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Birefringence and dichroism in X-rays passing through magnetic material.

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ABSTRACT

We present a framework for describing polarization-dependent attenuation and retardation of X-rays, by materials which are anisotropic and/or magnetic. Classical optical calculus is employed to relate observable quantities to atomic variables of the sample. As an explicit example, we consider the case of the biaxial magnetic crystal, ferrous niobate.

1. Background and orientation

Recent years have witnessed an explosion in the number and variety of X-ray experiments in which the polarization of the beam reveals important information about the electronic configuration of atoms in the solid state. For each class of measurement, the challenge is to relate observable quantities - intensity, Stokes parameters etc. - to atomic variables and symmetries of the sample. Fortunately, the subject of polarization in optics is a mature one. An armoury of well-proven theoretical tools, equally applicable at optical and X-ray wavelengths, exists in numerous texts [1,2,3,4]. At the most fundamental level, however, the physical origin of optical constants tends to be quite different, with X-rays being sensitive primarily to the configuration of individual atoms [5,6]. Interpretation of X-ray data therefore hinges on the relationship between atomic and optical variables, and the main goal of the present work is to develop a framework for exploring these connections.

The remainder of this paper is divided into four sections. In section 2 we relate the resonant forward scattering amplitude to reduced dipole-dipole matrix elements via the Kramers-Heisenberg formula, thus providing a link between the rank-two Cartesian tensor that describes these elements, with Jones and Mueller matrices. The transmittance and polarization of X-ray photons, attenuated by a uniform, anisotropic material, are thus obtained for incident beams of arbitrary partial polarization.

Section 3 deals with the passage of X-ray beams through materials which are magnetic and, generally, completely anisotropic. The dipole-dipole tensor is written as the sum of a scalar (giving spatially averaged properties), a symmetric tensor who's non-vanishing elements depend on the point group symmetry of the environment of the resonant ion, and an axial vector that defines the axis of magnetic quantization. The rotational properties and eigenstates of the symmetric tensor are discussed for various symmetries, and we establish a connection between the tensor (a property only of the sample) and the 2x2 scattering matrix, from which the results of X-ray optical measurements are derived.

Atomic models for the dipole-dipole tensor vary enormously in complexity, depending on the level of detail required to describe observable quantities. Section 4

describes five levels of approximation, varying from a completely isotropic sample with no polarization or energy selectivity, to detailed structure in dichroic spectra arising from exchange splitting in the atomic core level. Results encompass some well-documented sum-rules, where tensor elements are given by various ground-state atomic moments.

The paper is brought to a close with the example of ferrous niobate - a crystal which is biaxial and magnetic. Tensor components responsible for linear and circular dichroism are derived from the wavefunction of the ferrous ion.

2. The interpretation of transmission experiments

Our treatment of X-ray transmission through a foil is based on the Kramers – Heisenberg dispersion formula, in which the absorption process is an electric-dipole (E1) event [2,7]. In consequence, magnetic properties of the resonant ion manifest themselves in the formula through dipole matrix-elements for the valence shell which accepts the core electron, ejected by a photon from an initially complete core level.

A photon in the beam of X-rays incident on the foil has a wave vector, $\mathbf{q}$, and a polarization vector, $\boldsymbol{\varepsilon}$, which is taken to be a row vector with two components. The objective of an experiment is to investigate the properties of the equilibrium state of the resonant ion, for which there are degenerate states $\{|\mu>\}$. Attenuation and retardation of the X-ray beam engages quasi-discrete states, denoted here by the Greek letter η, comprised of a core level with one unfilled state and a valence shell with one additional electron. The rate of decay of such an intermediate state is $\gamma_\eta / \hbar$.

Let the dipole operator for the resonant ion at the position in the unit cell defined by the vector $\mathbf{d}$ be $\hat{\mathbf{R}}(\mathbf{d})$. The strength of the E1 event is determined by the radial integral for the core and valence levels, R_{cl}. With this notation, the Kramers-Heisenberg formula expressed as the resonant contribution to the scattering length is,

$$f_{\text{res}} = -(eq)^2 \, R_{\text{cl}}^2 \sum_{\text{d}} \sum_{\eta} (<\mu \,|\, \varepsilon' \cdot \hat{\text{R}} \,|\, \eta> <\eta \,|\, \varepsilon \cdot \hat{\text{R}} \,|\, \mu>) \,/\, (E + E_\mu - E_\eta + \text{i}\gamma_\eta / 2) \,. \tag{2.1}$$

Here, it is assumed that the energy of the X-rays and the energy of the resonance are nearby, i.e. $E = (\hbar cq) \approx E_\eta - E_\mu$. The prime on the polarization vector denotes the transpose, and $\boldsymbol{\varepsilon}' \, \boldsymbol{\varepsilon}$ is a square matrix.

Let σ and π be orthogonal unit-vectors in the plane normal to the wave vector, $\mathbf{q}$. Taking successively $\boldsymbol{\varepsilon} = \boldsymbol{\sigma}$ and $\boldsymbol{\pi}$, and $\boldsymbol{\varepsilon}' = \boldsymbol{\sigma}' = \boldsymbol{\sigma}$ and $\boldsymbol{\pi}'$ one constructs four values of f_{res} that together form a square matrix. In the limit $\gamma_\eta = 0$, the square matrix is Hermitian and some of its properties are gathered in the appendix to the paper. This limit is realized by working far from any resonance feature.

Our expression for f_{res} can be obtained from the scattering length, $f = f' + \text{i} f''$, by equating the wave vectors for the primary and secondary beams (the forward-scattering geometry) and setting aside all contributions to f other than the one enhanced by the resonance condition. The real and imaginary parts of f satisfy a dispersion relation, also known as a Kramers-Kronig transform. The scattered intensity, $f^+ f$, considered as a function of the states of polarization is a 2 x 2 Hermitian matrix. It can be diagonalized, and the ratio of its two principal values, denoted in the appendix by λ_+ and λ_-, gives the degree of depolarization, while their sum is proportional to the total intensity.

Attenuation (dichroism) and retardation (birefringence) in the foil are determined by its refractive index, denoted here by $n = n' + \text{i} \, n''$. The relation between n and f is taken to be,

$$n = 1 + (2\pi\rho_{\text{o}} / q^2) f, \tag{2.2}$$

in which ρ_{o} is the density of resonant ions present in the foil. With use of the optical theorem,

$$n'' = (2\pi\rho_o / q^2) f''_{res} = \frac{1}{2q}\gamma, \tag{2.3}$$

where the attenuation coefficient, γ, has the dimension of a wavevector.

As a function of E, f''_{res} is a palisade of Lorentzians centred at $\Delta_\eta = (E_\eta - E_\mu)$ with a width proportional to γ_η. More than one product of dipole matrix elements will likely contribute to the weight of a Lorentzian, and for a particular resonance we need to calculate for each ion the dimensionless quantity,

$$< Z > = \overline{\sum_{\eta(\Delta)} (< \mu | \boldsymbol{\varepsilon}' \cdot \hat{\mathbf{R}} | \eta > < \eta | \boldsymbol{\varepsilon} \cdot \hat{\mathbf{R}} | \mu >)}, \tag{2.4}$$

where the notation $\eta\ (\Delta)$ indicates a sum on η restricted to intermediate states which contribute to the resonance centred at the energy Δ, and the horizontal bar denotes an average with respect to the condition of polarization.

The physical significance of <Z>, defined in (2.4), in the interpretation of transmission experiments can be made quite clear. For, if the dichroic signal is integrated with respect to energy, over an interval of energy that spans the intermediate states which contribute to the sum defined by $\eta\,(\Delta)$, then <Z> is the weight of the integrated signal, apart from unimportant factors. It is standard practice to call <Z> a sum-rule, in keeping with the Kuhn-Thomas sum-rule for oscillator strengths, and we have more to say on this subject in section 4.

As we shall see in section 4, use of an atomic model enables one to express <Z> in terms of the mean values of operators associated with the valence shell of the resonant ion, e.g. the mean value of the orbital angular momentum operator. The number of different operators, and hence the degree of information about the valence shell carried by <Z> depend on the extent of the sum over the intermediate states in (2.4). An unrestricted sum removes the entire spectrum of the intermediate states, for the closure conditions is, $\sum_\eta |\eta > < \eta| = 1$. The corresponding expression for <Z> is

devoid of explicit information about the magnetic state of the valence shell. Hence, usually an unrestricted sum of the intermediate states is not adequate for the interpretation of data.

An average of a physical quantity with respect to the condition of polarization in the primary beam of X-rays is accomplished with a density matrix, μ, whose properties are reviewed in the appendix (in classical optics it is customary to describe polarization by a coherence matrix proportional to μ);

$$\overline{(\cdots)} = \mathrm{tr}.\mu(\cdots), \tag{2.5}$$

where tr. is the trace operation. The density matrix can be expressed in the form,

$$\mu = \tfrac{1}{2}(I + \mathbf{P}\cdot\boldsymbol{\sigma}), \tag{2.6}$$

where I is the unit matrix, and σ_1, σ_2, and σ_3 are Pauli matrices chosen as,

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_2 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{2.7}$$

The parameters (j = 1, 2 and 3),

$$P_j = \mathrm{tr}.(\mu\sigma_j), \tag{2.8}$$

are Stokes parameters for the primary beam. While $\mathbf{P} = (P_1, P_2, P_3)$ appears as a vector in (2.6) it is not a vector of any standard type; in particular, $\mathbf{P}$ is not an axial or a polar vector.

Prior to moving on, we briefly review properties of the Stokes parameters. P_1 and P_3 are measures of the linear polarization. In the right-handed and orthogonal set of co-ordinates $(\boldsymbol{\sigma}, \boldsymbol{\pi}, \hat{\mathbf{q}})$ P_1 describes linear polarization along directions at angles $\pm\frac{\pi}{4}$ to the σ- axis. The parameter P_3 describes polarization along the

$\sigma-$ and $\pi-$ axis; $P_3 = +1$ corresponds to complete polarization in the $\sigma-$ direction, and $P_3 = -1$ corresponds to complete polarization in the $\pi-$ direction. The parameter P_2 measures the degree if circular polarization. Here, it is defined to be the mean value of the helicity operator. The parameters satisfy $\left(P_1^2 + P_2^2 + P_3^2\right) \leq 1$, and the equality is achieved for a completely polarized beam.

All three parameters are even with respect to the reversal of the direction of time. However, with respect to the parity operation, that changes a right-handed co-ordinate system to a left-handed co-ordinate system (and equivalent to an inversion of the co-ordinate system), P_1 and P_3 are unchanged while P_2 changes its sign. Hence, P_1 and P_3 behave with respect to parity as true scalar qualities. On the other hand, P_2 is not a true scalar with respect to parity and it is usual to refer to such a quantity as a pseudo-scalar. There are several arguments that quickly show that P_2 is a pseudo-scalar. For example, it is the mean helicity, and the helicity operator is the scalar product of **q** (a polar vector) and the operator for angular momentum (an axial vector, also known as a pseudo-vector). From this definition one can see that P_2 is indeed even with respect to the reversal of the direction of time, since the helicity operator is the product of two variables that each change sign under the time-reversal operation, i.e. the wave vector **q** and the operator for orbital angular momentum are odd with respect to time reversal. (The helicity and spin operators have opposite behaviour with respect to time reversal.)

Of central importance in the interpretation of experiments is a transmission matrix, Ω [3, 4, 8, 9]. First, the average electric energy density of the transmitted beam is proportional to,

$$k = \overline{|\Omega|^2} = \mathrm{tr.}\left(\Omega^+ \mu \Omega\right), \tag{2.9}$$

where Ω^+ is the Hermitian conjugate of Ω. The physical significance of (2.9) is made apparent on noting that the primary and transmitted complex electric fields $\mathcal{E}$ and $\mathcal{E}'$, respectively, are related through $\mathcal{E}' = \mathcal{E}\Omega$, and the energy density in the transmitted beam is proportional to $(\mathcal{E}')^+ \mathcal{E}' = \Omega^+ \mathcal{E}^+ \mathcal{E}\Omega$. (NB the electric fields are row vectors.)

Secondly, the Stokes parameters of the transmitted beam are ($j = 1, 2$ and 3),

$$P'_j = \frac{1}{k}\,\mathrm{tr.}(\Omega^{+}\mu\Omega\sigma_j) = \mathrm{tr.}(\mu'\sigma_j), \tag{2.10}$$

where the second equality defines the density matrix of the transmitted beam, μ'. In the absence of a foil, $\Omega = I$, and any phase shift introduced by Ω is taken with respect to the unperturbed beam.

A perfect polarizer is represented by a transmission matrix which is both idempotent and singular. Physically the idempotent property of Ω refers to the fact that a beam emerging from a polarizer is unaffected by passage through a second identical polarizer. The singular property of Ω arises because the perfect polarizer destroys all information about the original state of polarization. A device which introduces a phase shift between the components of the complex electric field directed along $\boldsymbol{\sigma}$ and $\boldsymbol{\pi}$ is called a compensator. In the ideal case, there is no attenuation of the beam and a perfect compensator is represented by an Ω which is unitary.

We will express Ω in terms of a matrix which arises in the Jones calculus. Another approach to the description of optical devices uses the Mueller calculus [4]. One fundamental difference between the two calculi is found in the addition of waves; Jones calculus assumes a coherent addition whereas Mueller calculus assumes an incoherent addition. A relation between the calculi, appropriate to record at this juncture, is obtained from a consideration of the Stokes parameters (2.8) and (2.10). For this purpose, let $j = 1, 2$ and 3 and define,

$$s_j = s_0 P_j, \text{ and } s'_j = s'_0 P'_j, \tag{2.11}$$

where $k = s'_0 / s_0$. In terms of the parameters $\{s_h\}$ and $\{s'_h\}$ with $h = 0, 1, 2$ and 3 the degree of polarization of the primary beam, P, is,

$$P = \frac{1}{s_0}\sqrt{(s_1^2 + s_2^2 + s_3^2)} = \sqrt{(\mathbf{P}\cdot\mathbf{P})}, \tag{2.12}$$

and there is a similar expression for P' in terms of $\{s'_h\}$. The 4 x 4 Mueller matrix $\{M_{hh'}\}$ has elements,

$$M_{hh'} = \tfrac{1}{2}\,\mathrm{tr.}\{\sigma_h \Omega^+ \sigma_{h'} \Omega\}, \tag{2.13}$$

and it possesses the property,

$$s'_h = \sum_{h'=0}^{3} M_{hh'} s_{h'}\,. \tag{2.14}$$

In (2.13), $\sigma_0 = I$ and the three Pauli matrices are defined in (2.7).

From the identity $\det.\mu' = (1 - P'^2)\,/\,4$ and the definition of μ' in terms of μ and Ω we find,

$$k^2 (1 - P'^2) = (1 - P^2)\;|\det.\Omega|^2. \tag{2.15}$$

Evidently, for the case of a completely polarized beam (P = 1), likewise, the beam transmitted by the foil is completely polarized. In addition we mention two cases where P' takes special values. First, the ideal polarizer always gives P' = 1, for in this case Ω is singular and $\det.\Omega = 0$. Secondly, the ideal compensator and the ideal rotator always gives $P = P'$, for in this case Ω is unitary, $|\det.\Omega| = 1$ and $k = 1$ since $\Omega^+\Omega = 1$. To achieve depolarization of a completely polarized beam the foil must exhibit some randomness. Such a foil is represented by some statistical ensemble of transmission matrices, not a single matrix of the type we consider. In the event that the degree of polarization in the primary beam is not complete, and $P < 1$, there is no particular constraint from (2.15) on the value of P'.

Bulk optical properties of a foil appear in the calculus in a 2 x 2 Jones matrix, denoted by **J**, and,

$$\Omega = \exp(t\,\mathbf{J}). \tag{2.16}$$

The thickness of the foil, t, is taken to be small. A real foil is modelled by a stratified unit comprised of several lamella, each possessing one desired bulk property. One finds for the Jones matrix,

$$t\,\mathbf{J} = b\,I + \mathbf{a}\cdot\boldsymbol{\sigma} = \begin{pmatrix} b + a_3 & a_1 - \mathrm{i}a_2 \\ a_1 + \mathrm{i}a_2 & b - a_3 \end{pmatrix}. \tag{2.17}$$

In general, $\mathbf{a}$ and b are complex and the Jones matrix contains eight independent parameters [8]. However, for many experiments, the overall phase factor does not influence the observed quantity and it can be set equal to zero leaving b purely real. An example in which the overall phase does influence the observation is two-beam interferometry [10]. For our part, we henceforth take b purely real, and find,

$$b = -\tfrac{1}{2}qt\,(n''_\pi + n''_\sigma) = -qtn'' = -\tfrac{1}{2}t\gamma, \tag{2.18}$$

with (j = 1, 2 and 3),

$$a_j = -\tfrac{\mathrm{i}}{2}\,qt\,\Delta\,n_j,$$

where $\Delta n_j = \{n(P_j) - n(-P_j)\}$ is the difference in complex refractive indices picked out by the polarization described by the Stokes parameter P_j. The relation (2.2) together with (2.18) completes the connection between bulk optical properties of the foil, described by Jones matrices, and atomic properties of the resonant ion which appear in the scattering length.

It is often convenient to use the expression, derived as described in the appendix from (2.16) and (2.17),

$$\Omega = \exp\,(b)\,\{\mathcal{C}\,I + \mathcal{S}\,\mathbf{a}\cdot\boldsymbol{\sigma}\}, \tag{2.19}$$

where $\mathcal{C} = \cosh \zeta$, $\mathcal{S} = (\sinh \zeta) / \zeta$ and $\zeta^2 = \mathbf{a} \cdot \mathbf{a}$. For the transmittance ratio and the Stokes parameters of the transmitted beam one obtains from (2.19),

$$k = \mathrm{e}^{2b} \left\{ |\mathcal{C}|^2 + |\mathcal{S}|^2 [\mathbf{a} \cdot \mathbf{a}^* + \mathrm{i}\mathbf{P} \cdot (\mathbf{a} \times \mathbf{a}^*)] + 2\,\mathrm{Re.}(\mathcal{C}^* (\mathbf{P} \cdot \mathbf{a}) \mathcal{S}) \right\}, \tag{2.20}$$

and (j = 1, 2 and 3),

$$P'_j = \tfrac{1}{k} \mathrm{e}^{2b} \Big\{ 2\,\mathrm{Re.}(\mathcal{C}^* \mathcal{S}\, a_j) + |\mathcal{S}|^2 \left[-\mathrm{i}(\mathbf{a} \times \mathbf{a}^*)_j - \mathbf{a} \cdot \mathbf{a}^* P_j + 2\,\mathrm{Re.}(a_j^* (\mathbf{a} \cdot \mathbf{P})) \right]$$

$$+ |\mathcal{C}|^2 P_j + 2\,\mathrm{Im.}(\mathcal{C}^* \mathcal{S} (\mathbf{a} \times \mathbf{P})_j) \Big\}. \tag{2.21}$$

The Stokes parameters P'_j do not depend on b, as one might expect. On taking the limit $t \to 0$ and retaining terms up to order t,

$$k \to 1 - t\,\gamma + qt \sum_j P_j\, \Delta n''_j, \tag{2.22}$$

and,

$$P'_j \to 2a'_j + P_j \{1 - 2(\mathbf{a}' \cdot \mathbf{P})\} + 2(\mathbf{a}'' \times \mathbf{P})_j = P_j + 2a'_j (1 - P^2)$$

$$+ 2\,\{\mathbf{P} \times (\mathbf{a}' \times \mathbf{P})\}_j + 2\,(\mathbf{a}'' \times \mathbf{P})_j\,. \tag{2.23}$$

Here, $\mathbf{a} = \mathbf{a}' + \mathrm{i}\mathbf{a}''$, and $\mathbf{a}'$ represents attenuation and $\mathbf{a}''$ represents retardation of a beam passing through a foil. It is to be noted that, attenuation of a beam on passage through a foil creates polarization in the emerging beam (dichroism).

Algebra similar to that used in the derivation of (2.20) and (2.21) enables one to compute the Mueller matrix elements (2.13).

3. Passage through magnetic material

This section displays some general properties of attenuation and birefringence due to E1 events in a magnetic material.

The quantity in the numerator of the Kramers-Heisenberg formula is made up of the product of polarization vectors $\varepsilon'_\alpha\ \varepsilon_\beta$, and the product of atomic matrix elements,

$$T_{\alpha\beta} = \sum_{\eta(\Delta)} < \mu \,|\, \hat{R}_\alpha \,|\, \eta > < \eta \,|\, \hat{R}_\beta \,|\, \mu >, \tag{3.1}$$

where the notation $\eta(\Delta)$ is defined following (2.4). In these expressions, α and β label Cartesian components of a vector. With the X-ray energy in the vicinity of a single atomic resonance at the energy Δ,

$$f_{\text{res}}\,(E) = -\,(eq)^2\, R_{\text{cl}}^2\, \frac{\sum_{\mathbf{d}} \varepsilon'_\alpha \varepsilon_\beta T_{\alpha\beta}(\mathbf{d})}{(E - \Delta + \mathrm{i}\,\Gamma/2)} \tag{3.2}$$

The Einstein summation convention is employed, and the umbral Cartesian index is summed over its three values.

An important aspect of our $T_{\alpha\beta}$, defined by equation (3.1), is that there is a sum over some of the quasi-discrete intermediate states. Using an atomic model, several detailed calculations of (3.1) have demonstrated that it transforms as a tensor, and we will assume $T_{\alpha\beta}$ has this property. The standard argument which is used to verify the transformation property of Placzek's tensor, namely,

$$\sum_{\eta} \frac{\hat{R}_\alpha \,|\, \eta > < \eta \,|\, \hat{R}_\beta}{(E + E_\mu - E_\eta)},$$

exploits the closure condition for the intermediate states [7]. Likewise, the detailed calculations of $T_{\alpha\beta}$ to which we refer exploit the restricted sum over intermediate states in the definition (3.1).

In short, $T_{\alpha\beta}$ is henceforth taken to be a tensor of rank two in a space with three dimensions. Like every even rank tensor, the physical properties it describes are centrosymmetrical.

On using the Hermitian property of $\hat{\mathbf{R}}$,

$$T^{*}_{\beta\alpha} = T_{\alpha\beta} \,. \tag{3.3}$$

Hence, the real and imaginary parts of $T_{\alpha\beta}$, defined by $T_{\alpha\beta} = T'_{\alpha\beta} + \mathrm{i}T''_{\alpha\beta}$, satisfy the relations,

$$T'_{\alpha\beta} = T'_{\beta\alpha}, \text{ and } T''_{\alpha\beta} = -T''_{\beta\alpha}. \tag{3.4}$$

Next, we consider the behaviour of $T_{\alpha\beta}$ as a function of the polarity of a magnetic field, denoted by **H** (not to be confused with the weak variable field of the photon wave). The behaviour of interest is found to follow from the assumed invariance to a change in the sign of the time variable of the equations of motion determining physical properties. One consequence of the invariance is that, a spontaneous magnetization reverses its polarity under the time-reversal operation. As far as $T_{\alpha\beta}$ is concerned what matters is that it contains a product of two identical operators. Using **H** to represent an applied field or a spontaneous magnetization, one finds,

$$T_{\alpha\beta}(\mathbf{H}) = T_{\beta\alpha}(-\mathbf{H}), \tag{3.5}$$

and so,

$$T'_{\alpha\beta}(\mathbf{H}) = T'_{\alpha\beta}(-\mathbf{H}),\ \ T''_{\alpha\beta}(\mathbf{H}) = -T''_{\alpha\beta}(-\mathbf{H}). \tag{3.6}$$

The behaviour of $T''_{\alpha\beta}(\mathbf{H})$ with respect to the polarity of the field might be anticipated. For, any antisymmentrical tensor of rank two is equivalent to some axial vector, and **H** is here an axial vector. We will use this property of an antisymmetrical tensor of rank two later in the section.

For the product of polarization vectors we use the identity,

$$\varepsilon'_\alpha\varepsilon_\beta = \tfrac{1}{3}\delta_{\alpha\beta}(\boldsymbol{\varepsilon}'\cdot\boldsymbol{\varepsilon}) + \tfrac{1}{2}(\varepsilon'_\alpha\varepsilon_\beta - \varepsilon'_\beta\varepsilon_\alpha) + \tfrac{1}{2}(\varepsilon'_\alpha\varepsilon_\beta + \varepsilon'_\beta\varepsilon_\alpha - \tfrac{2}{3}\ (\boldsymbol{\varepsilon}'\cdot\boldsymbol{\varepsilon})\delta_{\alpha\beta}). \tag{3.7}$$

The identity expresses the representation of a tensor of rank two as the sum of three independent parts. The three parts are a scalar, an antisymmetrical tensor and an irreducible symmetrical tensor (the trace is zero). For the antisymmetrical tensor we employ a second identity,

$$\varepsilon'_\alpha\varepsilon_\beta - \varepsilon'_\beta\varepsilon_\alpha = \varepsilon_{\alpha\beta\gamma}(\boldsymbol{\varepsilon}'\mathrm{x}\ \boldsymbol{\varepsilon})_\gamma, \tag{3.8}$$

where $\varepsilon_{\alpha\beta\gamma}$ is the completely antisymmetrical unit pseudo-tensor of rank three. (Under rotations of the co-ordinate system, the quantities $\varepsilon_{\alpha\beta\gamma}$ do not change, whereas the components of a tensor should change sign. This special property of $\varepsilon_{\alpha\beta\gamma}$ is recognized by calling it a pseudo-tensor.) Also, we define a symmetrical tensor of rank two,

$$X_{\alpha\beta} = \tfrac{1}{2}\left(\tfrac{3}{2}\right)^{1/2}\left(\varepsilon'_\alpha\varepsilon_\beta + \varepsilon'_\beta\varepsilon_\alpha - \tfrac{2}{3}(\boldsymbol{\varepsilon}'\cdot\boldsymbol{\varepsilon})\,\delta_{\alpha\beta}\right), \tag{3.9}$$

with obvious property $X_{\alpha\alpha} = 0$.

Assembling the expressions in the quantity of interest one finds,

$$\varepsilon'_\alpha \varepsilon_\beta \, T_{\alpha\beta} = \tfrac{1}{3}(\boldsymbol{\varepsilon}' \cdot \boldsymbol{\varepsilon}) \, T'_{\alpha\alpha} + \tfrac{i}{2} \, \varepsilon_{\alpha\beta\gamma} \, T''_{\alpha\beta} (\boldsymbol{\varepsilon}' \times \boldsymbol{\varepsilon})_\gamma + \left(\tfrac{2}{3}\right)^{1/2} X_{\alpha\beta} \, T'_{\alpha\beta}. \tag{3.10}$$

For future purposes, it is useful to define two atomic quantities; and axial vector with components,

$$\Lambda_\gamma = \frac{1}{\sqrt{2}} \varepsilon_{\alpha\beta\gamma} \, T''_{\alpha\beta}, \tag{3.11}$$

or, in components, $T''_{xy} = \Lambda_z / \sqrt{2}$ etc., and, following the definition used for $X_{\alpha\beta}$, an irreducible symmetrical tensor of rank two,

$$A_{\alpha\beta} = \left(\frac{3}{2}\right)^{1/2} \left(T'_{\alpha\beta} - \frac{1}{3} \delta_{\alpha\beta} \, T'_{\gamma\gamma} \right). \tag{3.12}$$

(The square root of fractions in the definitions of Λ_γ and $A_{\alpha\beta}$ arise because these quantities are Cartesian components of tensors of rank one and rank two, respectively, and the atomic matrix elements in the definition of $T_{\alpha\beta}$, from which they are constructed, are naturally calculated using spherical (atomic) tensors.)

The expression (3.10) is a fundamental material property. However, it cannot describe the scattering of light directly since it is three-dimensional, while light is two-dimensional (there is no component of the electric field in the direction of propagation; see, also, the discussion in the appendix).

For the interpretation of an experiment one requires the scattering length averaged with respect to the polarization in the primary beam of X-rays. A natural choice of co-ordinates in which to effect the averaging is ($\boldsymbol{\sigma}$, $\boldsymbol{\pi}$, $\hat{\mathbf{q}}$). In this system of orthogonal unit vectors the polarization vectors take the values $\boldsymbol{\sigma}$ or $\boldsymbol{\pi}$, and $\varepsilon'_\alpha \, \varepsilon_\beta \, T_{\alpha\beta}$ can be represented as a 2 x 2 matrix. The details are (the summation convention does not apply to σ and π),

$$\varepsilon'_\alpha \varepsilon_\beta \, T_{\alpha\beta} = \tfrac{1}{2}(T'_{\sigma\sigma} + T'_{\pi\pi}) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \tfrac{i}{\sqrt{2}} \hat{\mathbf{q}} \cdot \mathbf{\Lambda} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

$$+ \begin{pmatrix} \frac{1}{2}(T'_{\sigma\sigma} - T'_{\pi\pi}) & T'_{\sigma\pi} \\ T'_{\sigma\pi} & -\tfrac{1}{2}(T'_{\sigma\sigma} - T'_{\pi\pi}) \end{pmatrix}. \tag{3.13}$$

Note that the coefficient of $\hat{\mathbf{q}} \cdot \mathbf{\Lambda}$ is proportional to the helicity operator defined in (A21). The average of (3.13) is obtained by multiplying it by the density matrix for the polarization of the primary beam and taking the trace of the product, as in (2. 5). For the quantity <Z>, defined in (2.4), one finds,

$$< Z > \; = \overline{\varepsilon'_\alpha \varepsilon_\beta \, T_{\alpha\beta}} = \text{tr.}\, \mu \varepsilon'_\alpha \varepsilon_\beta \, T_{\alpha\beta} = \tfrac{1}{2}\left(T'_{\sigma\sigma} + T'_{\pi\pi}\right)$$

$$- \tfrac{1}{\sqrt{2}} P_2 \left(\hat{\mathbf{q}} \cdot \mathbf{\Lambda}\right) + P_1 \, T'_{\sigma\pi} + \tfrac{1}{2} P_3 \, (T'_{\sigma\sigma} - T'_{\pi\pi}). \tag{3.14}$$

The dichroic signal is the part of <Z> picked out by the polarization. We see in (3.14) that the circular dichroic signal is proportional to $\hat{\mathbf{q}} \cdot \mathbf{\Lambda}$, and the linear ($P_3$) dichroic signal is proportional to $(T'_{\sigma\sigma} - T'_{\pi\pi})$.

Several comments are appropriate at this juncture. The symmetrical and antisymmetrical components of $T_{\alpha\beta}$, respectively, are even and odd under the operation which reverses the direction of time. All the Stokes parameters are even with respect to time reversal, and $\hat{\mathbf{q}}$ is odd with respect to this operation. By construction, $\mathbf{\Lambda}$ is also odd with respect to time reversal and an axial vector (also called a pseudo-vector). The properties of $\mathbf{\Lambda}$ mean that the contribution to <Z> in P_2 is indeed unchanged under the time-reversal and the parity operations.

Like every symmetrical tensor of rank two, $T'_{\alpha\beta}$ can be brought to diagonal form by a suitable choice of the Cartesian co-ordinate axes [2, 11, 12]. Hence, there are

three independent quantities in $T'_{\alpha\beta}$. There is one less independent quantity in $A_{\alpha\beta}$, constructed from $T'_{\alpha\beta}$ according to the expression (3.12), since it is a tensor whose trace is zero. The linear dichroic signals permit the measurement of the components $A_{\sigma\pi}$ and ($A_{\sigma\sigma} - A_{\pi\pi}$), and no other components are accessible. Shortly, we shall see that $A_{\sigma\pi}$ is obtained from ($A_{\sigma\sigma} - A_{\pi\pi}$). The co-ordinate axes in which $T'_{\alpha\beta}$ is diagonal have directions that are mutually perpendicular, and often they are referred to as the principal co-ordinate axes.

Let the principal axes be obtained from the orthogonal axes ($\sigma, \pi, \hat{\mathbf{q}}$) by a rotation specified by Euler angles α, β and γ (not to be confused with Cartesian labels). Expression (3.12) is used to define rank-two atomic quantities whose mean values, $\langle A_{\alpha\beta} \rangle$, are the subject of sections 4 and 5. The principal axes are labelled a, b and c. We find,

$$(A_{\sigma\sigma} - A_{\pi\pi}) = \left(\tfrac{3}{2}\right)^{1/2} \left(T'_{\sigma\sigma} - T'_{\pi\pi}\right) = (\tfrac{3}{2} \cos 2\alpha \sin^2 \beta) < A_{cc} >$$
$$+ \left(-\sin 2\alpha \cos\beta \sin 2\gamma + \tfrac{1}{4} \cos 2\alpha \, (3 + \cos 2\beta) \cos 2\gamma\right)(< A_{aa} > - < A_{bb} >). \tag{3.15}$$

The corresponding expression for $A_{\sigma\pi}$ is equal to ($A_{\sigma\sigma} - A_{\pi\pi}$)/2 evaluated at the Euler angles $\alpha - \frac{\pi}{4}, \beta, \gamma$.

In visualizing the constraints on $T'_{\alpha\beta}$ arising from the point-group symmetry it is helpful to observe that, in a space x, y, z,

$$\varepsilon_\alpha \varepsilon_\beta T'_{\alpha\beta} = x^2 T_{xx} + 2xy T_{xy} + \cdots,$$

is an ellipsoid whose principal axes are those in which $T'_{\alpha\beta}$ is diagonal [11]. By the Neumann principle [11, 12, 13] the ellipsoid must exhibit the symmetry of the environment of the resonant ion. Hence, $\varepsilon_\alpha \varepsilon_\beta \, T'_{\alpha\beta}$ is isotropic in a cubic system since the ellipsoid compatible with cubic symmetry is a sphere. For a uniaxial crystal the ellipsoid has two principal axes the same length, and in lower symmetry all three

principal axes of the ellipsoid have different lengths. Figure 1 illustrates the surface of second degree associated with cubic, tetragonal, orthorhombic and triclinic systems.

In the event that the symmetrical tensor $T'_{\alpha\beta}$ is referred to arbitrary axes (such axes are sometimes called oblique axes) the number of independent quantities is six. Principal axes are defined relative to oblique axes by three parameters, and in the principal axes $T'_{\alpha\beta}$ is specified by three independent quantities. Thus, in the latter scheme there are also six independent quantities, namely, three parameters for the specification of the principal axes relative to the oblique axes and three atomic quantities for $T'_{\alpha\beta}$. In so-called biaxial crystals (triclinic, monoclinic and orthorhombic systems) all three principal values of the tensor are different. For crystals with such a low symmetry $A_{\alpha\beta}$ is specified by two independent qualities and (3.15) is required in its full form. Crystals with symmetry higher than biaxial possess the property $< A_{aa} > = < A_{bb} >$ and, in this instance, $A_{\sigma\pi}$ and $(A_{\sigma\sigma} - A_{\pi\pi})$ are proportional to $< A_{cc} >$ (for uniaxial crystals (tetragonal, hexagonal and trigonal systems) the c-axis is taken to be the principal axis of symmetry of the crystal and thus $< A_{aa} > = < A_{bb} >$). It is perhaps useful to note that the orientation of the c-axis is independent of the Euler angle γ; the result is.

$$\mathbf{c} = (\cos\alpha \sin\beta, \sin\alpha \sin\beta, \cos\beta). \tag{3.16}$$

In this context, note that the coefficient of $< A_{cc} >$ in (3.15) is independent of γ, and a function of α and β which is zero for $\beta = 0$ and π. Hence, for crystals with a point group symmetry higher than biaxial the contribution to the attenuation coefficient picked out by linear polarization (P_1 and P_3) is zero if the principal axis is parallel to the beam of X-rays. With this particular experimental geometry the linear dichroic signals from biaxial crystals can be different from zero.

By way of an example, let us consider a monoclinic (biaxial) crystal. For this case there are three independent entries in $A_{\alpha\beta}$. One finds for $A_{\alpha\beta}$,

$$\begin{pmatrix} \langle A_{xx} \rangle & 0 & \langle A_{xz} \rangle \\ 0 & \langle A_{yy} \rangle & 0 \\ \langle A_{xz} \rangle & 0 & -\langle A_{xx} + A_{yy} \rangle \end{pmatrix}$$

and,

$$\varepsilon'_\alpha \varepsilon_\beta A_{\alpha\beta} = \tfrac{1}{2}\langle A_{xx} + A_{yy} \rangle (\boldsymbol{\varepsilon}' \cdot \boldsymbol{\varepsilon} - 3\varepsilon'_z \varepsilon_z) + \tfrac{1}{2}\langle A_{xx} - A_{yy} \rangle (\varepsilon'_x \varepsilon_x - \varepsilon'_y \varepsilon_y)$$

$$+ \langle A_{xz} \rangle (\varepsilon'_x \varepsilon_z + \varepsilon'_z \varepsilon_x).$$

This expression takes a much simpler form in the case of a uniaxial crystal since $\langle A_{xz} \rangle = \langle A_{xx} - A_{yy} \rangle = 0$. The orientation factor $(\boldsymbol{\varepsilon}' \cdot \boldsymbol{\varepsilon} - 3\varepsilon'_z \varepsilon_z)$ is familiar as the linear dichroic term in the scattering length for magnetic scattering and absorption where the unique axis is the preferred magnetic axis.

In the foregoing discussion use is made of angular brackets to denote the mean value of the enclosed quantity. For example, $< A_{aa} >$ is the mean value, which is equivalent to a time average, of a component of the rank-two symmetrical tensor $A_{\alpha\beta}$, defined in (3.12), evaluated in the principal axes. An explicit expression is,

$$< A_{aa} > = \sum_{\mu} p_\mu < \mu | A_{aa} | \mu >, \tag{3.17}$$

where p_μ is proportional to the Boltzmann factor for the equilibrium state labelled by μ, and $\Sigma\, p_\mu = 1$. It is to be noted that, the mean values of operators encountered in the interpretation of attenuation relate to the valence shell which accommodates the photo-ejected core electron. Details about the core level are largely removed by the sum on γ in the definition of $T_{\alpha\beta}$, equation (3.1), and remain in $< Z >$ only to the extent that the sum is restricted to states which contribute to a resonance labelled by quantum numbers for a core level. In general, the mean value of an atomic quantity depends on temperature, through the Boltzmann factor in (3.17), and all states of the ligand crystal-field appropriate to the resonant ion.

It is useful to record an identity for a mean value that stems from the invariance of equations of motion for material properties to a change in the direction of time. Let O be any quantum mechanical operator, O^+ its Hermitian conjugate and $\overline{O}$ the operator obtained from O by the operation of time reversal. With this notation, the identity of interest is,

$$< O >_{\mathbf{H}} = < \left\{ \overline{O} \right\}^{+} >_{-\mathbf{H}}. \tag{3.18}$$

All observable quantities are represented by Hermitian operators. One such case is the magnetization, **M**, for which the operator is odd with respect to time reversal; the identity (3.18) yields **M** (**H**) = –**M**(–**H**), a result noted at the beginning of the section.

For materials in which the magnetic moments assume a spatial order the full symmetry is a union of the point group and the symmetry element resulting from the reversal of all currents. The resultant space-time symmetry depends on the directions assumed by the moments, i.e. the spatial configuration of the magnetic moments. In the case of ferromagnetic or ferrimagnetic configurations consideration must be given to the influence on the configuration from any applied field. A sufficiently strong applied field can reorientate the ferromagnetic component of the magnetization. Thereby, the space-time symmetry is changed to one dictated by the direction of the applied field relative to the crystallographic axes; in fact, properties of the saturated material are governed by the structural crystal class and the direction of the applied field. Symmetry considerations are less helpful for multidomain crystals, which possess a far lower symmetry than the structural crystal class of the material. The latter might be adequate for the interpretation of experiments on a demagnetized material.

The behaviour of the atomic quantities $\mathbf{\Lambda}$ and $A_{\alpha\beta}$ with respect to **H** follows from their definitions in terms of the imaginary and real parts of $T_{\alpha\beta}(\mathbf{H})$. From the property (3.6) and the definition (3.11) and (3.12), $\mathbf{\Lambda}$ is an odd function of **H** and $A_{\alpha\beta}$ is an even function of **H**. In consequence, expansions of these quantities in powers of **H** begin with $\mathbf{\Lambda}$ linear in the field and $A_{\alpha\beta}$ equal to a constant plus a correction

quadratic in the field. Expressions for the atomic quantities correct at the first order in the field are, most likely, adequate, and we only need to consider $\mathbf{\Lambda}$.

Let,

$$\Lambda_\alpha = K_{\alpha\beta}\ H_\beta, \tag{3.19}$$

where $K_{\alpha\beta}$ is a tensor of rank two, in general not symmetrical in the Cartesian indices. From the transformation properties of Λ_α and H_β it follows that, $K_{\alpha\beta}$ is a polar tensor which is invariant (even) with respect to the operation of time reversal. $K_{\alpha\beta}$ is similar in respect to these transformations to the magnetic permeability tensor which, however, is symmetrical. There is no class of the point group for which $K_{\alpha\beta}$ is identically zero, in contrast, say, to an axial tensor of rank two.

By way of example, let us briefly consider a monoclinic system (a biaxial crystal) in which z labels the two-fold axis. In this case, $K_{\alpha\beta}$ at most contains five independent quantities and it has the form,

$$\begin{pmatrix} K_{xx} & K_{xy} & 0 \\ K_{yx} & K_{yy} & 0 \\ 0 & 0 & K_{zz} \end{pmatrix}.$$

The result applies to a magnetic phase of haematite, which exhibits a corundum-type crystal structure and the Fe^{3+} spins form an antiferromagnetic configuration. In the temperature range defined by the Néel temperature = 950K and the Morin temperature = 260K the symmetry is C_{2h}, and $K_{\alpha\beta}$ has the form indicated. Associated with this phase is an anisotropic exchange interaction, usually called the Dzyaloshinsky-Moriya interaction, and a small spontaneous ferromagnetism, parasitic to the antiferromagnetism, and perpendicular to the spin axis of the antiferromagnetism. Below the Morin temperature the symmetry is D_{3d}, and for this symmetry $K_{\alpha\beta}$ is zero apart from three elements on the diagonal and two of these are equal, $K_{xx} = K_{yy}$.

Weak ferromagnetism does not coexist with the symmetry D_{3d}. In its low-temperature phase, haematite is a fully compensated antiferromagnet and the circular dichroic signal is zero.

Many ferromagnetic materials possess a cubic crystal structure, and the point group symmetry is O_h. In this instance, non-diagonal components of $K_{\alpha\beta}$ are zero and the diagonal components are equal. Hence, $\mathbf{\Lambda} = K_0\mathbf{H}$ where K_0 is the magnitude of the diagonal components of $K_{\alpha\beta}$.

4. Atomic models for <Z>

Several methods have been used to calculate the matrix elements of the dipole operators in the resonant scattering length. The methods include multiple scattering, and various computer codes for individual ions that differ in their treatment of electron correlations and the influence of the ion's environment.

Using individual ions as a starting point has proved successful in the interpretation of the magnetic properties of many materials, and it is adopted in this section. It has been known for a long time that algebraic results for $T_{\alpha\beta}$ can be derived [14, 15]. The actual handling levied on the sum over the intermediate states in $T_{\alpha\beta}$ gives rise to different expressions for it, as we shall see. In all cases, the handling of the intermediate states makes $T_{\alpha\beta}$ a tensor, as we assumed in previous sections.

(I) A sum over all the intermediate states associated with a valence shell, and they are labelled here by η, followed by a spatial average reduces $T_{\alpha\beta}$ to a quantity proportional to the number of holes in the shell which accommodates the photo-ejected core electron. Here, and subsequent sub-sections, we make explicit the dependence of <Z> on the spectrum of intermediate states it contains by writing it as $< Z_\eta >$. Denoting the number of holes in the valence shell by n_h,

$$\left(\sum_{\eta} < Z_{\eta} >\right)_{av} = \tfrac{1}{3}\, n_h . \tag{4.1}$$

(II) Summing over all the intermediate states alone, and no spatial average, leads to an expression that depends on n_h and the quadrupole moment of the valence shell. The latter is a spherical tensor of rank two, and we denote the mean value of the tensor by <**Q**>.

To give an explicit expression for the symmetrical tensor $A_{\alpha\beta}$ in $< Z_{\eta} >$ we need formulae that relate $A_{\alpha\beta}$ to spherical components of a second-rank spherical tensor $< A_{\upsilon}^{(2)} >$ where $\upsilon = 0$, ± 1, and ± 2:

$$A_{xy} = \tfrac{i}{2}\left(\tfrac{3}{2}\right)^{\frac{1}{2}} < \left(A_{-2}^{(2)} - A_{+2}^{(2)}\right) > , \quad A_{xz} = \tfrac{1}{2}\left(\tfrac{3}{2}\right)^{\frac{1}{2}} < \left(A_{-1}^{(2)} - A_{+1}^{(2)}\right) >$$

$$A_{yz} = \tfrac{i}{2}\left(\tfrac{3}{2}\right)^{\frac{1}{2}} < \left(A_{-1}^{(2)} + A_{+1}^{(2)}\right) > , \quad A_{xx} - A_{yy} = \left(\tfrac{3}{2}\right)^{\frac{1}{2}} < \left(A_{+2}^{(2)} + A_{-2}^{(2)}\right) > \tag{4.2}$$

and,

$$A_{zz} = < A_{o}^{(2)} > .$$

It is interesting to note that tensors of higher rank, encountered in absorption by an electric quadrupole (E2) event, do not have unique relations in Cartesian and spherical co-ordinates.

At the second level of sophistication in handling the sum over intermediate states one arrives at the atomic quantities in $\Sigma < Z_{\eta} >$. One finds,

$$T'_{\alpha\alpha} = n_{h} , \text{ and } \Lambda = 0 . \tag{4.3}$$

The construction of $A_{\alpha\beta}$ uses the identity,

$$\sum_{\alpha\beta} X_{\alpha\beta} A_{\alpha\beta} = \tfrac{3}{2}\mathbf{X}^{(2)}.\mathbf{A}^{(2)} = \tfrac{3}{2}\sum_{\upsilon} (-1)^{\upsilon} X_{\upsilon}^{(2)} A_{-\upsilon}^{(2)} , \tag{4.4}$$

and (4.2) gives the rules for spherical and Cartesian components of a second-rank tensor. Our result is,

$$< A_{\upsilon}^{(2)} >= -2\left(\tfrac{2}{3}\right)^{\frac{1}{2}} \frac{1}{(2l-1)(2l+3)} < Q_{\upsilon} >, \tag{4.5}$$

where l is the angular momentum of the valence shell orbitals (the angular momentum of the core level orbital is taken to be $l - 1$). An alternative way of expressing (4.5) is to say that the Cartesian tensor,

$$T'_{\alpha\beta} - \tfrac{1}{3}\delta_{\alpha\beta} T'_{\gamma\gamma} = \left(\tfrac{2}{3}\right)^{1/2} A_{\alpha\beta} ,$$

has spherical components,

$$\left(\tfrac{2}{3}\right)^{1/2} \left\langle A_{\upsilon}^{(2)} \right\rangle = -\frac{4}{3(2l-1)(2l+3)} \left\langle Q_{\upsilon} \right\rangle ,$$

which are used in the formulae (4.2). The definition of $<\mathbf{Q}>$ is such that for $\upsilon = 0$,

$$< Q_{o} > \equiv < Q_{z} > = \tfrac{1}{2} < \sum_{j} \{3l_{z}^{2} - l(l+1)\}_{j} >, \tag{4.6}$$

and the sum runs over all the unoccupied states in the valence shell. The remaining four components of $< Q_{\upsilon} >$, with $\upsilon = \pm 1$ and ± 2, contain the reduced matrix element in $< Q_{o} >$, i.e. the Wigner-Eckart theorem applies to every contribution to $< Q_{\upsilon} >$. In the principal axes there are at most three

different quantities, namely $< A_{aa} >, < A_{bb} >$ and $< A_{cc} >$, and we have seen that these do not depend on $< Q_{\pm 1} >$.

(III) At the next level of sophistication in handling the sum over the intermediate states η is restricted to states that contribute to a resonance labelled by the total angular momentum of the core level, $\bar{J}$; $\bar{J} = \bar{l} \pm \frac{1}{2}$ and $\bar{l} = l - 1$. If we denote the mean value of the energy at which the resonance is observed by Δ, the notation, $\sum_{\eta(\Delta)}$ means a sum on γ restricted to the states that contribute to the structure around $\Delta = \Delta(\bar{J})$. The value of, $\sum_{\eta(\Delta)} < Z_\eta >$, is the weight of the integrated absorption signal, and the following expressions include results from the first investigation of the associated sum-rule [5].

One finds,

$$T'_{\alpha\alpha} \equiv \sum_{\alpha=x,y,z} T'_{\alpha\alpha} = \frac{l}{(2l+1)} n_h, \tag{4.7}$$

$$\mathbf{\Lambda} = \frac{1}{(2l+1)\sqrt{2}} < \mathbf{L} >, \text{ with } T''_{xy} = \frac{\langle L_z \rangle}{2(2l+1)} \text{ etc.} \tag{4.8}$$

and,

$$< A_\upsilon^{(2)} > = -\left(\frac{2}{3}\right)^{\frac{1}{2}} \frac{1}{(4l^2-1)} < Q_\upsilon >, \tag{4.9}$$

where the quadrupole tensor is defined in part II of this section. At the third level of sophistication, the forward scattering-length reveals information on the orbital contribution, $< \mathbf{L} >$, to the magnetic moment carried by the valence shell. The coefficient of P_2 in (3.14) is, $-\frac{1}{2(2l+1)} \hat{\mathbf{q}} \cdot < \mathbf{L} >$. In other words, the circular dichroic signal is sensitive to the projection onto the direction of the X-ray beam of the orbital moment.

In the case of 3d transition ions it is customary to find, $<\mathbf{L}> = (g_o - 2) <\mathbf{S}>$, where g_o is the gyromagnetic factor and $\mathbf{S}$ is the total spin operator for the valence shell. Lanthanide ions are distinguished by a very strong spin-orbit interaction in the valence shell, and $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is a good quantum number (to a very good approximation). The Landé factor, g, satisfies $g\,\mathbf{J} = (\mathbf{L} + 2\mathbf{S})$, and $\mathbf{L} = (2 - g)\mathbf{J}$.

With the present level of sophistication, the spherical components of,

$$T'_{\alpha\beta} - \tfrac{1}{3}\delta_{\alpha\beta}T'_{\gamma\gamma} \quad \text{are,} \quad -\frac{2}{3(4l^2-1)}\langle Q_\upsilon \rangle.$$

Next, we look at the coefficient of P_3 in (3.14). Let the symmetry of the crystal be higher than biaxial (results for a biaxial crystal are given in the next section); from (3.15), (4.2) and (4.9),

$$\frac{1}{\sqrt{6}}\left(A_{\sigma\sigma} - A_{\pi\pi}\right) = \frac{3}{2\sqrt{6}} < A_{cc} > \cos 2\alpha \sin^2\beta = \tfrac{1}{2}\left(\tfrac{3}{2}\right)^{\frac{1}{2}} < A_o^{(2)} > \cos 2\alpha \sin^2\beta$$

$$= -\frac{1}{2(4l^2-1)} < Q_o > \cos 2\alpha \sin^2\beta,$$

where $< Q_o >$ is defined in (4.6). As mentioned previously, the linear dichroic signal is zero if the principal axis is parallel to the beam of X-rays. The direction of the principal axis of symmetry is specified in (3.16).

(IV) The spin-orbit coupling on the core level makes $\bar{J}$ a good quantum number and the states $\bar{J} = \bar{l} \pm \frac{1}{2}$ have different energies. In consequence, with sufficient resolution in energy, it is possible to investigate the absorption at the two spin-orbit split partners. The weights for the partners are, $\sum_{\eta(\pm)} < Z_\eta >$ and one finds [6];

$$T'_{\alpha\alpha} = \frac{1}{2}\frac{l}{(4l^2-1)}\left\{(2\bar{J}+1)n_h \pm 4\left(\frac{l-1}{l}\right) < \Sigma \mathbf{s.l} >\right\}, \tag{4.10}$$

where $< \Sigma \mathbf{s.l} >$ is the mean value of the spin-orbit operator,

$$\mathbf{\Lambda} = \frac{1}{2\sqrt{2}}\frac{1}{(4l^2-1)}\{(2\bar{J}+1) < \mathbf{L} > \pm \frac{4}{3}(l-1)[l < \mathbf{S} > +(2l+3) < \mathbf{T} >]\}, \tag{4.11}$$

and,

$$< A_\upsilon^{(2)} > = -\frac{1}{\sqrt{6}}\frac{1}{(2l-1)^2(2l+1)}\{(2\bar{J}+1) < Q_\upsilon > \pm \frac{4}{5}[(l-1)(2l-1) < P_\upsilon > +3 < R_\upsilon >]\}. \tag{4.12}$$

Recall that, in the principal axes the two independent quantities in the symmetrical tensor $A_{\alpha\beta}$ depend only on $< A_o^{(2)} >$ and $< A_{\pm 2}^{(2)} >$. When summed over the two values of $\bar{J}$ the foregoing expressions for $T'_{\alpha\alpha}, \mathbf{\Lambda}$ and $< A_\upsilon^{(2)} >$ reduce to the expression in III, as expected.

The rank-one operator $\mathbf{T}$ (not to be confused with the tensor $T_{\alpha\beta}$) and the rank-two operators $\mathbf{P}$ and $\mathbf{R}$ are completely specified by the expressions,

$$< T_o > \equiv < T_z > = - < \sum_j \{3\hat{R}_z(\hat{\mathbf{R}} \cdot \mathbf{s}) - s_z\}_j >, \tag{4.13}$$

$$< P_o > = \tfrac{1}{2} < \sum_j \{3 s_z l_z - \mathbf{s} \cdot \mathbf{l}\}_j >, \tag{4.14}$$

$$< R_o > = -\tfrac{1}{2} < \sum_j \{(2l(l+1)+1)s_z l_z + (l(l+2)-2)\mathbf{s} \cdot \mathbf{l} - 5 l_z (\mathbf{s} \cdot \mathbf{l}) l_z\}_j >. \tag{4.15}$$

Values of $< \mathbf{T} >, < \mathbf{P} >$ and $< \mathbf{R} >$ for a 3d-transition ion are given in the next section.

(V) The spin projection of the core state, $\overline{M}$, can take $(2\overline{J}+1)$ values. The degeneracy of the states labelled by $\overline{M}$ is removed by the exchange field acting on the core level. To take this fine structure into account one needs the weights, $\sum_{\eta(\overline{M})} < Z_\eta >$. For each weight there is in f''_{res} one Lorentzian function of energy, i.e. the energy dependence of a spin-orbit split partner is modelled by $(2\overline{J}+1)$ Lorentzian functions. We shall not give the corresponding expressions for $T'_{\alpha\alpha}$, Λ and $\left\langle A_\upsilon^{(2)} \right\rangle$ simply because they are lengthy. Examples of the expressions appropriate for a 3d ion and a lanthanide ion are found in [6,16].

5. Example: a biaxial crystal

The transition-metal niobates crystallize in the columbite structure, which is an orthorhombic system and thus biaxial. Below 4.9K, ferrous niobate exhibits antiferromagnetic order with a canted spin configuration. For a fully compensated spin configuration the circular dichroic signal is zero. A non-zero signal can be created by application of the magnetic field, and in the case of ferrous niobate at 2.0K the field-induced magnetization is significant for modest fields. The critical value of the magnetic field and the magnetization depends on the orientation of the applied field relative to the crystal axes. The anisotropy in the magnetization is mirrored in the gyromagnetic factors; in the principal axes, the gyromagnetic tensor of the ferrous ion has values $g_a = 2.0$, $g_b = 2.37$ and $g_c = 3.09$.

The results given below are based on a model of ferrous niobate in which the degrees of freedom of the orbital angular momentum of the ferrous ion are explicitly taken into account [17]. The model is consistent with a wealth of experimental data, including the magnetization, susceptibility and neutron diffraction pattern of a single crystal.

To obtain the results of this section, the wave function of the ferrous ion is calculated by perturbation theory, correct to the first-order in the spin-orbit coupling. The mean values of the atomic quantities, introduced in part IV of section 4, are

correct to the same order of approximation. Results here are for a single ferrous ion; the field-induced magnetization and the relative orientation of the two ions in the unit cell are given in reference [17].

We begin with the atomic quantities in $\mathbf{\Lambda}$, equation (4.11). In the principal axes, (a, b, c), one finds

$$< L_c > = (g_c - 2) < S_c >, \tag{5.1}$$

and,

$$< T_c > = \tfrac{1}{14} \{1 - \tfrac{3}{4}(g_b - 2)\} < S_c > . \tag{5.2}$$

Because $(g_a - 2) = 0$ there is no contribution to the anisotropy tensor, $< \mathbf{T} >$, from the component of the moment in the **a**-direction. The remaining Cartesian components of $\mathbf{\Lambda}$ are zero. Using the values quoted for the gyromagnetic factors $< T_c > = 0.047 < L_c >$. (Results for $< \mathbf{T} >$ for other 3d-transition ions are found in [6,18,19].)

The quadrupole moment, which appears in the symmetrical tensor $A_{\alpha\beta}$, is independent of the temperature. The spherical components $< Q_\upsilon >$ different from zero are $< Q_o > = 3/2$ and $< Q_{\pm 2} > = -(3/2)^{3/2}$, and these particular values are indicative of the main component of the ground-state orbital, which is the $| yz >$ orbital in the Γ_5 triplet.

The remaining rank-two tensors depend on temperature through $< S_c^2 >$. Thus, in the paramagnetic phase the symmetrical tensor $A_{\alpha\beta}$ is different from zero, unlike $\mathbf{\Lambda}$. One finds,

$$< P_o > + < R_o > = -\frac{5}{4}\left\{(g_c - 2) < S_c^2 > + \frac{1}{4}(g_b - 2)[< S_c^2 > - S(S+1)]\right\}, \tag{5.3}$$

and,

$$< P_{\pm 2} > + < R_{\pm 2} > = \tfrac{5}{16}\left(\tfrac{3}{2}\right)^{\frac{1}{2}}(g_{\mathrm{b}} - 2)[S(S+1) - < S_{\mathrm{c}}^2 >], \tag{5.4}$$

where $S = 2$ is the spin of the ferrous ion.

Combining the results for $< \mathbf{Q} >$, and $(< \mathbf{P} > + < \mathbf{R} >)$ in (4.12) and using (4.2), we arrive at expressions for the quantities in the dichroic signal picked out by linear polarization, namely,

$$\tfrac{1}{\sqrt{6}} < A_{\mathrm{cc}} > = \tfrac{1}{180}\left\{-(2\overline{J}+1) \pm 2[(g_{\mathrm{c}} - 2) < S_{\mathrm{c}}^2 > + \tfrac{1}{4}(g_{\mathrm{b}} - 2)\{< S_{\mathrm{c}}^2 > - S(S+1)\}]\right\},$$

and, (5.6)

$$\tfrac{1}{\sqrt{6}} < A_{\mathrm{aa}} - A_{\mathrm{bb}} > = \tfrac{1}{60}\left\{(2\overline{J}+1) \pm \tfrac{1}{2}(g_{\mathrm{b}} - 2)[< S_{\mathrm{c}}^2 > - S(S+1)]\right\}.$$

These expressions inserted in (3.15) give the coefficient of P_3 in $< Z >$, found in (3.14). The dependence on temperature of the linear dichroic signal is not simple; in particular, the signal is not proportional to $< S_{\mathrm{c}}^2 >$. In the limit of an infinite temperature $< S_{\mathrm{c}}^2 > \rightarrow S(S+1)/3$, and the approach to this value depends on the strong uniaxial magnetic anisotropy in ferrous niobate. A value of $< A_{\mathrm{aa}} - A_{\mathrm{bb}} >$ different from zero reflects the low symmetry of the crystal. Another point to note is that, the linear dichroic signal is not zero for a compensated antiferromagnetic configuration of the moments, whereas the circular dichroic is zero for such a configuration. The geometrical factor in the circular dichroic signal is simple, being the projection of $\mathbf{\Lambda}$ on the direction of propagation of the X-ray beam. When the projection is zero the linear dichroic signal is non-zero. Note that there is no simple geometry which renders the contribution from $< A_{\mathrm{aa}} - A_{\mathrm{bb}} >$ zero, and this signature of a biaxial crystal is omnipresent in the linear dichroic signal.

6. Conclusions

Classical optical techniques, including Jones and Mueller calculi, are equally applicable to X-rays and visible light. One can employ such well-established techniques to provide a complete description of the passage of X-rays through a material which is anisotropic and magnetic, including all polarization-dependent effects. The scattering amplitude matrix, from which Jones and Mueller matrices can be derived, is related to components of the dipole-dipole tensor. We describe a range of atomic models for these same tensor components, thus providing a complete link between atomic variables and observable quantities in X-ray attenuation and retardation. The chosen example of ferrous niobate illustrates how, armed with the appropriate electronic wavefunction, one can model X-ray attenuation, including linear and circular dichroism.

Because the present treatment is restricted to rank-two tensors, appropriate for pure dipolar events, effects such as natural circular dichroism [20] are not accessible.

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Figure Caption:

Figure 1

The ellipsoid formed by $\varepsilon_\alpha \varepsilon_\beta T'_{\alpha\beta}$, for an ion in various crystalline environments. With cubic symmetry, the ellipsoid becomes a sphere (there is no linear dichroism). An ion in a tetrahedral environment has two principal axes the same length. Dichroism is observed upon rotation about any axis other than the unique axis. Orthorhombic symmetry leads to all three principal axes being different, with each being parallel to symmetry directions of the ion. Any rotation leads to dichroism and $T'_{\alpha\beta}$ has three independent elements. The final illustration shows an ion in a triclinic environment. Again, the three principal axes are of different length, but they no longer lie along symmetry directions. The tensor $T'_{\alpha\beta}$ has six independent elements, equivalent to three principal axis lengths and three angles.

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Appendix

Consider a square matrix of order two,

$$G = \begin{pmatrix} b + a_3 & a_1 - \mathrm{i}a_2 \\ a_1 + \mathrm{i}a_2 & b - a_3 \end{pmatrix}, \tag{A1}$$

where, for the moment, a_1, a_2, a_3 and b are purely real. We note that G is Hermitian and,

$$G \equiv bI + \mathbf{a} \cdot \boldsymbol{\sigma}, \tag{A2}$$

where I is the unit matrix, and σ_1, σ_2 and σ_3 are standard Pauli matrices defined in (2.6). In (A2) we employ the shorthand notation $\mathbf{a} \cdot \sigma = \sum a_j \sigma_j$, j = 1, 2 and 3. The determinant of G is,

$$\det. G = b^2 - \zeta^2, \tag{A3}$$

with $\zeta^2 = \mathbf{a} \cdot \mathbf{a}$, and the trace is,

$$\mathrm{tr}. G = 2b. \tag{A4}$$

(A3) and (A4) are invariants of G and they are unchanged when G is the subject of a unitary transformation, like a rotation of the axes that span its two-dimensional space.

The two eigenvalues of G are denoted by λ_+ and λ_- and have the values,

$$\lambda_\pm = b \pm \zeta, \tag{A5}$$

which satisfy,

$$\det. G = \lambda_+ \lambda_-, \tag{A6}$$

and,

$$\mathrm{tr.}\, G = \lambda_+ + \lambda_-. \tag{A7}$$

Using the fact that G satisfies the eigenvalue equation one finds,

$$G^2 = 2bG - (b^2 - \zeta^2)I. \tag{A8}$$

The corresponding eigenvectors of G are,

$$\begin{pmatrix} n_1(\pm) \\ n_2(\pm) \end{pmatrix} \tag{A9}$$

with $n_1(+) = (a_1 - \mathrm{i}a_2)C_+, \quad n_2(+) = (\zeta - a_3)\, C_+$

$$n_1(-) = -(a_1 - \mathrm{i}a_2)C_-, \quad n_2(-) = (\zeta + a_3)\, C_- \tag{A10}$$

in which,

$$C_\pm = \left\{2\zeta\left(\zeta \mp a_3\right)\right\}^{-1/2}. \tag{A11}$$

The two eigenvectors are orthogonal, and each one is normalized to the value 1.

The matrix,

$$U = \begin{pmatrix} n_1(+) & n_1(-) \\ n_2(+) & n_2(-) \end{pmatrix} \tag{A12}$$

is unitary, $U^+ = U^{-1}$, and satisfies, $U^+ \; U = I$. Of course,

$$U^+ G U = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix}, \tag{A13}$$

and,

$$G^{-1} = U\begin{pmatrix} 1/\lambda_+ & 0 \\ 0 & 1/\lambda_- \end{pmatrix}U^{-1} = \begin{pmatrix} b-a_3 & -a_1+\mathrm{i}a_2 \\ -a_1-\mathrm{i}a_2 & b+a_3 \end{pmatrix}(b^2-\zeta^2)^{-1}. \qquad \text{(A14)}$$

It is interesting to note that the eigenvectors, and hence U, do not depend on b, the coefficient of the unit matrix in (A2).

The matrix formed with the symmetrical elements, ½ ($G_{\alpha\beta}$ + $G_{\beta\alpha}$) is purely real, namely,

$$G_s = \begin{pmatrix} b+a_3 & a_1 \\ a_1 & b-a_3 \end{pmatrix}. \qquad \text{(A15)}$$

Let,

$$\zeta' = (a_1^2+a_3^2)^{1/2},\ C'_\pm = \{2\zeta'(\zeta' \mp a_3)\}^{-1/2},\ \cos\phi = a_1 C'_+ = (\zeta'+a_3)C'_-,$$

and, (A16)

$$\sin\phi = a_1 C'_- = (\zeta'-a_3)C'_+.$$

Taking $a_2 = 0$ in foregoing results one finds,

$$G_s = \begin{pmatrix} \lambda'_+\cos^2\phi + \lambda'_-\sin^2\phi & \frac{1}{2}\sin(2\phi)(\lambda'_+-\lambda'_-) \\ \frac{1}{2}\sin(2\phi)(\lambda'_+-\lambda'_-) & \lambda'_+\sin^2\phi + \lambda'_-\cos^2\phi \end{pmatrix}, \qquad \text{(A17)}$$

with $\lambda'_\pm = b \pm \zeta'$, and,

$$\begin{pmatrix} \lambda'_+ & 0 \\ 0 & \lambda'_- \end{pmatrix} = \begin{pmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{pmatrix} G_s \begin{pmatrix} \cos\phi & -\sin\phi \\ \sin\phi & \cos\phi \end{pmatrix}. \qquad \text{(A18)}$$

The vectors (cosϕ, sinϕ) and (–sinϕ, cosϕ) define a set of principal axes in which G_s is diagonal.

The matrix formed with the antisymmetrical elements, ½ ($G_{\alpha\beta}$ – $G_{\beta\alpha}$), has two elements and it is purely imaginary. If the elements $\varepsilon_{12} = -\varepsilon_{21} = 1$ define the unit antisymmetrical tensor,

$$\tfrac{1}{2}(G_{\alpha\beta} - G_{\beta\alpha}) = -\mathrm{i}a_2\varepsilon_{\alpha\beta}\,. \tag{A19}$$

For the case in hand, the quantity a_2 is a pseudo-scalar because the rank of the antisymmetrical tensor on the left-hand side of (A19) is equal to the dimension of the space in which it is defined. Specifically, the electric field that accompanies a photon is described with two basis-vectors (usually called the polarization vectors) and the scattering length, and the density matrix for the states of polarization, are tensors of rank two.

By definition,

$$G = G_s + G_a\,, \tag{A20}$$

and,

$$G_a = -\mathrm{i}a_2\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = a_2\Sigma\ , \tag{A21}$$

The second equality in (A21) defines Σ which is found to be the operator for the helicity of a photon. Note that the matrix representation of Σ is identical to the Pauli matrix σ_2.

Define angles ψ and η such that,

$$n_1(+) = \exp(\mathrm{i}\eta)\cos\psi, \;\; n_2(+) = \sin\psi,$$
$$n_1(+)/n_2(-) = -n_1(-)/n_2(+) = \frac{(a_1 - \mathrm{i}a_2)}{(a_1^2 + a_2^2)^{1/2}} = \exp(\mathrm{i}\eta). \tag{A22}$$

Observe that exp (iη) is the value of the determinant of U defined by (A12). One finds,

$$G = \begin{pmatrix} \lambda_+ \cos^2\psi + \lambda_- \sin^2\psi & \frac{1}{2}\mathrm{e}^{\mathrm{i}\eta}\sin(2\psi)(\lambda_+ - \lambda_-) \\ \frac{1}{2}\mathrm{e}^{-\mathrm{i}\eta}\sin(2\psi)(\lambda_+ - \lambda_-) & \lambda_+ \sin^2\psi + \lambda_- \cos^2\psi \end{pmatrix}, \tag{A23}$$

where, as before, $\lambda_\pm = b \pm \zeta$, and now the orthogonality condition is,

$$\mathbf{n}(+) \cdot \mathbf{n}^*(-) = 0.$$

In the main text we are led to consider the matrix,

$$\Omega = \exp(G) = \exp(b\,I)\exp(\mathbf{a}\cdot\boldsymbol{\sigma}). \tag{A24}$$

Using $\sigma_j^2 = I$ and $(\mathbf{a}\cdot\boldsymbol{\sigma})^2 = \zeta^2 I$, or (A8), one finds for Ω,

$$\Omega = \exp(b)\left\{ I\cosh(\zeta) + \mathbf{a}\cdot\boldsymbol{\sigma}\,\tfrac{1}{\zeta}\sinh(\zeta)\right\}. \tag{A25}$$

This important result is valid for complex **a** and b. Note that Ω has exactly the same mathematical structure as G, cf. (A2). So, all previous results in the appendix apply to Ω on making the replacements,

$$b \rightarrow \exp(b)\cosh(\zeta) \quad \text{and} \quad \mathbf{a} \rightarrow \mathbf{a}\exp(b)\tfrac{1}{\zeta}\sinh(\zeta). \tag{A26}$$

In particular,

$$\mathrm{tr}.\Omega = 2\exp(b)\cosh(\zeta), \tag{A27}$$

and,

$$\det.\Omega = \exp(2b), \tag{A28}$$

and if b is purely real it follows from (A28) that Ω is a non-singular matrix.

The density matrix for states of polarization in a beam of photons, μ, has the structure of the matrix G, defined in (A1) and (A2), and **a** and b purely real. In this instance,

$$\mu = \tfrac{1}{2}(I + \mathbf{P}\cdot\boldsymbol{\sigma}), \tag{A29}$$

where $\mathbf{P} = (P_1, P_2, P_3)$ is the so-called Stokes vector. One sees that $\mathrm{tr}.\mu = 1$, and $\det.\mu = (1 - P^2)/4 \geq 0$ where $P = \sqrt{(\mathbf{P}\cdot\mathbf{P})}$. For a completely polarized beam $P = 1$ and for an unpolarized beam $P = 0$.

Let **u** be a unit vector with purely real components $u_j = P_j/P$. Then,

$$\mu = \tfrac{1}{2}(1-P)I + \tfrac{1}{2}P(I + \mathbf{u}\cdot\boldsymbol{\sigma}), \tag{A30}$$

in which the matrix $(I + \mathbf{u}\cdot\boldsymbol{\sigma})/2$ is idempotent, a useful property in manipulations involving μ. A physical interpretation of (A30) is that μ is an incoherent mixture of a completely polarized state (often called a pure state, and achieved when a photon is described by a wave function), and a completely unpolarized state.

The average of a quantity Y, say, with respect to the polarization described by **P** is,

$$\overline{Y} = \quad \mathrm{tr}.\mu Y = \mathrm{tr}.Y\mu. \tag{A31}$$

Taking Y to be a Pauli matrix,

$$\overline{\sigma}_j = P_j . \tag{A32}$$

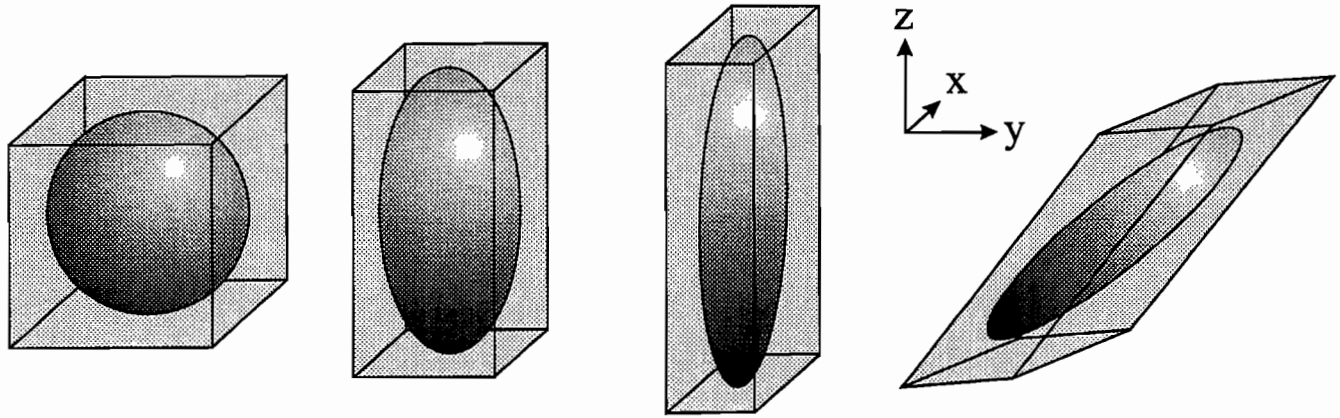
The combination of the three Stokes parameters P_1, P_2 and P_3 into a "vector" **P** is, of course, purely formal and is done only for convenience of notation. As we have seen, P_2 is a pseudo-scalar, and P_1 and P_3 are true scalars. A second property of the Stokes parameters which demonstrate that **P** is not a true vector stems from crossing symmetry. From the latter symmetry one finds the *modulus* of the scattering length is invariant under the transformation expressed by,

$$E \leftrightarrow -E', \quad \mathbf{q} \leftrightarrow -\mathbf{q}', \quad P_1 \leftrightarrow P_1', \quad P_2 \leftrightarrow -P_2', \quad P_3 \leftrightarrow P_3'. \tag{A33}$$

Here, the energy of a photon with wavevector **q** is $E = \hbar c|\mathbf{q}|$, and primed quantities relate to the condition of the secondary beam. It is readily shown that, under the reversal of the direction of time all three Stokes parameters are even.

It is interesting to note that, for neutrons and photons the formal mathematical structures of the density matrices are the same. However, the physical significance of **P** differs for the two types of particle. In the case of a beam of neutrons **P** is twice the mean value of the spin variable for neutrons in the beam. **P**, therefore, is odd with respect to the reversal of the direction of time, and a pseudo-vector (also called an axial vector). Thus, under the parity transformation, which inverts spatial coordinates and so changes a right-handed system of coordinates to a left-handed system of coordinates and vice versa, the polarization of neutrons is unchanged. Under the parity transformation, the Stokes parameters P_1 and P_3 are unchanged, whereas P_2, the mean helicity, changes its sign, i.e. P_1 and P_3 are true scalars and P_2 is a pseudo-scalar. The change in sign of P_2 is evident from its relation to helicity, the operator for which is the scalar product of a polar vector (the photon wavevector) and an axial vector (the photon spin). With regard to spatial symmetries for the two types of particles it is relevant that the symmetry group for the density matrix of photons is SO(2), while for neutrons the symmetry group is SU(2), of course. For one thing, the dimension of SO(2) equals the rank of the density matrix and, from this alone, we have noted that the Stokes parameter P_2 is a pseudo-scalar.

Cubic (isotropic)	Tetragonal (uniaxial)	Orthorhombic (biaxial)	Triclinic (biaxial)



$$T' = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix} \quad T' = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & c \end{pmatrix} \quad T' = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix} \quad T' = \begin{pmatrix} a & d & e \\ d & b & f \\ e & f & c \end{pmatrix}$$