(\omega_h)}\right)S_m$$
(10.60)

At normal incidence this expression reduces to the formula in Eq. (10.58), as expected. Eq. (10.60) is important to the characterization of materials with  $\mu \neq 1$  since the AOSM condition may not always occur at normal incidence. At AOI where the AOSM condition is not met, the above equations provide expressions for AOS in reflection which will also assist in the proper characterization throughout the AOI domain.

Also using Eq. (8.5), the AOSM condition at normal incidence (AOI=0) can be expressed for an anisotropic material. Since the tensor components which enter into  $r_{ss}$ are  $\mu_{xx}$  and  $\varepsilon_{yy}$ , the AOSM condition becomes:

$$S_{m_{xx}} \varepsilon_{yy} \left( \omega_h \right) = S_{e_{yy}} \mu_{xx} \left( \omega_h \right) \tag{10.61}$$

The foregoing analysis relating the AOSM condition and the tendency toward cancellation of modes in Reflectivity can be also qualitatively understood based on Veselago's approach for light propagation in an isotropic, semi-infinite medium with  $\mu(\omega) \neq 1$ . This approach was discussed previously and involves a simple replacement of the refractive index: for Fresnel's reflection coefficient,  $n(\omega) \rightarrow \sqrt{\varepsilon(\omega)/\mu(\omega)}$  [36, 37]. Using the Lorentzian formulas in Eq. (10.52), it can be shown that the hybrid resonance can be described with an AOS in reflection of  $S_R = (\mu_{\infty} \cdot S_e - \varepsilon_{\infty} \cdot S_m)/\mu_{\infty}^2$  [2].

## 10.5.2 Thin Film Configuration and Hybrid Modes

For the case of coincident natural frequencies for the magnetic and dielectric oscillators in thin films, the partial derivative expansions for reflectivity and transmission are:

$$\frac{dR_{ss}}{d\omega} \cong r_{ss}^{*} (S_{2}) + r_{ss} (S_{2})^{*}$$

$$\frac{dT_{ss}}{d\omega} \cong t_{ss}^{*} (S_{3}) + t_{ss} (S_{3})^{*}$$
(10.62)

where  $S_2$  and  $S_3$  are given by:

$$S_{2} = -\frac{2\omega_{h}}{\gamma_{h}^{2}} \frac{\alpha_{e}^{R_{TF}}(\omega_{h})}{\sqrt{\mu(\omega_{h})\varepsilon(\omega_{h})}} \left(\mu(\omega_{h})S_{e} + \varepsilon(\omega_{h})S_{m}\frac{\alpha_{m}^{R_{TF}}(\omega_{h})}{\alpha_{e}^{R_{TF}}(\omega_{h})}\right)$$

$$S_{3} = -\frac{2\omega_{h}}{\gamma_{h}^{2}} \frac{\alpha_{e}^{T}(\omega_{h})}{\sqrt{\mu(\omega_{h})\varepsilon(\omega_{h})}} \left(\mu(\omega_{h})S_{e} + \varepsilon(\omega_{h})S_{m}\frac{\alpha_{m}^{T}(\omega_{h})}{\alpha_{e}^{T}(\omega_{h})}\right)$$

$$(10.63)$$

In Eq. (10.63), the bracketed terms are the Adjusted Oscillator Strengths for thin film reflection and transmission,  $S_R$  and  $S_T$ . As in the semi-infinite case, the  $\alpha$  terms are

components of the reflection and transmission coefficient derivatives with respect to the response functions. Here, *TF* denotes the thin film configuration. For materials with non-

negligible film thickness, 
$$\frac{\alpha_m^{R_{TF}}(\omega_h)}{\alpha_e^{R_{TF}}(\omega_h)}$$
 and  $\frac{\alpha_m^{T}(\omega_h)}{\alpha_e^{T}(\omega_h)}$  are negative and positive, respectively,

with absolute value approximately equal to 1. The AOSM condition for thin films is therefore:

$$\mu(\omega_h)S_e = -\varepsilon(\omega_h)S_m \frac{\alpha_m^{R_2}(\omega_h)}{\alpha_e^{R_2}(\omega_h)}$$
(10.64)

The  $\alpha$  ratio term is retained in Eq.(10.64) because its value, while close to -1, is dependent on film thickness. The fact that the  $\frac{\alpha_m^T(\omega_h)}{\alpha_e^T(\omega_h)}$  term is positive at hybrid

resonance sets up the interesting result that while hybrid modes in reflection tend to cancel, in transmission they are additive. This additive conclusion can also be understood qualitatively based on Veselago who suggested that if light propagation in transmission is mainly driven by exponential decay and the extinction coefficient,  $T_{ss}(\omega)$  becomes a function of  $\varepsilon(\omega) \cdot \mu(\omega)$ . Using the expansion outlined in Ref. [2], the AOS in transmission is:  $S_T \approx S_e \cdot \mu_{\infty} + S_m \cdot \varepsilon_{\infty}$  with the two factors in  $S_T$  being additive. Since most experiments in Transmission are carried out at normal incidence, we do not consider the variable AOI case for the thin film configuration.

The expressions for  $S_R$  and  $S_T$  allow for analysis of the interesting case of hybrid modes which cancel or disappear in reflectivity but remain strong in transmission combining the magnetic and electric oscillator strengths. The case where hybrid mode magnetic and electric dipole contributions completely cancel in reflection ( $S_R = 0$ ) but add to  $S_T$  in transmission requires the solution of the following simultaneous equation:

$$\mu(\omega_{h})S_{e} + \varepsilon(\omega_{h})S_{m}\frac{\alpha_{m}^{R_{TF}}(\omega_{h})}{\alpha_{e}^{R_{TF}}(\omega_{h})} = 0$$

$$\mu(\omega_{h})S_{e} + \varepsilon(\omega_{h})S_{m}\frac{\alpha_{m}^{T}(\omega_{h})}{\alpha_{e}^{T}(\omega_{h})} = S_{T}$$
(10.65)

For 
$$\frac{\alpha_m^{R_2}(\omega_h)}{\alpha_e^{R_2}(\omega_h)} \approx -1$$
,  $\frac{\alpha_m^{T}(\omega_h)}{\alpha_e^{T}(\omega_h)} \approx 1$ ,  $\mu(\omega_h) \approx 1$  and  $\varepsilon(\omega_h) \approx \varepsilon_{\infty}$ , Eq. (10.65) has the

approximate solution:  $S_e \cong \frac{S_T}{2}$  and  $S_m \cong \frac{S_T}{2\varepsilon_{\infty}}$ . The key implication of Eq. (10.65) to

experimentalists is that experimental data for both Reflectivity and Transmission are needed for proper characterization of a hybrid mode.

#### **10.6 Mueller Matrix Simulations**

Based on the foregoing analysis, electric, magnetic, hybrid, electromagnon and chirality excitations in the optical spectra can be simulated. The Mueller Matrices of a chiral multiferroic crystal in 222 point group symmetry (see Case 4) in a semi-infinite configuration are modeled. The material is assumed to have two main oscillators: a magnetic dipole mode at 60 cm<sup>-1</sup> and an electric mode at 80 cm<sup>-1</sup>. A hybrid mode at 70 cm<sup>-1</sup> is modeled to illustrate the AOSM condition. In addition, a number of scenarios addressing electromagnons and chirality are analyzed in both the frequency and AOI

$$\hat{\alpha}(\omega) = f_m \cdot \sqrt{\hat{\varepsilon}(\omega)} \cdot \hat{\mu}(\omega)$$

$$\hat{\alpha}'(\omega) = f_e \cdot \sqrt{\hat{\varepsilon}(\omega)} \cdot \hat{\mu}(\omega)^T$$

$$\hat{\xi}(\omega) = \sum_{j=1}^N \frac{S_{j,\xi} \omega^2}{(\omega^2 - \omega_{j,\xi^0})^2 - i\gamma_{j,\xi} \omega)}$$
(10.66)

In Eq. (10.66),  $f_{e,m}$  are prefactors which are modeled as either 0 or 1. The model for chirality follows a Pendry approach so that the static value is 0.  $S_{\xi}$  is the chiral oscillator strength,  $\omega_{\xi_0}$  is the chiral natural frequency and  $\gamma_{\xi}$  is the chiral damping coefficient.

Figure 10.6 illustrates the MM of the two main oscillators at normal incidence. Only the diagonal MM elements are populated due to the absence of cross polarization terms. The Reflectivity spectra can be seen in M11 where the opposite Lorentzian shapes of the magnetic and electric dipoles are evident.



**Figure. 10.6** AOI=0. MM of electric and magnetic excitations at 80 and 60 cm<sup>-1</sup>.  $\varepsilon_{\infty} = 10$ ,  $S_e = 0.2$  and  $S_m = 0.0168$ . Only diagonal elements are populated due to the absence of cross polarization terms. The opposite Lorentzian shapes of the magnetic and electric oscillators are evident in M11.

Figure 10.7 illustrates a hybrid mode with coincident electric excitation (e) with  $S_e = 0.2$  and magnetic excitation (m) with  $S_m = 0.0168$  at 70 cm<sup>-1</sup> (green). With  $\varepsilon_{\infty} = 10$ , an initial observation would suggest that the AOSM condition should only be met if  $S_m = 0.02$ . It must be remembered, however that the coupling occurs with the actual  $\varepsilon(\omega_h)$  at the hybrid frequency which is approximately 10.86 in this case. Accordingly,  $S_m$  must be less than 0.02 for perfect matching to occur. With  $S_m = 0.0168$ , the oscillator

strengths meet the AOSM condition. The hybrid mode at 70 cm<sup>-1</sup> disappears in the MM spectra.



**Figure 10.7** AOI=0. Two main electric and magnetic excitations at 80 and 60 cm<sup>-1</sup> (blue).  $\varepsilon_{\infty} = 10$ ,  $S_e = 0.2$  and  $S_m = 0.0168$ . Two main excitations together with coincident electric excitation (e) with  $S_e = 0.2$  and magnetic excitation (m) with  $S_m = 0.0168$  at 70 cm<sup>-1</sup> (green). Oscillator strengths meet the AOSM condition. The hybrid mode at 70 cm<sup>-1</sup> disappears in the MM spectra.

Figure 10.8 illustrates the effect of electromagnons on the MM spectra in the frequency domain. In addition to the two main oscillators (blue), a electromagnon excitation is added to the magnetic oscillator (*mem*) at 60 cm<sup>-1</sup> (green). This results in a non-zero  $\hat{\alpha}$  tensor. Off diagonal elements of the MM become populated due to presence of cross polarization terms. Electromagnons result in visible peaks at the two resonances in M14

and M41. These peaks exist because both the resonances of  $\varepsilon$  and  $\mu$  are incorporated into the equation for  $\hat{\alpha}$ . It should be noted that M14 and M41 have opposite signs. This observation is important in distinguishing dynamic magneto-electric activity from chiral activity.



**Figure 10.8** AOI=45. Electric and magnetic excitations at 80 and 60 cm<sup>-1</sup> (blue).  $\varepsilon_{\infty} = 10$ ,  $S_e = 0.2$  and  $S_m = 0.0168$ . Two main oscillators together with a magneto-electromagnon (*mem*) (green). In *mem*,  $\alpha(\omega) = \sqrt{\varepsilon(\omega)\mu(\omega)}$ . Certain off diagonal elements of the MM are populated due to the presence of cross polarization terms. The electromagnon results in peaks at the two resonances in M14 and M41.

Figure 10.9 illustrates the effect of chiral activity on the MM spectra in the frequency domain. An oblique angle is used to better analyze the chirality. In addition to the two

main oscillators (blue), chiral excitations are added to the electric oscillator at 80 cm<sup>-1</sup> and magnetic oscillator at 60 cm<sup>-1</sup> (green). Off diagonal elements of the MM become populated due to presence of cross polarization terms. Chiral excitations result in visible peaks at the two resonances in M14 and M41. It is important to note that the peaks in M14 and M41 are not inverted as in the case of the electro-magnon spectra.



**Figure 10.9** AOI=45°. Electric and magnetic excitations at 80 and 60 cm<sup>-1</sup> (blue).  $\varepsilon_{\infty} = 10$ ,  $S_e = 0.2$  and  $S_m = 0.0168$ . Two main oscillators together with chiral excitations at 60 and 80 cm<sup>-1</sup> (green) each having  $S_{\xi} = 0.2$ . Off diagonal elements of the MM are populated due to the presence of cross polarization terms. The chiral excitations result in peaks at the two resonances in M14 and M41.

Figure 10.10 illustrates the MM of the two main electric and magnetic excitations at 80 and 60 cm<sup>-1</sup> in the AOI domain. These coincident excitations are measured at 60 cm<sup>-1</sup> (green) and 80 cm<sup>-1</sup> (blue). Off diagonal elements are non-zero at varying AOI because of

differences between  $r_{pp}$  and  $r_{ss}$ . We note that M34 results in opposite signs for each of the two resonances.



**Figure 10.10** MM of coincident electric and magnetic excitations at 80 and 60 cm<sup>-1</sup> in the AOI domain.  $\varepsilon_{\infty} = 10$ ,  $S_e = 0.2$  and  $S_m = 0.0168$ . Simulated at  $\omega = 60$  cm<sup>-1</sup> and  $\omega = 80$  cm<sup>-1</sup>. Off diagonal elements M12 and M34 become populated at varying AOI because of differences between  $r_{pp}$  and  $r_{ss}$ .

	11	
Line Description	Excitation	Measured at
		Frequency
Green	Magnetic at 60 cm <sup>-1</sup> Electric at 80 cm <sup>-1</sup>	$60 \text{ cm}^{-1}$
Blue	Magnetic at 60 cm <sup>-1</sup> Electric at 80 cm <sup>-1</sup>	80 cm <sup>-1</sup>

Figure 10.11 illustrates the effect of electromagnons on the MM spectra in the AOI domain. In addition to the two main oscillators, electromagnon excitations are added: *(eem)* (blue) and *(mem)* (green). Since the analysis is done in the AOI domain, it is

critical to identify the frequency with which the simulation takes place. We have chosen the two resonance frequencies of 60 cm<sup>-1</sup> and 80 cm<sup>-1</sup> for analysis. This configuration produces four separate curves: *mem* simulated at the two resonances and *eem* simulated at the two resonances. All off diagonal elements of the MM are populated due to presence of cross polarization terms. This figure suggests that it is possible to distinguish between a *mem* and *eem* excitation through the analysis of M14 or M34 at the different resonance frequencies. For both M14 and M34, the *mem* measured at 60 cm<sup>-1</sup> (thick green) has the opposite sign to the *eem* measured at 80 cm<sup>-1</sup> (dotted blue). As in the case of electromagnon activity in the frequency domain, we see again that M14 and M41 are inverted.



**Figure 10.11** MM of electric and magnetic excitations at 80 and  $60 \text{cm}^{-1}$  ( $\varepsilon_{\infty} = 10$ ,  $S_e = 0.2$  and  $S_m = 0.0168$ ) in the AOI domain together with an electro-electromagnon *(eem)* (blue) and a magneto-electromagnon *(mem)* (green). For *eem*,  $\alpha'(\omega) = \sqrt{\varepsilon(\omega)\mu(\omega)}$ . For *mem*,  $\alpha(\omega) = \sqrt{\varepsilon(\omega)\mu(\omega)}$ . All 16 MM elements are populated when the electromagnons are active. The possibility of distinguishing between *eem* and *mem* is suggested through the asymmetric shapes in M34 for *eem* and *mem*.

Line Description	Excitation	Measured at	
		Frequency	
Thick green	тет	$60 \text{ cm}^{-1}$	
Thin green	тет	$80 \text{ cm}^{-1}$	
Solid blue	eem	$60 \text{ cm}^{-1}$	
Dotted blue	eem	$80 \text{ cm}^{-1}$	

Figure 10.12 illustrates the effect of chiral excitations in the MM spectra in the AOI domain. To the main magnetic and electric oscillators, chiral excitations with  $S_{\xi} = 0.20$  are added at each of 60 and 80 wave numbers. From Fig. 10.9, we use the two

frequencies which produce maximum amplitude for the chiral oscillators in M14. This is 61.5 cm<sup>-1</sup> for the chiral oscillator with natural frequency of 60 cm<sup>-1</sup> and 83.5 cm<sup>-1</sup> for the chrial oscillator with natural frequency of 80 cm<sup>-1</sup>. These combinations result in the simulation of four separate curves. When the chiral excitations are active, all 16 elements of the MM are populated. This figure also suggests the possibility of using M24 to distinguish between the two chiral excitations. In M24, the chiral excitation at 60 cm<sup>-1</sup> and measured at 61.5 cm<sup>-1</sup> (thick green) is of opposite sign to the chiral excitation at 80 and measured at 83.5 cm<sup>-1</sup> (dotted blue) for low angles of incidence. As in the case of chiral activity in the frequency domain, we see again that M14 and M41 are of the same sign and not inverted. Accordingly, in both the frequency and AOI domains, it is possible to distinguish between the magneto-electric and chirality effects by examing the relationship between M14 and M41.



**Figure 10.12** MM of electric and magnetic excitations at 80 and 60 cm<sup>-1</sup> ( $\varepsilon_{\infty} = 10$ ,  $S_e = 0.2$  and  $S_m = 0.0168$ ) in the AOI domain together with chiral excitations at 60 cm<sup>-1</sup> and 80 cm<sup>-1</sup>.  $S_{\xi} = 0.20$ ,  $\gamma_{\xi} = 2$ . Note that all 16 MM elements are populated when chiral excitations are active.

Line Description	$\mathcal{O}_{\xi_0}$	Measured at
		Frequency
Thick green	$60 \text{ cm}^{-1}$	$61.5 \text{ cm}^{-1}$
Thin green	$60 \text{ cm}^{-1}$	83.5 cm <sup>-1</sup>
Solid blue	$80 \text{ cm}^{-1}$	$61.5 \text{ cm}^{-1}$
Dotted blue	$80 \text{ cm}^{-1}$	83.5 cm <sup>-1</sup>

# **10.7 Chapter Summary**

In this Chapter, we have used  $4\times4$  matrix formalism to analyze electromagnetic wave propagation and the optical spectra of complex media. We have demonstrated that a complete description requires the calculation of eigenvalues and eigenvectors of the  $\tilde{\Delta}$  matrix using all four response functions. We have used 5 cases to describe the interesting optical effects when additional components are added to the optical matrix. These effects include birefringence, non-reciprocity, divergence between the wave vector and Poynting vector, NIR, opposing Lorentzian shapes for magnetic and dielectric excitations, and AOSM. For *RE*MnO<sub>3</sub> compounds with cycloidal magnetic order (having off diagonal magneto-electric tensors in the dynamic state) the following results have been derived analytically for the first time:

- the eigenvectors for *p* and *s* polarizations
- the complex reflection coefficients for *p* and *s* polarizations for the semi-infinite case
- the Poynting Vector for *p* and *s* polarizations
- proof of birefringence for the *p* polarization state but not for the *s* polarization state
- the complex reflection and transmission coefficients for *p* and *s* polarizations for the thin film case
- the cutoff wave vector which separates propagating waves from decaying waves in the medium for both right handed and left handed conditions

For a multiferroic material with anisotropic  $\hat{\varepsilon}$ ,  $\hat{\mu}$ ,  $\hat{\rho}$  and  $\hat{\rho}'$  tensors, the  $\tilde{\Delta}$  matrix has been derived. In addition, we have shown how a full Mueller Matrix analysis assists in the proper characterization of the material properties of such media. For example, although the effects of electro-electromagnons and magneto-electromagnons are difficult to distinguish in the reflectivity spectra, it is possible to distinguish them using full Mueller Matrix analysis over varying AOI. We have also derived the AOSM condition at varying AOI. These derivations will assist in the characterization of metamaterials and multiferroic materials.

## CHAPTER 11

## THESIS SUMMARY

After a review of background material in Chapters 1-7, the following original results were presented in Chapters 8-10.

- formulae for the complex reflection and transmission coefficients have been derived for materials with μ≠1 in the thin film configuration having orthorhombic symmetry or higher. These formulae incorporate the case of non-vacuum incident and substrate media.
- the behavior of Mueller matrix components for a planar metamaterial in proximity to resonance has been illustrated at varying AOI.
- for the first time, the separation of dielectric and magnetic contributions in the optical spectra of a magnetic material has been demonstrated by performing MM simulations at varying AOI
- for the first time, the identification of the Negative Index of Refraction condition in the optical spectra of thin films with μ≠1 is illustrated by performing MM simulations at varying AOI.
- for the first time, Adjusted Oscillator Strength (AOS) formulas for a multiferroic material have been derived for reflection in the semi-infinite configuration and reflection and transmission in the thin film configuration.
- for the first time, the Adjusted Oscillator Strength Matching (AOSM) condition  $\mu(\omega_h) \cdot S_e = \varepsilon(\omega_h) \cdot S_m$  has been applied to explain the behavior of the hybrid modes in the optical spectra of Dy-IG.

- For *RE*MnO<sub>3</sub> compounds with cycloidal magnetic order (having off diagonal magnetoelectric tensors in the dynamic state) the following results are derived analytically for the first time:
  - the eigenvectors for *p* and *s* polarizations
  - the complex reflection coefficients for *p* and *s* polarizations for the semi-infinite case having oblique angles of incidence
  - the Poynting Vector for *p* and *s* polarizations
  - proof of birefringence for the p polarization state but not for the s polarization state
  - the complex reflection and transmission coefficients for *p* and *s* polarizations for the thin film configuration having oblique angles of incidence
  - the cutoff wave vector which separates propagating waves from decaying waves in the medium for both right handed and left handed conditions
- For a multiferroic material with anisotropic ε, μ, ρ and ρ' tensors, the Del matrix has been derived.

## **APPENDIX A**

## ERROR ANALYSIS FOR DY-IG REFLECTIVITY FIT

# **A.1 Fitting Procedures**

The experimental results for the Reflectivity spectra for Dy-IG are illustrated in Figure A.1.



Figure A.1 Experimental results for Reflectivity for Dy-IG.

The fitting for this spectra was done using the Levenberg Marquardt fitting algorithm. In order to determine an initial parameter vector for the fitting process, we developed a program which simulates the reflectivity spectra for a given set of parameters. This simulation program also returns a  $\chi^2$  value for the objective function. Accordingly, determining an initial parameter vector was essentially a 'by hand' procedure. For the majority of the fitting process, unconstrained optimization techniques were used. By this we mean that all parameters were allowed to 'float' until convergence. However, later in the fitting procedure, it was necessary to constrain certain parameters within specified upper and lower bounds. For example, it is now understood that the magnetic and dielectric oscillators for a hybrid mode are additive in transmission. Therefore, the total value of the Adjusted Oscillator Strength (AOS) for transmission could not exceed its actual experimentally determined value. Accordingly, upper bounds for the oscillator strengths of the magnetic and dielectric oscillators were required. Another example is that the damping parameter for each of the magnetic and dielectric oscillators needed to be roughly the same for a hybrid mode in order to correctly model the lifetime of the excitation. A function called 'check\_bounds' was created to ensure that targeted parameters stayed within pre-specified limits. This was called by the LM parent program 'mrqmin'. The disadvantage of this approach, however, as compared to unconstrained optimization, is that for any given constrained parameter, its partial derivative approached zero as it neared or exceeded its upper or lower bound. This made convergence slow since the step in parameter space is proportional to the Jacobian. In addition, it made inversion of the Hessian more difficult. The inverse of the Hessian provides the covariance matrix which, in turn, provides the standard errors of the parameters. As a result, it was necessary to use a combination of the constrained and unconstrained optimization procedures to properly calculate the error bars for the parameters.

#### A.2. Error Analysis for Main Magnetic and Dielectric Oscillators

The error bars for the magnetic oscillator at 59.5 cm<sup>-1</sup> and the dielectric oscillator at 81.3 cm<sup>-1</sup> were determined using the analytical procedure discussed previously. The dielectric oscillator strength for the hybrid mode at 73.5 cm<sup>-1</sup> was fixed at 0.0400 (ie. ix=0 for this parameter which indicates that this parameter is not to be fitted). Subject to this single condition, the unconstrained optimization procedure was used. The objective function was calculated according to the formula:

$$F(\vec{x}) = \chi^{2}(\vec{x}) = \frac{1}{N - m - 1} \sum_{i=1}^{m} \left( \frac{y_{i} - y(t_{i}, (x_{1}, x_{2}, x_{3} \dots x_{M}))}{\sigma_{i}} \right)^{2}$$
(A.1)

In (A.1), N is 209 which is the number of data points and m is 68 which is the number of parameters to be fitted.  $\sigma_i$  was taken to be .0005 for all data points. For the magnetic oscillator strength,  $S_m$ , the process returned 0.0017±0.0006. For the dielectric oscillator strength,  $S_e$ , the process returned 0.0988±0.0143. The error bars represent the standard error. When all parameters were subject to their upper and lower bounds,  $S_m$  returned 0.0018 and  $S_e$  returned 0.0873. Using the same proportionality as for the unconstrained results, we finalized the error bars for the magnetic oscillator strength to be 0.0018±0.0006 and for the dielectric oscillator, 0.0873±0.0126.

#### A.3. Error Analysis for Hybrid Modes

The error analysis for the hybrid modes must take into account that these oscillators are essentially acting as coupled oscillators. For the purposes of illustration, the hybrid oscillator at 73.5 cm<sup>-1</sup> is analyzed. With  $S_e$  fixed at 0.0400,  $S_m$  is returned as  $.0035\pm.0008$ . In doing this analysis, it was necessary to force the damping parameters to be the same for both oscillators. With these values for  $S_m$  and  $S_e$ , the total adjusted oscillator strength matching condition is exceeded which cannot represent a physically realizable condition. However, the result is still useful to provide proportionality for the error bar in  $S_m$ . The constrained optimization results returned .0025 for  $S_m$ . Using the same proportionality as for the unconstrained case, the error bar for the magnetic oscillator strength becomes: .0025±.0006. We expect that the AOSM condition will also apply to the error bars in a hybrid mode since:

$$\mu (S_e + \Delta S_e) - \varepsilon (S_m + \Delta S_m) = (\mu S_e - \varepsilon S_m) + (\mu \Delta S_e - \varepsilon \Delta S_m) = 0$$
(A.2)

Under unconstrained optimization, we found that the ratio of the error bars for the hybrid modes is virtually the same as the ratio of the parameters which suggests that the rule in (A.2) is followed for both the parameters and their errors. Using this approach, the results for the magnetic oscillator strength are:  $.0400 \pm .0091$ .

### A.4. The Impact of Random Errors

We adjusted the experimental data for random errors by applying up to a  $\pm 10\%$  change for every data point. The results of this process are illustrated in Figure A.2.



Figure A.2 Random errors applied to experimental data.

At first glance, the Figure A.2. looks like it represents a linear relationship between reflection and frequency with positive slope. Parameters were fitted with the LM fitting algorithm with the results shown in Figure A.3.



Figure A.3 Results of fitting experimental results with random error.

The magnetic oscillator strength was calculated to be  $0.0015 \pm 0.0007$  and the dielectric oscillator strength was calculated to be  $0.0919 \pm .0195$ . Note that the range of outcomes includes that of the non-randomized case. The error bars for the dielectric case are slightly higher than for the non-randomized case.

## **APPENDIX B**

## MATLAB SCRIPTS USED IN LEVENBERG MARQUARDT FITTING ALGORITHM

## **B.1 Pseudo-Code and Numerical Implementation of Levenberg Marquardt Method**

Pseudo-code for the LM implementation consists of the steps outlined in the following table [55]:

**Table B.1** Pseudo Code for Levenberg Marquardt Implementation.

- 1. Choose starting parameter vector,  $\vec{x}$ . Initialize  $\lambda = .001$ .
- 2. Calculate  $\chi^2(\vec{x})$ .
- 3. Solve Eq. (7.15) for  $h_{lm}$ . Evaluate  $\chi^2(\vec{x} + \vec{h}_{lm})$ .
- 4. If  $\chi^2(\vec{x} + \vec{h}_{lm}) \ge \chi^2(\vec{x})$  then decrease  $\lambda$  by a factor of 10. This sends the step back in the direction of steepest descent. Repeat step 3.
- 5. If  $\chi^2(\vec{x} + \vec{h}_{lm}) < \chi^2(\vec{x})$  then increase  $\lambda$  by a factor of 10. This sends the step in the direction of the Gauss Newton step for quicker convergence. Repeat step 3.
- 6. Cease iterating when user defined stopping criteria are met.

We have implemented this code using a number of Matlab functions. Table B.2 gives an explanation of each of the functions.

## **B.2 List of Matlab Scripts Used in Fitting**

Table B.2 below provides a list of Matlab scripts used in fitting.

1	Matlab Script	Functionality
2	Main_MM_to_Eps_Mu_Isotropic Main_MM_to_Eps_Mu_Anisotropic	Loads Mueller Matrix data across a frequency spectrum.
		Using LM method, calculates $\varepsilon$ and $\mu$ using isotropic and anisotropic models.
		Creates a data file of calculated $\varepsilon$ and $\mu$ .
3	fit_exact_Mueller_to_Eps_Mu_ISOTROPIC	Called by #1. Calculates the
5	fit_exact_Mueller_to_Eps_Mu_ANISOTROPIC	residual error function, $f_i$ .
4	fit_Eps_Mu_to_Parameters_ISOTROPIC	Called by #2. Calculates the
	fit_Eps_Mu_to_Parameters_ANISOTROPIC	residual error function, $f_i$ .
5	funcsv2(fun,x0,omega,y,cf)	Required function in LM implementation [55].
		For fun defined as #3 or #4 calculates initial values of residual error function.
6	mrqminv5_bounded(alamda,ix, mx,ndata,fun,x0, opts, sig,theta1,y, cf,lb,ub)	Implements major steps of LM method as outlined in Table B.1.
7	mrqcofv5(fun,sig,ndata,x,ix,mx,opts,omega,y,cf)	Called by #6. Returns Hessian and Jacobian matrices in addition to residual error vector.
8	jacobianv5(fun,f,x,mx,ix,mfit,opts,omega,y,cf);	Called by #7. Calculates the Jacobian matrix for parameters to be fitted.
9	gaussjmatlabv2(alpha,dx,alamda)	Called by #6. Calculates next step in LM method.
10	check_bounds(x,lb,ub)	Called by #6. Checks that current iteration of $\vec{x}$ is within user defined bounds and adjusts vector if required.

 Table B.2
 Matlab scripts used in Levenberg Marquardt Implementation.

#### **APPENDIX C**

# ADJUSTED OSCILLATOR STRENGTH MATCHING FOR HYBRID MAGNETIC AND ELECTRIC EXCITATIONS IN DY<sub>3</sub>FE<sub>5</sub>O<sub>12</sub> GARNET

Expressions for the Adjusted Oscillator Strength (AOS) and the Adjusted Oscillator Strength Matching (AOSM) condition are developed for materials with  $\mu \neq 1$ . V. G. Veselago's results for semi-infinite magnetic materials [36, 37] together with analytic expressions obtained by the authors in Ref. [1] are used in this treatment. A Lorentzian oscillator model is used in the formulas below for magnetic and dielectric excitations. For a single hybrid excitation, the dielectric and magnetic contributions are given in Eq. (9.2), where N = M = 1,  $\omega_{e0} = \omega_{m0} = \omega_h$ , and  $\gamma_e = \gamma_m = \gamma$ .

The semi-infinite case for normal incident radiation (AOI=0) is examined first. Based on Veselago's work, it is assumed that the *s* polarized reflection intensity  $R_{ss}(\omega)$  is a function of  $\sqrt{\varepsilon(\omega)/\mu(\omega)}$  [36, 37]. Then, in the proximity of a resonance with a single hybrid mode

$$R_{ss}(\omega) = f\left(\sqrt{\frac{\varepsilon(\omega)}{\mu(\omega)}}\right) = f\left(\sqrt{\frac{\varepsilon_{\infty} + \frac{S_e \omega_h^2}{(\omega_h^2 - \omega^2 - i\gamma\omega)}}{\mu_{\infty} + \frac{S_m \omega_h^2}{(\omega_h^2 - \omega^2 - i\gamma\omega)}}}\right) \approx (C.1)$$

$$f\left(\sqrt{\frac{\varepsilon_{\infty}}{\mu_{\infty}} + \frac{(\mu_{\infty}S_e - \varepsilon_{\infty}S_m)\omega_h^2}{\mu_{\infty}^2(\omega_h^2 - \omega^2 - i\gamma\omega)}}\right) = f\left(\sqrt{\frac{\varepsilon_{\infty}}{\mu_{\infty}} + \frac{S_R \omega_h^2}{(\omega_h^2 - \omega^2 - i\gamma\omega)}}\right),$$

where  $f(x) = |(1-x)/(1+x)|^2$ . The expansion in Eq. (C.1) is justified since  $S_m \ll \mu_\infty$  for the magnetic modes (see Table 9.1). In general, the hybrid resonance can be described with an AOS in reflection:  $S_R = (\mu_\infty \cdot S_e - \varepsilon_\infty \cdot S_m)/\mu_\infty^2$ . We have also derived a similar expression for  $S_R$  by analyzing the derivative of the exact complex reflection coefficient

with respect to frequency for the thin film configuration, which will be described below. The AOSM condition,  $S_m \varepsilon_{\infty} = S_e \mu_{\infty}$ , is immediately apparent from Eq. (C.1). Under this condition, the hybrid mode disappears from reflectivity and reflectivity becomes a function of  $\varepsilon_{\infty}$  and  $\mu_{\infty}$  only:  $R_{ss}(\omega_h) = f(\sqrt{\varepsilon_{\infty}/\mu_{\infty}})|_{S_m \varepsilon_{\infty} = S_e \mu_{\infty}}$ .

For a pure magnetic dipole at  $\omega_h = \omega_{m0}$ , Eq. (C.1) can be approximated for  $S_e = 0$  and  $\mu_{\infty} = 1$  as:

$$R_{ss}(\omega) = f\left(\sqrt{\varepsilon_{\infty} - \frac{\varepsilon_{\infty}S_{m}\omega_{m}^{2}}{(\omega_{m0}^{2}(1+S_{m}) - \omega^{2} - i\gamma\omega)}}\right) \approx f\left(\sqrt{\varepsilon_{\infty} - \frac{\varepsilon_{\infty}S_{m}\omega_{m}^{2}}{(\omega_{L0}^{2} - \omega^{2} - i\gamma\omega)}}\right).$$
(C.2)

The negative sign in Eq. (C.2) corresponds to the inverted Lorentzian shape of a pure magnetic dipole with AOS:  $S_R = S_m \cdot \varepsilon_\infty$ . For hybrid modes, this inverted shape provides for the partial or complete cancellation of the electric and magnetic components at resonance. As is evident from Eq. (C.2), a pole in the effective dielectric function measured, for example, in RAE experiments, is shifted from  $\omega_{m0}$ , appearing at the longitudinal frequency  $\omega_{LO} = \omega_{m0} \cdot \sqrt{1 + S_m}$ . Note that this frequency shift is small due to  $S_m << \mu_\infty$  for magnetic modes.

If light propagation in transmission is mainly driven by exponential decay and the extinction coefficient, according to Veselago,  $T_{ss}(\omega)$  becomes a function of the product  $\varepsilon(\omega) \cdot \mu(\omega)$ :

$$T_{ss}(\omega) = F\left(\sqrt{\varepsilon(\omega)} \cdot \mu(\omega)\right) = F\left(\sqrt{\left(\varepsilon_{\infty} + \frac{S_{e}\omega_{h}^{2}}{(\omega_{h}^{2} - \omega^{2} - i\gamma\omega)}\right)} \cdot \left(\mu_{\infty} + \frac{S_{m}\omega_{h}^{2}}{(\omega_{h}^{2} - \omega^{2} - i\gamma\omega)}\right)\right)}$$

$$= F\left(\sqrt{\varepsilon_{\infty}} \cdot \mu_{\infty} + \frac{\left(S_{e} \cdot \mu_{\infty} + S_{m} \cdot \varepsilon_{\infty}\right) \cdot \omega_{h}^{2}}{(\omega_{h}^{2} - \omega^{2} - i\gamma\omega)} + \delta}\right) \approx F\left(\sqrt{\varepsilon_{\infty}} + \frac{S_{T} \cdot \omega_{h}^{2}}{(\omega_{h}^{2} - \omega^{2} - i\gamma\omega)}\right).$$
(C.3)

For strong absorption at the hybrid mode, when one can neglect multiple reflections,

$$F(y) = |(1-r^2)t(y)|^2$$
 where  $y = \sqrt{\varepsilon \cdot \mu}$ ,  $t(y) = \exp\left(i\frac{\omega}{c}yd\right)$ , and  $r$  is the complex

reflection coefficient. We note that at  $\omega_h$ , the reflection intensity  $R(\omega)$  as described by Eq. (C.1) does not change significantly. As one can see from Eq. (C.3), the AOS in transmission is  $S_T \approx S_e \cdot \mu_{\infty} + S_m \cdot \varepsilon_{\infty}$ . In contrast to  $S_R$ , the magnetic and electric oscillator strengths in  $S_T$  are additive. Note that the contribution of the magnetic oscillator strength in  $S_T$  is "enhanced" by  $\varepsilon_{\infty}$ . The expressions for  $S_R$  and  $S_T$  allow for analysis of the interesting case of hybrid modes which can cancel or disappear in reflectivity but remain strong in transmission. Note that the exact analytical expression for F(y) in the general case of multiple reflections is complicated and will be discussed below.

A complete analysis of thin film reflectivity and transmission must involve the reflection from the backside of the sample, which depends on the thickness d. The opposing shapes of the Lorentzian profile of the magnetic and electric excitations motivate the calculation of  $\frac{\partial R_{ss}(\omega_h)}{\partial \omega}$  and  $\frac{dT_{ss}(\omega_h)}{d\omega}$ . The two total derivatives require partial derivative expansion of the response functions as well as those of  $r_{ss}$  and  $t_{ss}$ , the complex reflection and transmission coefficients. For a magnetic thin film whose principal axes are coincident with the laboratory system,  $r_{ss}$  and  $t_{ss}$  are given by [1]:

$$r_{ss} = \frac{q_{zs} \cos(q_{zs}d)(k_{z0} - k_{z2}) + i\left(\frac{q_{zs}^2}{\mu_{xx}} - k_{z0}k_{z2}\mu_{xx}\right)\sin(q_{zs}d)}{q_{zs}\cos(q_{zs}d)(k_{z0} + k_{z2}) - i\left(\frac{q_{zs}^2}{\mu_{xx}} + k_{z0}k_{z2}\mu_{xx}\right)\sin(q_{zs}d)}, \quad (C.4)$$

$$t_{ss} = \frac{2k_{z0}q_{zs}}{q_{zs}\cos(q_{zs}d)(k_{z0} + k_{z2}) - i\left(\frac{q_{zs}^2}{\mu_{xx}} + k_{z0}k_{z2}\mu_{xx}\right)\sin(q_{zs}d)},$$

where  $k_{z0}$ ,  $q_{zs}$  and  $k_{z2}$  are the *z* components of the wave vector in the incident, thin film and substrate media, respectively. At hybrid resonance, the following expressions for the two total derivatives are obtained:

$$\frac{dR_{ss}}{d\omega} \cong r_{ss}^* \cdot S_2 + r_{ss} \cdot S_2^* \quad \text{and} \quad \frac{dT_{ss}}{d\omega} \cong t_{ss}^* \cdot S_3 + t_{ss} \cdot S_3^* \tag{C.5}$$

where  $S_2$  and  $S_3$  are given by:

$$S_{2} = -\frac{2\omega_{h}}{\gamma_{h}^{2}} \frac{\alpha_{e}^{R_{TF}}(\omega_{h})}{\sqrt{\mu(\omega_{h})\varepsilon(\omega_{h})}} \left( \mu(\omega_{h})S_{e} + \varepsilon(\omega_{h})S_{m} \frac{\alpha_{m}^{R_{TF}}(\omega_{h})}{\alpha_{e}^{R_{TF}}(\omega_{h})} \right)$$

$$S_{3} = -\frac{2\omega_{h}}{\gamma_{h}^{2}} \frac{\alpha_{e}^{T}(\omega_{h})}{\sqrt{\mu(\omega_{h})\varepsilon(\omega_{h})}} \left( \mu(\omega_{h})S_{e} + \varepsilon(\omega_{h})S_{m} \frac{\alpha_{m}^{T}(\omega_{h})}{\alpha_{e}^{T}(\omega_{h})} \right)$$

$$(C.6)$$

The four  $\alpha$  terms are components of the partial derivatives of the complex reflection and transmission coefficients taken with respect to the two response functions. Analytic solutions for these terms can be obtained starting from  $r_{ss}$  and  $t_{ss}$ . For the material parameters of Dy<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> sample with the thickness of 0.55 mm,  $\frac{\alpha_m^{R_{TF}}(\omega_h)}{\alpha_e^{R_{TF}}(\omega_h)}$  and  $\frac{\alpha_m^T(\omega_h)}{\alpha_e^T(\omega_h)}$  are negative and positive, respectively, with absolute value equal to 1 (see FIG. C.1). When these values are inserted into Eq. (9.A6), the upper and lower bracketed terms can

be identified with the  $S_R$  and  $S_T$  terms discussed in the Veselago qualitative analysis above. These results are also consistent with the subtraction and addition of the AOS components in reflectivity and transmission, respectively.



**Fig. C.1** Variability of the ratio of  $\alpha$  terms with thin film thickness,  $d \, \cdot \, \varepsilon_{\infty} = 15.85$ ,  $S_e = 0.100$ ,  $S_m = 0.0063$  and  $\omega_h = 78 \text{ cm}^{-1}$ .  $\frac{\alpha_m^{R_{TT}}(\omega_h)}{\alpha_e^{R_{TT}}(\omega_h)}$  is the bottom solid red line.  $\frac{\alpha_m^T(\omega_h)}{\alpha_e^T(\omega_h)}$  is the top blue dashed line. For the Dy<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> sample with thickness d = 0.55 mm, the opposite signs of these two ratios account for the subtraction of AOS contributions in reflectivity and the addition of the AOS contributions in transmission.

The case where hybrid mode magnetic and electric dipole contributions completely cancel in reflection ( $S_R = 0$ ) but add to  $S_T$  in transmission requires the solution of the following simultaneous equation:

$$\mu(\omega_{h})S_{e} + \varepsilon(\omega_{h})S_{m}\frac{\alpha_{m}^{R_{TF}}(\omega_{h})}{\alpha_{e}^{R_{TF}}(\omega_{h})} = 0$$

$$\mu(\omega_{h})S_{e} + \varepsilon(\omega_{h})S_{m}\frac{\alpha_{m}^{T}(\omega_{h})}{\alpha_{e}^{T}(\omega_{h})} = S_{T}$$
(C.7)

For the case of the fitted parameters for Dy-IG,  $\frac{\alpha_m^{R_{TF}}(\omega_h)}{\alpha_e^{R_{TF}}(\omega_h)} \approx -1$ ,  $\frac{\alpha_m^{T}(\omega_h)}{\alpha_e^{T}(\omega_h)} \approx 1$ ,  $\mu(\omega_h) \approx 1$  and  $\varepsilon(\omega_h) \approx \varepsilon_{\infty}$ , Eq. (C.7) has the approximate solution:  $S_e \cong \frac{S_T}{2}$  and  $S_m \cong \frac{S_T}{2\varepsilon_{\infty}}$ .

#### **APPENDIX D**

# DERIVATION OF ADJUSTED OSCILLATOR STRENGTH MATCHING CONDITION USING DERIVATIVE APPROACH

#### **D.1 Introduction**

Berreman's 4×4 matrix formalism can be used to analyze the optical properties of a crystal with  $\mu \neq 1$ . This technique can always return numerical solutions which describe wave propagation in the material. However, for many crystal symmetries, including those of orthorhombic and higher, closed form solutions for the complex reflection coefficients of a semi-infinite material and the complex reflection and transmission coefficients of a thin film can be obtained. These formulas are appropriate for the case where the principal axes of the crystal are coincident with the laboratory axes. From these formulas, expressions for the derivatives with respect to  $\omega$  of  $R_{ss}(\omega)$  and  $T_{ss}(\omega)$  can be calculated.  $R_{ss}(\omega)$  and  $T_{ss}(\omega)$  are the Reflection and Transmission intensities, respectively.

Focus is on the derivative calculations for two reasons. First, while it is possible to obtain exact analytical expressions for the complex reflection and transmission coefficients, analytical expressions for  $R_{ss}(\omega)$  and  $T_{ss}(\omega)$  are more difficult to obtain. Second, for materials with  $\mu \neq 1$ , an examination of the variation of intensity with respect to the frequency of incident radiation gives important information regarding the interaction between the magnetic and dielectric oscillators used in modeling optical properties. The derivative approach allows for the interesting property of Adjusted Oscillator Strength (AOS) for each of the magnetic and dielectric oscillators to be identified. In turn, AOS gives rise to the fascinating case of Adjusted Oscillator Strength Matching (AOSM) for hybrid modes. When the AOSM condition is fulfilled, the hybrid modes can be completely cancelled in the Reflection spectra but are additive in the Transmission spectra.

### **D.2.** Key Results From 4×4 Matrix Formalism

For readability, key results from Berreman's 4×4 matrix formalism are included to make this Appendix self consistent.  $q_{zp}$  and  $q_{zs}$  are the eigenvalues associated with p and spolarizations, respectively and constitute the z components of the wave vectors in the medium. These are:

$$q_{zp} = \frac{\omega}{c} \sqrt{\varepsilon_{xx}} \sqrt{\mu_{yy} - \frac{N_0^2 \sin^2(\theta_0)}{\varepsilon_{zz}}}$$
(D.1)

$$q_{zs} = \frac{\omega}{c} \sqrt{\mu_{xx}} \sqrt{\varepsilon_{yy} - \frac{N_0^2 \sin^2(\theta_0)}{\mu_{zz}}}$$
(D.2)

For a semi-infinite medium, the complex reflection coefficients are determined to be:

$$r_{pp} = \frac{\varepsilon_{xx}k_{z0} - N_0^2 q_{zp}}{\varepsilon_{xx}k_{z0} + N_0^2 q_{zp}}$$
(D.3)

$$r_{ss} = \frac{\mu_{xx}k_{z0} - q_{zs}}{\mu_{xx}k_{z0} + q_{zs}},\tag{D.4}$$

where  $N_0$  is the index of refraction of the incident medium and  $k_{z0}$  is the *z* component of the incident wave vector. In the case of thin films, the complex reflection and transmission coefficients are calculated using 4×4 matrix formalism to be:

$$r_{pp} = \frac{q_{zp} \cos(q_{zp}d) \left(\frac{N_2}{N_0} k_{z0} - \frac{N_0}{N_2} k_{z2}\right) + i \left(\frac{N_0 N_2 q_{zp}^2}{\varepsilon_{xx}} - \frac{\varepsilon_{xx} k_{z0} k_{z2}}{N_0 N_2}\right) \sin(q_{zp}d)}{q_{zp} \cos(q_{zp}d) \left(\frac{N_2}{N_0} k_{z0} + \frac{N_0}{N_2} k_{z2}\right) - i \left(\frac{N_0 N_2 q_{zp}^2}{\varepsilon_{xx}} + \frac{\varepsilon_{xx} k_{z0} k_{z2}}{N_0 N_2}\right) \sin(q_{zp}d)}$$
(D.5)

$$t_{pp} = \frac{2k_{z0}q_{zp}}{q_{zp}\cos(q_{zp}d)\left(\frac{N_2}{N_0}k_{z0} + \frac{N_0}{N_2}k_{z2}\right) - i\left(\frac{N_0N_2q_{zp}^2}{\varepsilon_{xx}} + \frac{\varepsilon_{xx}k_{z0}k_{z2}}{N_0N_2}\right)\sin(q_{zp}d)}$$

and

$$r_{ss} = \frac{q_{zs} \cos(q_{zs}d)(k_{z0} - k_{z2}) + i\left(\frac{q_{zs}^{2}}{\mu_{xx}} - k_{z0}k_{z2}\mu_{xx}\right)\sin(q_{zs}d)}{q_{zs} \cos(q_{zs}d)(k_{z0} + k_{z2}) - i\left(\frac{q_{zs}^{2}}{\mu_{xx}} + k_{z0}k_{z2}\mu_{xx}\right)\sin(q_{zs}d)}$$

$$t_{ss} = \frac{2k_{z0}q_{zs}}{q_{zs}\cos(q_{zs}d)(k_{z0} + k_{z2}) - i\left(\frac{q_{zs}^{2}}{\mu_{xx}} + k_{z0}k_{z2}\mu_{xx}\right)\sin(q_{zs}d)}$$
(D.6)

where  $N_2$  is the index of refraction of the substrate medium and  $k_{z2}$  is the *z* component of the wave vector in the substrate.

# **D.3** Approach to the Calculation of Derivatives of $R_{ss}(\omega)$ and $T_{ss}(\omega)$ .

Magnetic and dielectric excitations are modeled as Lorentzian oscillators:

$$\mathcal{E}(\omega) = \mathcal{E}_{\infty} + \sum_{j=1}^{N} \frac{S_{j,e} \omega_{j,e0}^{2}}{(\omega^{2} - \omega_{j,e0}^{2} - i\gamma_{j,e} \omega)},$$

$$\mu(\omega) = 1 + \sum_{j=1}^{M} \frac{S_{j,m} \omega_{j,m0}^{2}}{(\omega^{2} - \omega_{j,m0}^{2} - i\gamma_{j,m} \omega)},$$
(D.7)
where  $\varepsilon_{\infty}$  is the infinite-frequency of the dielectric function,  $S_{e,m}$  is the corresponding mode oscillator strength,  $\gamma_{e,m}$  is the damping constant, and  $\omega_{0e,m}$  is the resonance frequency.

 $R_{ss}(\omega)$  and  $T_{ss}(\omega)$  are the *s* polarized reflection and transmission intensities, respectively. Both are real valued functions of their associated complex coefficients:

$$R_{ss}(\omega) = r_{ss}(\omega) \times r_{ss}(\omega)^{*}$$

$$T_{ss}(\omega) = t_{ss}(\omega) \times t_{ss}(\omega)^{*}$$
(D.8)

The asterisk in (D.8) indicates the complex conjugate operation. Expressions for  $\frac{\partial R_{ss}(\omega)}{\partial \omega}$ 

and  $\frac{dT_{ss}(\omega)}{d\omega}$  will be developed in parallel.

From (D.8), the derivative chain rule for complex variables is used to obtain:

$$\frac{\partial R_{ss}(\omega)}{\partial \omega} = r_{ss}(\omega)^* \frac{\partial r_{ss}(\omega)}{\partial \omega} + r_{ss}(\omega) \frac{\partial r_{ss}(\omega)^*}{\partial \omega}$$

$$\frac{\partial T_{ss}(\omega)}{\partial \omega} = t_{ss}(\omega)^* \frac{\partial t_{ss}(\omega)}{\partial \omega} + t_{ss}(\omega) \frac{\partial t_{ss}(\omega)^*}{\partial \omega}$$
(D.9)

In (D.9),  $r_{ss}$  and  $t_{ss}$  are functions of  $\varepsilon$  and  $\mu$  and  $\varepsilon$  and  $\mu$ , in turn, are functions of  $\omega$ .

Accordingly, the formulas for  $\frac{dR_{ss}(\omega)}{d\omega}$  and  $\frac{dT_{ss}(\omega)}{d\omega}$  require expansion in partial

derivatives. The following expressions are used in this analysis:

$$\frac{dR_{ss}}{d\omega} = r_{ss}^{*} \left( \frac{\partial r_{ss}}{\partial \varepsilon} \frac{\partial \varepsilon}{d\omega} + \frac{\partial r_{ss}}{\partial \mu} \frac{\partial \mu}{d\omega} \right) + r_{ss} \left( \frac{\partial r_{ss}}{\partial \varepsilon} \frac{\partial \varepsilon}{d\omega} + \frac{\partial r_{ss}}{\partial \mu} \frac{\partial \mu}{d\omega} \right)^{*}$$
(D.10)  
$$\frac{dT_{ss}}{d\omega} = t_{ss}^{*} \left( \frac{\partial t_{ss}}{\partial \varepsilon} \frac{\partial \varepsilon}{d\omega} + \frac{\partial t_{ss}}{\partial \mu} \frac{\partial \mu}{d\omega} \right) + t_{ss} \left( \frac{\partial t_{ss}}{\partial \varepsilon} \frac{\partial \varepsilon}{d\omega} + \frac{\partial t_{ss}}{\partial \mu} \frac{\partial \mu}{d\omega} \right)^{*}$$

For both semi-infinite and thin film configurations, the procedure to calculate these derivatives begins with analytical expressions for  $r_{ss}$  and  $t_{ss}$ . From these expressions, the required partial derivatives can be calculated. It is possible for some simplifications to be obtained in (D.10) if the response functions are analyzed at magnetic and dielectric resonance.

#### **D.4** Semi-infinite configuration – separate modes

For the semi-infinite case, the *s* polarized eigenvalue,  $q_{zs}$ , is given in Eq. (D.2) and the general equation for the *s* polarized complex reflection coefficient is given in Eq. (D.4). For simplification, an isotropic material is modeled using one magnetic and one dielectric Lorentzian oscillator whose natural frequencies are separated by at least  $3 \gamma_{e,m}$ .

In addition, only normally incident radiation is considered.  $\frac{dR_{ss}}{d\omega}$  is analyzed at each of magnetic and dielectric resonance with the terms  $\frac{\partial \varepsilon}{d\omega}$  and  $\frac{\partial \mu}{d\omega}$  being considered first. At magnetic resonance, the term  $\frac{\partial \varepsilon}{d\omega}$  is negligible. At dielectric resonance, the term  $\frac{\partial \mu}{d\omega}$  is negligible. At each of their respective resonances, the derivatives can be approximated by the following real valued expressions:

$$\frac{d\varepsilon}{d\omega}\Big|_{\omega \in 0} \cong -\frac{2S_e \omega_{e0}}{\gamma_e^2}$$
(D.11)  
$$\frac{d\mu}{d\omega}\Big|_{\omega_{m0}} \cong -\frac{2S_m \omega_{m0}}{\gamma_m^2}$$

Expressions for  $\frac{dr_{ss}}{d\varepsilon}$  and  $\frac{dr_{ss}}{d\mu}$  are given by:

$$\frac{dr_{ss}}{d\varepsilon}\Big|_{\omega_{e0}} = \sqrt{\frac{\mu(\omega_{e0})}{\varepsilon(\omega_{e0})}} \alpha_{e}^{R_{st}}(\omega_{e0})$$

$$\frac{dr_{ss}}{d\mu}\Big|_{\omega_{m0}} = \sqrt{\frac{\varepsilon(\omega_{m0})}{\mu(\omega_{m0})}} \alpha_{m}^{R_{st}}(\omega_{m0})$$
(D.12)

where the  $\alpha$  terms are defined as:

$$\alpha_{e,m}^{R_{SI}} = \frac{\mp 1}{\left(\sqrt{\varepsilon} + \sqrt{\mu}\right)^2} \tag{D.13}$$

In Eq. (D.13), the terms associated with the dielectric (magnetic) oscillator are given by the upper (lower) sign. The *SI* (meaning semi-infinite) subscript in Eq. (D.12) is used to distinguish this term from its thin film counterpart which will be discussed below. Note that the expressions for  $\alpha_e^{R_{SI}}$  and  $\alpha_m^{R_{SI}}$  are of opposite sign. It is this factor which accounts for the differing Lorentzian profiles for magnetic and dielectric excitations in the Reflection spectra. Inserting Eq. (D.11) and Eq. (D.12) into Eq. (D.10) produces:

$$\frac{dR_{ss}}{d\omega}\Big|_{\omega_{e0}} \approx -\frac{2\omega_{e0}}{\gamma_{e}^{2}} \left( r_{ss}^{*} \left( \frac{\sqrt{\mu(\omega_{e0})}}{\sqrt{\varepsilon(\omega_{e0})}} \alpha_{e}^{R_{st}}(\omega_{e0}) S_{e} \right) + r_{ss} \left( \frac{\sqrt{\mu(\omega_{e0})}}{\sqrt{\varepsilon(\omega_{e0})}} \alpha_{e}^{R_{st}}(\omega_{e0}) S_{e} \right)^{*} \right)$$

$$\frac{dR_{ss}}{d\omega}\Big|_{\omega_{m0}} \approx -\frac{2\omega_{m0}}{\gamma_{m}^{2}} \left( r_{ss}^{*} \left( \frac{\sqrt{\varepsilon(\omega_{m0})}}{\sqrt{\mu(\omega_{m0})}} \alpha_{m}^{R_{st}}(\omega_{m0}) S_{m} \right) + r_{ss} \left( \frac{\sqrt{\varepsilon(\omega_{m0})}}{\sqrt{\mu(\omega_{m0})}} \alpha_{m}^{R_{st}}(\omega_{m0}) S_{m} \right)^{*} \right)$$
(D.14)

We are motivated to find the ratio of these two derivatives. For modes with similar  $\gamma_{e,m}$ , it is evident that the ratio of the size of the excitations at magnetic and dielectric resonance is directly proportional to the ratio of  $\frac{dR_{ss}}{d\omega}$  calculated at each resonance. When the imaginary components in Eq. (D.14) are small compared to their real counterparts, the ratio of these derivatives can be approximated as:

$$\frac{\sqrt{\mu(\omega_{e^0})\mu(\omega_{m^0})}}{\sqrt{\varepsilon(\omega_{e^0})\varepsilon(\omega_{m^0})}}\frac{\alpha_e^{R_{SI}}(\omega_{e^0})}{\alpha_m^{R_{SI}}(\omega_{m^0})}\frac{S_e}{S_m}\frac{\omega_{e^0}}{\omega_{m^0}}\frac{\gamma_m^2}{\gamma_e^2}$$
(D.15)

If it is further assumed that: (i)  $\gamma_e \approx \gamma_m \approx \gamma$ ; and (ii) the first term in the bracket can be approximated by the ratio of the background response functions  $\frac{\mu_{bg}}{\varepsilon_{bg}}$ , then a good first

order approximation of the ratio of the derivatives at the two resonances is given by:

$$\frac{\frac{dR_{ss}}{d\omega}}{\frac{dR_{ss}}{d\omega}} \approx \frac{\mu_{bg}}{\varepsilon_{bg}} \frac{S_e}{S_m} \frac{\alpha_e^{R_{st}}(\omega_{e0})}{\alpha_m^{R_{st}}(\omega_{m0})} \frac{\omega_{e0}}{\omega_{m0}}$$
(D.16)

It is important to note in Eq. (D.16), that the ratio is not simply proportional to the ratio of oscillator strengths but rather to the ratio of the oscillator strengths *adjusted* by their constitutive complement. This is an important observation. It suggests that even when

 $S_m \ll S_e$ , the impact of the magnetic oscillator in Reflection can be brought to the same order as that of the dielectric oscillator as a result of its multiplication by  $\varepsilon_{bg}$ . The role of this adjustment becomes even more apparent when consideration is given to hybrid modes.

# D.5. Semi-infinite configuration - hybrid modes

The interesting case of coincident natural frequencies for the magnetic and dielectric oscillators is now examined. This case is referred to as the hybrid mode. The assumption that  $\frac{\partial \varepsilon}{\partial \omega}$  and  $\frac{\partial \mu}{\partial \omega}$  are negligible at magnetic and dielectric resonance, respectively, can no longer be made given coincident resonances. The partial derivative expansion requires a second term and becomes:

$$\frac{dR_{ss}}{d\omega}\Big|_{\omega_h} \cong -\frac{2\omega_h}{\gamma_h^2} \frac{1}{\sqrt{\mu(\omega_h)\varepsilon(\omega_h)}} \Big(r_{ss}^* S_1 + r_{ss} S_1^*\Big), \tag{D.17}$$

where,

$$S_{1} = \alpha_{e}^{R_{SI}} (\omega_{h}) \left( \mu(\omega_{h}) S_{e} + \varepsilon(\omega_{h}) \frac{\alpha_{m}^{R_{SI}} (\omega_{h})}{\alpha_{e}^{R_{SI}} (\omega_{h})} S_{m} \right)$$
(D.18)

In Eq.(D.18), the bracketed term is identified as the Net Adjusted Oscillator strength for reflection and we define this term as  $S_R$ . At hybrid frequency,  $\alpha_e^R(\omega_h) = -\alpha_m^R(\omega_h)$  and  $S_R$  can be further reduced to:

$$S_{R}(\omega_{h}) = (\mu(\omega_{h})S_{e} - \varepsilon(\omega_{h})S_{m}).$$
(D.19)

In Eq. (D.19), the two components are identified as the Adjusted Oscillator Strengths (AOS) for the individual modes. The term  $\mu(\omega_h)S_e$  is identified as the AOS of the

dielectric oscillator. The term  $\varepsilon(\omega_h) S_m$  is identified as the AOS of the magnetic oscillator. This equation also suggests that the AOS for the contributing modes tend to cancel in Reflection. This motivates examination of the interesting case when the AOS for the two modes are exactly matched. In this case,  $\frac{dR_{ss}}{d\omega}\Big|_{\omega_h} = 0$  and occurs when the adjusted oscillator strengths satisfy the simple condition:  $S_m \varepsilon(\omega_h) = S_{\varepsilon} \mu(\omega_h)$ . We define this condition as Adjusted Oscillator Strength Matching (AOSM). Notwithstanding that there are two oscillators active at  $\omega_h$ , when AOSM is satisfied, they interact in such a way as to have no net impact on the background reflectivity at that point in the spectra. Note that in deriving Eq. (D.19), no assumptions have been made about the relationship of the imaginary and real components in the equation. In other words, to establish the AOSM condition perfectly, both the real and imaginary components in Eq. (D.19) must be identical.

### **D.6.** Thin film configuration – separate modes

The general equations for the complex reflection and transmission coefficients for s polarized radiation incident upon a thin film of thickness d are given in Eq. (D.6). As for the semi-infinite case, an isotropic material is modeled using one magnetic and one dielectric Lorentzian oscillator whose natural frequencies are separated by at least  $3\gamma_{e,m}$ . Radiation is again incident normally. Both expressions in (D.9) and (D.10) will be developed in parallel. Since the same Lorentzian oscillator models will be used, the analysis for  $\frac{\partial \varepsilon}{d\omega}$  and  $\frac{\partial \mu}{d\omega}$  is identical to the semi-infinite case. Analytical formulas for

the other derivatives are more complicated than those of the semi-infinite case and are given below:

$$\frac{\partial r_{ss}(\omega)}{\partial \varepsilon} = \sqrt{\frac{\mu}{\varepsilon}} \alpha_{e}^{R_{TF}} \qquad \frac{\partial t_{ss}}{\partial \varepsilon} = \sqrt{\frac{\mu}{\varepsilon}} \alpha_{e}^{T} \qquad , \qquad (D.20)$$

$$\frac{\partial r_{ss}(\omega)}{\partial \mu} = \sqrt{\frac{\varepsilon}{\mu}} \alpha_{m}^{R_{TF}} \qquad \frac{\partial t_{ss}}{\partial \mu} = \sqrt{\frac{\varepsilon}{\mu}} \alpha_{m}^{T}$$

where the expressions for  $\alpha$  are calculated as:

$$\alpha_{e,m}^{R_{TF}} = \frac{\pm 2\left(\sqrt{\varepsilon\mu} \pm 2id\sqrt{\varepsilon}(\varepsilon - \mu)\sqrt{\mu\pi\omega}\right) \mp 2\sqrt{\varepsilon\mu} \text{Cos}\left[4d\sqrt{\varepsilon\mu\pi\omega}\right] \pm i(\varepsilon + \mu)\text{Sin}\left[4d\sqrt{\varepsilon\mu\pi\omega}\right]}{2\left(2\sqrt{\varepsilon\mu}\text{Cos}\left[2d\sqrt{\varepsilon\mu\pi\omega}\right] - i(\varepsilon + \mu)\text{Sin}\left[2d\sqrt{\varepsilon\mu\pi\omega}\right]\right)^{2}}$$
(D.21)  
$$\alpha_{e,m}^{T} = -\frac{i\left(2d\sqrt{\varepsilon\mu}(\varepsilon + \mu)\pi\omega\text{Cos}\left[2d\sqrt{\varepsilon\mu\pi\omega}\right] + (\pm\varepsilon\mp\mu - 4id\varepsilon\mu\pi\omega)\text{Sin}\left[2d\sqrt{\varepsilon\mu\pi\omega}\right]\right)}{\left(2i\sqrt{\varepsilon\mu}\text{Cos}\left[2d\sqrt{\varepsilon\mu\pi\omega}\right] + (\varepsilon + \mu)\text{Sin}\left[2d\sqrt{\varepsilon\mu\pi\omega}\right]\right)^{2}}$$

In the above equations, the subscript TF (meaning thin film) is used to distinguish it from its semi-infinite counterpart. In Eq. (D.21), terms associated with the dielectric (magnetic) oscillator follow the upper (lower) signs.

As in the semi-infinite case, we are again motivated to examine  $\frac{dR_{ss}}{d\omega}$  at each resonance in order to estimate a ratio of the size of excitations in the Reflectivity spectra. With the exception of the  $\alpha$  terms, an expression identical in form to the semi-infinite case is obtained:

$$\frac{dR_{ss}}{d\omega}\Big|_{\omega_{e0}} \approx -\frac{2\omega_{e0}}{\gamma_{e}^{2}} \left( r_{ss}^{*} \left( \frac{\sqrt{\mu(\omega_{e0})}}{\sqrt{\varepsilon(\omega_{e0})}} \alpha_{e}^{R_{TF}}(\omega_{e0}) S_{e} \right) + r_{ss} \left( \frac{\sqrt{\mu(\omega_{e0})}}{\sqrt{\varepsilon(\omega_{e0})}} \alpha_{e}^{R_{TF}}(\omega_{e0}) S_{e} \right)^{*} \right)$$

$$\frac{dR_{ss}}{d\omega}\Big|_{\omega_{m0}} \approx -\frac{2\omega_{m0}}{\gamma_{m}^{2}} \left( r_{ss}^{*} \left( \frac{\sqrt{\varepsilon(\omega_{m0})}}{\sqrt{\mu(\omega_{m0})}} \alpha_{m}^{R_{TF}}(\omega_{m0}) S_{m} \right) + r_{ss} \left( \frac{\sqrt{\varepsilon(\omega_{m0})}}{\sqrt{\mu(\omega_{m0})}} \alpha_{m}^{R_{TF}}(\omega_{m0}) S_{m} \right)^{*} \right)$$
(D.22)

When the imaginary components in (D.22) are small compared to their real counterparts and we make similar assumptions as for the semi-infinite case concerning the  $\gamma$ ,  $\varepsilon_{bg}$  and  $\mu_{bg}$  parameters, the first order approximation to the ratio of these derivatives becomes:

$$\frac{\frac{dR_{ss}}{d\omega}}{\frac{dR_{ss}}{d\omega}} \approx \frac{\mu_{bg}}{\varepsilon_{bg}} \frac{S_e}{S_m} \frac{\alpha_e^{R_{TF}}(\omega_{e0})}{\alpha_m^{R_{TF}}(\omega_{m0})} \frac{\omega_{e0}}{\omega_{m0}}$$
(D.23)

In (D.23), the  $\frac{\alpha_e^{R_{TF}}(\omega_{e0})}{\alpha_m^{R_{TF}}(\omega_{m0})}$  term is again negative. It is through this factor that the opposite

slopes of the magnetic and dielectric resonances in Reflectivity are incorporated into the thin film configuration. Eq. (D.23) also shows that the AOS phenomenon is present for thin films. This again motivates an analysis of the interesting case of hybrid modes.

## **D.7.** Thin film configuration – hybrid modes

The case of coincident natural frequencies for the magnetic and dielectric oscillators in thin films is now examined. The partial derivative expansions for Reflection and Transmission for thin films are:

$$\frac{dR_{ss}}{d\omega} \cong r_{ss}^{*}(S_{2}) + r_{ss}(S_{2})^{*}$$

$$\frac{dT_{ss}}{d\omega} \cong t_{ss}^{*}(S_{3}) + t_{ss}(S_{3})^{*}$$
(D.24)

where  $S_2$  and  $S_3$  are given by:

$$S_{2} = -\frac{2\omega_{h}}{\gamma_{h}^{2}} \frac{\alpha_{e}^{R_{TF}}(\omega_{h})}{\sqrt{\mu(\omega_{h})\varepsilon(\omega_{h})}} \left(\mu(\omega_{h})S_{e} + \varepsilon(\omega_{h})S_{m}\frac{\alpha_{m}^{R_{TF}}(\omega_{h})}{\alpha_{e}^{R_{2}}(\omega_{h})}\right)$$

$$S_{3} = -\frac{2\omega_{h}}{\gamma_{h}^{2}} \frac{\alpha_{e}^{T}(\omega_{h})}{\sqrt{\mu(\omega_{h})\varepsilon(\omega_{h})}} \left(\mu(\omega_{h})S_{e} + \varepsilon(\omega_{h})S_{m}\frac{\alpha_{m}^{T}(\omega_{h})}{\alpha_{e}^{T}(\omega_{h})}\right)$$
(D.25)

In Eq. (D.25), the bracketed terms can be recognized as the contributions the Net Adjusted Oscillator Strength for Reflection and Transmission and can be defined for thin films as  $S_R$  and  $S_T$ . At hybrid resonance, while  $\frac{\alpha_m^{R_2}(\omega_h)}{\alpha_e^{R_2}(\omega_h)}$  is a negative term, it is no longer identically equivalent to -1 under all circumstances and will be retained in the following

expressions. The AOSM condition for thin films is therefore:

$$\mu(\omega_h)S_e = -\varepsilon(\omega_h)S_m \frac{\alpha_m^{R_2}(\omega_h)}{\alpha_e^{R_2}(\omega_h)}$$
(D.26)

At hybrid resonance, while the  $\frac{\alpha_m^T(\omega_h)}{\alpha_e^T(\omega_h)}$  term is positive, it is not identically equivalent to

unity and will also be retained. The fact that this latter ratio is positive sets up the interesting result that while the modes in reflection tend to cancel, in transmission the AOS for each mode is additive. We note again that no assumptions regarding the relationship between the real and imaginary components were made in deriving Eq.

(D.26). Accordingly, to establish AOSM perfectly, both the real and imaginary parts must match. The condition for AOSM in Reflectivity and additive modes in Transmission requires the solution of a simultaneous equation. Assume that the Transmission spectra for a material can be fitted using a dielectric oscillator strength of  $S_{Total}$ . At hybrid frequency, this result could also be obtained through a combination of one magnetic and one dielectric oscillator. Using the expressions for AOS derived above, the simultaneous equation can be written down as:

$$\mu(\omega_{h})S_{e} + \varepsilon(\omega_{h})S_{m}\frac{\alpha_{m}^{R_{TF}}(\omega_{h})}{\alpha_{e}^{R_{TF}}(\omega_{h})} = 0$$

$$\mu(\omega_{h})S_{e} + \varepsilon(\omega_{h})S_{m}\frac{\alpha_{m}^{T}(\omega_{h})}{\alpha_{e}^{T}(\omega_{h})} = S_{Total}$$
(D.27)

Eq. (D.27) has the solution:

$$S_{m} = \frac{S_{Total}}{\varepsilon(\omega_{h})} \frac{1}{\left(\frac{\alpha_{m}^{T}(\omega_{h})}{\alpha_{e}^{T}(\omega_{h})} - \frac{\alpha_{m}^{R_{TF}}(\omega_{h})}{\alpha_{e}^{R_{TF}}(\omega_{h})}\right)}$$
(D.28)  
$$S_{e} = -\frac{S_{Total}}{\mu(\omega_{h})} \frac{\alpha_{m}^{R_{TF}}(\omega_{h})}{\alpha_{e}^{R_{TF}}(\omega_{h})} \frac{1}{\left(\frac{\alpha_{m}^{T}(\omega_{h})}{\alpha_{e}^{T}(\omega_{h})} - \frac{\alpha_{m}^{R_{TF}}(\omega_{h})}{\alpha_{e}^{R_{TF}}(\omega_{h})}\right)}$$

Eq. (D.28) describes the coupling condition in a hybrid mode. It will produce a result where we clearly see a mode in transmission with oscillator strength  $S_{Total}$  but no commensurate mode in Reflectivity. For the Dy<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> fitted parameters,  $\frac{\alpha_m^{R_2}(\omega_h)}{\alpha_s^{R_2}(\omega_h)} \approx -1$ ,

$$\frac{\alpha_m^T(\omega_h)}{\alpha_e^T(\omega_h)} \approx 1, \, \mu(\omega_h) \approx 1 \text{ and } \varepsilon(\omega_h) \approx \varepsilon_{bg} \text{ . Eq. (D.28) can be simplified to: } S_e \cong \frac{S_{Total}}{2} \text{ and } \varepsilon(\omega_h) \approx \varepsilon_{bg} \text{ and } \varepsilon(\omega_$$

 $S_m \cong \frac{S_{Total}}{2\varepsilon_{bg}}$ . These simplified equations were used in the fitting of the Reflection and

Transmission spectra for  $Dy_3Fe_5O_{12}$  with  $\mu \neq 1$ .

## REFERENCES

- [1] P.D. Rogers, T.D. Kang, T. Zhou, M. Kotelyanskii, A.A. Sirenko, Thin Solid Films 519 (2011) 2668.
- [2] P.D. Rogers, Y.J. Choi, E. Standard, T.D. Kang, K.H. Ahn, A. Dubroka, P. Marsik, C. Wang, C. Bernhard, S. Park, S.-W. Cheong, M. Kotelyanskii, A.A. Sirenko, Physical Review B (2011).
- [3] S.M. O'Malley, Ph.D. Thesis, Applied Physics, New Jersey Institute of Technology, Newark, New Jersey, 2009.
- [4] H. Fujiwara, Spectroscopic Ellipsometry : Principles and Applications, John Wiley & Sons, Chichester, England ; Hoboken, NJ, 2007.
- [5] M. Schubert, Infrared Ellipsometry on Semiconductor Layer Structures : Phonons, Plasmons, and Polaritons, Springer, Berlin ; New York, 2004.
- [6] T. Driscoll, D.N. Basov, W.J. Padilla, J.J. Mock, D.R. Smith, Phys. Rev. B 75 (2007) 115114.
- [7] M. Born, E. Wolf, Principles of Optics : Electromagnetic Theory of Propagation, Interference and Diffraction of Light, Cambridge University Press, Cambridge ; New York, 1999.
- [8] C. Kittel, Introduction to Solid State Physics, Wiley, Hoboken, NJ, 2005.
- [9] S. Blundell, Magnetism in Condensed Matter, Oxford University Press, Oxford ; New York, 2001.
- [10] G.H. Dieke, H.M. Crosswhite, H. Crosswhite, Spectra and Energy Levels of Rare Earth Ions in Crystals, Interscience Publishers, New York, 1968.
- [11] D. Talbayev, A.D. LaForge, S.A. Trugman, N. Hur, A.J. Taylor, R.D. Averitt, D.N. Basov, Physical Review Letters 101/24 (2008) 247601.
- [12] R.P. Feynman, R.B. Leighton, M.L. Sands, The Feynman Lectures on Physics, Addison-Wesley, Redwood City, Calif., 1989.
- [13] M.A. Omar, Elementary Solid State Physics: Principles and Applications, Addison-Wesley Pub. Co., Reading, Mass., 1975.
- [14] T.D. Kang, E. Standard, K.H. Ahn, A.A. Sirenko, G.L. Carr, S. Park, Y.J. Choi, M. Ramazanoglu, V. Kiryukhin, S.W. Cheong, Phys. Rev. B 82/1 (2010) 014414.

- [15] S.J. Orfanidis, Electromagnetic Waves and Antennas, <u>www.filestube.com/.../Electromagnetic-waves-and-antenna-Rutgers-</u> <u>ORFANIDIS.html</u>., Rutgers University, 2002. Accessed March, 2009.
- [16] D.W. Berreman, J. Opt. Soc. Am. 62 (1972) 502.
- [17] R.M.A. Azzam, N.M. Bashara, Ellipsometry and Polarized Light, North-Holland, Amsterdam, 1977.
- [18] J.-P. Rivera, Eur. Phys. J. B 71/3 (2009) 299.
- [19] D. Khomskii, Physics 2 (2009) 20.
- [20] M. Wegener, S. Linden, Physics Today 63/10 (2010) 32.
- [21] W. Eerenstein, N.D. Mathur, J.F. Scott, Nature 442/7104 (2006) 759.
- [22] L.D. Landau, E.M. Lifshitz, L.P. Pitaevskii, Electrodynamics of Continuous Media, Pergamon, Oxford [Oxfordshire]; New York, 1984.
- [23] I.E. Dzyaloshinskii, Sov. Phys. JETP 10 (1959) 628. (English Translation).
- [24] D.N. Astrov, Sov. Phys. JETP 11 (1960) 708. (English Translation).
- [25] T.H. O'Dell, The Electrodynamics of Magneto-Electric Media, North Holland, Amsterdam, 1970.
- [26] H. Schmid, Ferroelectrics 162/1 (1994) 317
- [27] N.A. Spaldin, S.-W. Cheong, R. Ramesh, Physics Today 63/10 (2010) 38.
- [28] N.A. Hill, The Journal of Physical Chemistry B 104/29 (2000) 6694.
- [29] S.-W. Cheong, M. Mostovoy, Nat Matter 6/1 (2007) 13.
- [30] R.V. Aguilar, M. Mostovoy, A.B. Sushkov, C.L. Zhang, Y.J. Choi, S.W. Cheong, H.D. Drew, Phys. Rev. Lett. 102/4 (2009) 047203.
- [31] N. Hur, S. Park, P.A. Sharma, J.S. Ahn, S. Guha, S.W. Cheong, Nature 429/6990 (2004) 392.
- [32] A. Cano, Physical Review B 80/18 (2009) 180416.
- [33] J.F. Nye, Physical Properties of Crystals Their Representation by Tensors and Matrices, Oxford University Press, Oxford, 2006.
- [34] W.S. Weiglhofer, A. Lakhtakia, Introduction to Complex Mediums for Optics and Electromagnetics, SPIE Optical Engineering Press, Bellingham, Wash., 2003.

- [35] M. Fiebig, T. Lottermoser, D. Frohlich, A.V. Goltsev, R.V. Pisarev, Nature 419/6909 (2002) 818.
- [36] V.G. Veselago, Sov. Phys. Usp. 10 (1968) 509.
- [37] V. Veselago, L. Braginksy, V. Shklover, C. Hafner, Journal of Computational and Theoretical Nanoscience 3 (2006) 1.
- [38] J.B. Pendry, A.J. Holden, D.J. Robbins, W.J. Stewart, IEEE Trans. Microwave Theory Tech. 47 (1999) 2075.
- [39] D.R. Smith, W.J. Padilla, D.C. Vier, S.C. Nemat-Nasser, S. Schultz, Physical Review Letters 84/18 (2000) 4184.
- [40] V.M. Shalaev, Nat Photon 1/1 (2007) 41.
- [41] E. Georgieva, J. Opt. Soc. Am. A 12/10 (1995) 2203.
- [42] A.N. Grigorenko, A.K. Geim, H.F. Gleeson, Y. Zhang, A.A. Firsov, I.Y. Khrushchev, J. Petrovic, Nature 438 (2005) 335.
- [43] I.V. Lindell, Electromagnetic Waves in Chiral and Bi-Isotropic Media, Artech House, Boston, 1994.
- [44] D.R. Smith, D. Schurig, Phys. Rev. Lett. 90 (2003) 077405.
- [45] D.H. Goldstein, E. Collett, Polarized Light, Marcel Dekker, New York, 2003.
- [46] M. Schubert, T. Hofmann, C.M. Herzinger, J. Opt. Soc. Am. A 20/2 (2003) 347.
- [47] P.S. Hauge, Surface Science 96/1-3 (1980) 108.
- [48] A. De Martino, E. Garcia-Caurel, B. Laude, B. Drévillon, Thin Solid Films 455-456 (2004) 112.
- [49] <u>http://www.nsls.bnl.gov/beamlines/beamline.asp?blid=U12IR</u>. Accessed February 2011.
- [50] H. Kuzmany, Solid-State Spectroscopy : An Introduction, Springer Verlag, Berlinew York, 1998.
- [51] E. Hecht, Optics, Pearson Education, Inc., 2002.
- [52] W.A. Shurcliff, S.S. Ballard, Polarized Light, Published for the Commission on College Physics [by] D. Van Nostrand, Princeton, N.J., 1964.
- [53] T.D. Kang, E. Standard, G.L. Carr, T. Zhou, M. Kotelyanskii, A.A. Sirenko, Thin Solid Films 519/9 (2011) 2698.

- [54] P.R. Bevington, D.K. Robinson, Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill, Boston, 2003.
- [55] W.H. Press, Numerical Recipes in FORTRAN : The Art of Scientific Computing, Cambridge University Press, Cambridge [England] ; New York, NY, USA, 1992.
- [56] K. Madsen, H.B. Nielsen, O. Tingleff, Methods for Non-Linear Least Squares Problems, Department of Informatics and Mathematical Modeling, Technical University of Denmark, Copenhagen, 2004.
- [57] A. Kuzmenko, Guide to RefFIT Software to Fit Optical Spectra, 2009.
- [58] P.E. Frandsen, K. Jonassen, H.B. Nielsen, O. Tingleff, Unconstrained Optimization, Department of Informatics and Mathematical Modeling, Technical University of Denmark, Copenhagen, 2004.
- [59] G.E. Jellison, in: H.G. Tompkins, E.A. Irene (Eds.), Handbook of Ellipsometry, William Andrew, Inc., Norwich, 2005, p. 237.
- [60] T. Driscoll, G.O. Andreev, D.N. Basov, S. Palit, T. Ren, J. Mock, S.-Y. Cho, N.M. Jokerst, D.R. Smith, App. Phys. Lett. 90 (2007) 092508.
- [61] E. Altewischer, M.P. van Exter, J.P. Woerdman, J. Opt. Soc. Am. B 22 (2005) 1731.
- [62] M. Schubert, B. Rheinländer, J.A. Woollam, B. Johs, C.M. Herzinger, J. Opt. Soc. Am. A 13 (1996) 875.
- [63] A. Pimenov, A.A. Mukhin, V.Y. Ivanov, V.D. Travkin, A.M. Balbashov, A. Loidl, Nat Phys 2/2 (2006) 97.
- [64] A.B. Sushkov, R.V. Aguilar, S. Park, S.W. Cheong, H.D. Drew, Phys. Rev. Lett. 98/2 (2007) 027202.
- [65] Y. Takahashi, N. Kida, Y. Yamasaki, J. Fujioka, T. Arima, R. Shimano, S. Miyahara, M. Mochizuki, N. Furukawa, Y. Tokura, Physical Review Letters 101/18 (2008) 187201.
- [66] Y. Takahashi, S. Ishiwata, S. Miyahara, Y. Kaneko, N. Furukawa, Y. Taguchi, R. Shimano, Y. Tokura, Physical Review B 81/10 (2010) 100413.
- [67] A.M. Nicholson, G.F. Ross, IEEE Trans. Instr. Meas. IM-19 (1970).
- [68] C. Bernhard, J. Humlícek, B. Keimer, Thin Solid Films 455-456 (2004) 143.
- [69] F. Sayetat, J. of Mag. and Mag. Mat. 58/3-4 (1986) 334.
- [70] K.P. Belov, V.I. Sokolov, Sov. Phys. Usp. 20/2 (1977) 149.

- [71] R. Hock, H. Fuess, T. Vogt, M. Bonnet, J. of Sol. St. Chem. 84/1 (1990) 39.
- [72] M. Lahoubi, M. Guillot, A. Marchand, F. Tcheou, E. Roudault, IEEE Trans. Mag. 20/5 (1984) 1518.
- [73] Y. Tokunaga, S. Iguchi, T. Arima, Y. Tokura, Phys. Rev. Lett. 101/9 (2008) 097205.
- [74] N. Hur, S. Park, S. Guha, A. Borissov, V. Kiryukhin, S.-W. Cheong, App. Phys. Lett. 87 (2005).
- [75] A.J. Sievers, M. Tinkham, Phys. Rev. 129/5 (1963) 1995.
- [76] M. Tinkham, Phys. Rev. 124/2 (1961) 311.
- [77] J. Yamamoto, B.T. Smith, E.E. Bell, J. Opt. Soc. Am. 64/6 (1974) 880.
- [78] J. Kaplan, C. Kittel, J. of Chem. Phys. 21 (1953) 760.
- [79] N.T. McDevitt, J. Opt. Soc. Am. 59/9 (1969) 1240.
- [80] R.V. Aguilar, A.B. Sushkov, C.L. Zhang, Y.J. Choi, S.W. Cheong, H.D. Drew, Physical Review B 76/6 (2007) 060404.
- [81] Y. Takahashi, Y. Yamasaki, N. Kida, Y. Kaneko, T. Arima, R. Shimano, Y. Tokura, Physical Review B 79/21 (2009) 214431.
- [82] J.S. Lee, N. Kida, S. Miyahara, Y. Takahashi, Y. Yamasaki, R. Shimano, N. Furukawa, Y. Tokura, Physical Review B 79/18 (2009) 180403.
- [83] A. Shuvaev, F. Mayr, A. Loidl, A.A. Mukhin, A. Pimenov, ArXiv 1008.2064v1 (2010).
- [84] <u>http://web.njit.edu/~sirenko/SiMM\_web/SiMM.htm</u>. Accessed April, 10, 2011.
- [85] A. Konstantinova, K. Konstantinov, B. Nabatov, E. Evdishchenko, Crystallography Reports 47/4 (2002) 645.
- [86] A. Konstantinova, B. Nabatov, E. Evdishchenko, K. Konstantinov, Crystallography Reports 47/5 (2002) 815.
- [87] T.G. Mayerhöfer, S. Weber, J. Popp, Optics Communications 284/3 (2010) 719.
- [88] E. Bahar, J. Opt. Soc. Am. B 26/2 (2009) 364.
- [89] E. Bahar, J. Opt. Soc. Am. B 25/8 (2008) 1294.
- [90] E. Bahar, J. Opt. Soc. Am. B 24/11 (2007) 2807.

- [91] E. Bahar, J. Opt. Soc. Am. B 24/7 (2007) 1610.
- [92] E. Bahar, J. Opt. Soc. Am. B 25/2 (2008) 218.
- [93] O. Arteaga, Opt. Lett. 35/9 (2010) 1359.
- [94] O. Arteaga, A. Canillas, Opt. Lett. 35/4 (2010) 559.
- [95] O. Arteaga, A. Canillas, J. Opt. Soc. Am. A 26/4 (2009) 783.
- [96] O. Arteaga, A. Canillas, Opt. Lett. 35/20 (2010) 3525.
- [97] O. Arteaga, E. Garcia-Caurel, R. Ossikovski, J. Opt. Soc. Am. A 28/4 (2011) 548.
- [98] W.F. Brown, R.M. Hornreich, S. Shtrikman, Physical Review 168/2 (1968) 574.