Magnetic Effects in Anomalous Dispersion *

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Abstract

Spectacular enhancements of magnetic x-ray scattering have been predicted and observed experimentally. These effects are the result of resonant phenomena closely related to anomalous dispersion, and they are strongest at near-edge resonances. The theory of these resonances will be developed with particular attention to the symmetry properties of the scatterer. While the phenomena to be discussed concern magnetic properties the transitions are electric dipole or electric quadrupole in character and represent a subset of the usual anomalous dispersion phenomena. The polarization dependence of the scattering is also considered, and the polarization dependence for magnetic effects is related to that for charge scattering and to Templeton type anisotropic polarization phenomena. It has been found that the strongest effects occur in rare-earths and in actinides for M shell edges. In addition to the scattering properties the theory is applicable to "forward scattering" properties such as the Faraday effect and circular dichroism.

With the coming of age of synchrotron radiation sources of x-rays many phenomena which had barely been observable have become important research techniques. In particular, the high intensity of these sources has made possible the observation of x-ray scattering from the magnetization density in solids with relative ease [1–5]. By contrast, the initial experiments using conventional sources [2] required heroic efforts to observe the effects. Similarly, the tunability of synchrotron sources has made possible a much more detailed study of anomalous dispersion and related absorption and polarization phenomena. A consequence of these developments has been a closer look at the theoretical aspects of anomalous dispersion. The basic equations that will be used in many papers at this conference are more than sixty years old, and a number of the important developments to be discussed here could have been worked out at any time in this period. That they have not is an indication of the interplay between theory and experiment. The spectacular experimental developments made possible by synchrotron radiation sources have stimulated a reconsideration of theoretical terms that previously had to be dismissed as unobservable. In this process several effects which might in fact have been observed with conventional x-ray sources have been found.

In this paper I will discuss the theory of magnetic effects in anomalous dispersion, and in the process will develop equations which contain not only these magnetic terms but also the general theory of anomalous dispersion including charge effects.

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The coherent amplitude for scattering of a photon with wave vector $\boldsymbol{k}$ and polarization state λ to $\boldsymbol{k}'$ and λ' is shown in the appendix to be given by

$$A = -\frac{e^2}{mc^2}\varepsilon'^{\alpha *}_{\lambda'}\varepsilon^{\beta}_{\lambda}\sum_a p_a \Bigg\{ \langle a|\sum_i e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i}|a\rangle\delta^{\alpha\beta}$$
$$-i\frac{\hbar\omega}{mc^2}\langle a|\sum_i e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i}\left(\frac{-i(\boldsymbol{K}\times\boldsymbol{p}_j)^\gamma}{\hbar K^2}A^{\alpha\beta\gamma} + \boldsymbol{s}_j^\gamma B^{\alpha\beta\gamma}\right)|a\rangle$$
$$-\frac{1}{m}\sum_c\left(\frac{E_a-E_c}{\hbar\omega}\right)\frac{\langle a|O^{\alpha\dagger}(\boldsymbol{k}')|c\rangle\langle c|O^{\beta}(\boldsymbol{k})|a\rangle}{E_a-E_c+\hbar\omega-i\frac{\Gamma}{2}}$$
$$+\frac{1}{m}\sum_c\left(\frac{E_a-E_c}{\hbar\omega}\right)\frac{\langle a|O^{\beta}(\boldsymbol{k})|c\rangle\langle c|O^{\alpha\dagger}(\boldsymbol{k}')|a\rangle}{E_a-E_c-\hbar\omega}\Bigg\} \tag{1}$$

where $O^\beta(\boldsymbol{k}) = \sum_i e^{i\boldsymbol{k}\cdot\boldsymbol{r}_i}(\boldsymbol{p}_i^\beta - i\hbar(\boldsymbol{k}\times\boldsymbol{s}_i)^\beta)$, and the remainder of the notation used in equation (1) is defined in the appendix [7]. The first term in braces, proportional to $\langle a|\sum_i e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i}|a\rangle$, gives the charge scattering, and is usually the only term considered in the simplest "kinematical" theory of x-ray scattering. If the state $|a\rangle$ of the scatterer is spatially periodic it is easily shown that this term produces Bragg scattering. The second term, proportional to $i\frac{\hbar\omega}{mc^2}$, is the non-resonant magnetic scattering [1–5]. Notable in this term is the fact that the scattering from orbital and spin magnetization densities have different polarization factors ($A^{\alpha\beta\gamma}$ and $B^{\alpha\beta\gamma}$, respectively), raising the possibility of using polarization dependence to separate these densities [2,4]. The non-resonant magnetic scattering is much smaller than the charge scattering [4], but it is readily observable with the intensity of synchrotron radiation. It is most easily seen in an antiferromagnet or in a helical magnetic structure, where the charge and magnetic scattering Bragg peaks are separate. In a ferromagnet, where the weak magnetic scattering occurs at the same point in reciprocal space as the charge scattering, the two may interfere with one another, and the polarization dependence can be used to separate them. The third and fourth terms are responsible for anomalous dispersion—the energy dependence of the scattering and the subject of this conference. The bulk of this article will consider the properties of these terms.

We are concerned with the effects of resonance, when the photon energy $\hbar\omega$ is approximately equal to the energy difference $E_c - E_a$ of an excited state E_c above the ground state E_a. Then the final term in braces can be neglected compared to the next-to last, as the energy denominator of the latter can be close to zero. It might in some cases be necessary to include the non-resonant terms, particularly when looking at cases when the photon energy is far from resonance. This can be done in a straightforward way, and equation (A8) in the appendix gives the relevant formula.

In eq. (1) the quantum states $|a\rangle$ and $|c\rangle$ refer to states of the *entire* solid, and the sums over i and j are over *all* electrons in the scatterer. If the electron is associated with a specific atom we can write

$$\boldsymbol{r}_j = \boldsymbol{n} + \boldsymbol{d}_s + \boldsymbol{r}'_j, \tag{2}$$

where $\boldsymbol{n}$ is a vector to the n^{th} unit cell and $\boldsymbol{d}_s$ is a vector from the origin of the unit cell to the s^{th} atom in the cell. Finally, we approximate $e^{i\boldsymbol{k}\cdot\boldsymbol{r}'_i} \approx 1 + i\boldsymbol{k}\cdot\boldsymbol{r}'_i + \frac{1}{2}(i\boldsymbol{k}\cdot\boldsymbol{r}'_i)^2$.

Eq. (1) then becomes

$$A = -\frac{e^2}{mc^2}\varepsilon_{\lambda'}^{\prime\alpha *}\varepsilon_{\lambda}^{\beta}\sum_{n,s} e^{iK\cdot(n+d_s)-W_s}\sum_a p_a\Bigg\{\langle a|\sum_i{}^{(n,s)}e^{iK\cdot r_i}|a\rangle\delta^{\alpha\beta}$$
$$-i\frac{\hbar\omega}{mc^2}\langle a|\sum_i{}^{(n,s)}e^{iK\cdot r_i}\left\{\frac{-i(K\times p_i)^{\gamma}}{\hbar K^2}A^{\alpha\beta\gamma}+s_i^{\gamma}B^{\alpha\beta\gamma}\right\}|a\rangle$$
$$+m\sum_c\left(\frac{(E_c-E_a)^3}{\hbar^3\omega}\right)\frac{\langle a|\sum_i^{(n,s)}r_i^{\alpha}(1-\frac{1}{2}ik'\cdot r_i)|c\rangle\langle c|\sum_j^{(n,s)}r_j^{\beta}(1+\frac{1}{2}ik\cdot r_j)|a\rangle}{E_a-E_c+\hbar\omega-i\frac{\Gamma}{2}}\Bigg\} \quad (3)$$

with $\sum^{(n,s)}$ indicating a summation over electrons in the ion at $n+d_s$. While we have not derived it, it can be shown that the Debye-Waller factor W_s must be included, and we have written it in eq. (3). We have also dropped the primes on the r_j', and have omitted the spin and magnetic orbital parts in the dispersive term. The latter may have to be considered in special cases, particularly for visible light, but they are generally smaller in the VUV and x-ray regimes than the electric multipole transitions which we have retained.

Setting $\hbar\omega_{ca} = E_c - E_a(> 0)$, and writing

$$R_{ns}^{\alpha} = \sum_i{}^{(n,s)}r_i^{\alpha} \quad , \quad Q_{ns}^{\alpha\delta} = \sum_i{}^{(n,s)}r_i^{\alpha}r_i^{\delta},$$

the resonance term in (3) becomes

$$A_{res} = -\frac{e^2}{mc^2}\sum_{n,s} e^{iK\cdot(n+d_s)-W_s}\varepsilon_{\lambda'}^{\prime\alpha *}\varepsilon_{\lambda}^{\beta}$$
$$\times\frac{m}{\hbar}\sum_{ca}p_a\frac{\omega_{ca}^3}{\omega}\frac{\langle a|(R_{ns}^{\alpha}-\frac{1}{2}iQ_{ns}^{\alpha\delta}k'^{\delta})|c\rangle\langle c|(R_{ns}^{\beta}+\frac{1}{2}iQ_{ns}^{\beta\gamma}k^{\gamma})|a\rangle}{\omega-\omega_{ca}-i\frac{\Gamma}{2\hbar}} \quad (4)$$

This expression is the usual one (except for the factor $\frac{\omega_{ca}}{\omega}$) for the calculation of anomalous dispersion up to electric quadrupole emission and absorption. We can write

$$A_{res} = -\frac{e^2}{mc^2}\sum_{ns} e^{iK\cdot(n+d_s)-W_s}\varepsilon_{\lambda'}^{\prime\alpha *}\varepsilon_{\lambda}^{\beta}$$
$$\times\frac{m}{\hbar}\sum_{ca}p_a\frac{\omega_{ca}^3}{\omega}\Bigg\{\frac{\langle a|R_{ns}^{\alpha}|c\rangle\langle c|R_{ns}^{\beta}|a\rangle}{\omega-\omega_{ca}-i\frac{\Gamma}{2\hbar}}$$
$$+\frac{1}{2}i\left[\frac{\langle a|R_{ns}^{\alpha}|c\rangle\langle c|Q_{ns}^{\beta\gamma}k^{\gamma}|a\rangle-\langle a|Q_{ns}^{\alpha\gamma}k'^{\gamma}|c\rangle\langle c|R_{ns}^{\beta}|a\rangle}{\omega-\omega_{ca}-i\frac{\Gamma}{2\hbar}}\right]$$
$$+\frac{1}{4}\frac{\langle a|Q_{ns}^{\alpha\delta}k'^{\delta}|c\rangle\langle c|Q_{ns}^{\beta\gamma}k^{\gamma}|a\rangle}{\omega-\omega_{ca}-i\frac{\Gamma}{2\hbar}}\Bigg\}. \quad (5)$$

$$\equiv A_{res}^{dd} + A_{res}^{dq} + A_{res}^{qq},$$

where dd denotes dipole-dipole absorption and emission, dq the dipole-quadrupole cross-terms, and qq the pure quadrupole terms. Note that for an ordered crystal the R's and Q's are independent of the vector $\boldsymbol{n}$ of the unit cell: $R^{\alpha}_{\boldsymbol{n}s} = R^{\alpha}_{s}$ and $Q^{\alpha\delta}_{ns} = Q^{\alpha\delta}_{s}$. For a magnetic crystal in which the magnetic structure differs from the atomic structure (e.g. a spiral structure) the labels are necessary. We omit them in the following, but they should be restored where needed.

As a first application of symmetry we note that A^{dq}_{res} vanishes unless the atom is not at a center of symmetry. $Q^{\alpha\delta}$ will only connect states of the same parity and R^{α} only those of different parity. These terms will thus be small, but they are essential in that they are responsible for optical activity and (non-magnetic) circular dichroism.

DIPOLE TRANSITIONS

The dipolar terms are generally larger than the quadrupolar ones in the transitions for which they are allowed, and we will consider the dipolar terms first. We write

$$A^{dd}_{res} = -\frac{e^2}{mc^2} \sum_{ns} e^{i\boldsymbol{K}\cdot(\boldsymbol{n}+\boldsymbol{d}_s)-W_s} \varepsilon'^{\alpha *}_{\lambda'} \varepsilon^{\beta}_{\lambda} C^{\alpha\beta}_{s} \cdot \frac{m\omega_0^3}{\hbar\omega} \tag{6}$$

where $\omega_{ac} \approx \omega_0$, and

$$C^{\alpha\beta}_{s} = \sum_{ca} p_a \frac{\langle a|R^{\alpha}_{s}|c\rangle\langle c|R^{\beta}_{s}|a\rangle}{\omega - \omega_{ca} - i\frac{\Gamma}{2\hbar}}. \tag{7}$$

The states $|a\rangle$ and $|c\rangle$ between which resonance occurs involve levels which differ from one another by the change in state of a single electron. The sums over a and c are here taken only over a set of sublevels of the ground state $|a\rangle$ (for example over the magnetic quantum numbers of that state) and of a similar set of sublevels of the excited state $|c\rangle$. (It is important to be aware of the distinction between the many body state $|a\rangle$ and the approximate single particle states occupied by the electrons. The many body states may be specified by giving the occupancy of the single particle states by the electrons.) As an example we consider scattering from Holmium [8], which was the first material in which resonant magnetic scattering was observed at a magnetic Bragg peak. The single particle states of Ho are shown in figure 1. The ground state $|a\rangle$ is represented by the occupancy $(1s)^2(2s)^2(2p_{1/2})^2(2p_{3/2})^4\ldots(4f)^{10}$. The excited states of the L_{III} resonance have one fewer $2p_{3/2}$ electron and either one additional $5d$ electron or one additional $4f$ electron. The state with an additional $5d$ electron is reached by an electric dipole transition ($\Delta\ell = 1$ with a change of parity) while the state with an additional $4f$ electron requires an electric quadrupole transition. These transitions represent promotion of the inner shell electron to a bound or nearly bound level with a high density of states. They are related to the "white lines" in the near-edge absorption spectrum. The usual calculations of anomalous dispersion, on the other hand, involve promoting one of the inner shell electrons (such as a $2p_{3/2}$ or a $1s$ electron) into the continuum of Bloch states or free-particle plane wave states. In general the anomalous effects are much larger for the "white line" transitions, and the tunability of synchrotron radiation makes such studies relatively straightforward.

Returning to eq. (7) we may consider the decomposition of $C^{\alpha\beta}_{s}$, which is a second rank tensor [9], into three parts:

$$C_s^{\alpha\beta} = C_{0s}\delta^{\alpha\beta} + C_{-s}^{\alpha\beta} + C_{+s}^{\alpha\beta} \tag{8}$$

(recall that s labels the particular atom in the unit cell). Here $C_0 = \frac{1}{3}trC$, $C_-^{\alpha\beta} = -C_-^{\beta\alpha}$ is the antisymmetric part of C, and $C_+^{\alpha\beta} = C_+^{\beta\alpha}$ is the traceless symmetric part of C, so that

$$C_-^{\alpha\beta} = \frac{1}{2}(C^{\alpha\beta} - C^{\beta\alpha}),$$
$$C_+^{\alpha\beta} = \frac{1}{2}(C^{\alpha\beta} + C^{\beta\alpha}) - \frac{1}{3}(trC)\delta^{\alpha\beta}.$$

It is straightforward to deduce the form of the polarization dependence of the resonant scattering from the fact that C is a tensor, together with assumptions about the symmetry of the surroundings of the atom. Each atom in the unit cell will, in general, have a different tensor.

If the atom is in spherically symmetric surroundings, but possesses a magnetic moment, then

$$C_-^{\alpha\beta} \propto \varepsilon^{\alpha\beta\gamma} m^\gamma,$$
$$C_+^{\alpha\beta} \propto m^\alpha m^\beta - \frac{1}{3}m^2\delta^{\alpha\beta}, \tag{9}$$

since $\boldsymbol{m}$, the magnetic moment, is the only vector in the problem. Here $\varepsilon^{\alpha\beta\gamma}$ is the antisymmetric tensor of third rank. From eq. (6)

$$A_{res}^{dd} = -\frac{e^2}{mc^2}\sum_{ns} e^{i\boldsymbol{K}\cdot(\boldsymbol{n}+\boldsymbol{d}_s)-W_s}\frac{m\omega_0^3}{\hbar\omega}\Big(\boldsymbol{\varepsilon}_{\lambda'}'^* \cdot \boldsymbol{\varepsilon}_\lambda\, C_{0s}$$
$$+i(\boldsymbol{\varepsilon}_{\lambda'}'^* \times \boldsymbol{\varepsilon}_\lambda)\cdot \boldsymbol{m}_{ns}C_{1s} + \left[(\boldsymbol{\varepsilon}_{\lambda'}'^* \cdot \boldsymbol{m}_{ns})(\boldsymbol{\varepsilon}_\lambda \cdot \boldsymbol{m}_{ns}) - \frac{1}{3}m_{ns}^2 \boldsymbol{\varepsilon}_{\lambda'}'^* \cdot \boldsymbol{\varepsilon}_\lambda\right] C_{2s}\Big), \tag{10}$$

where C_{0s}, C_{1s}, and C_{2s} are constants (with energy denominators of the form $(\omega - \omega_0 - i\frac{\Gamma}{2\hbar})^{-1}$). Since the magnetic and chemical structures differ we have labeled $\boldsymbol{m}_{ns}$ as depending on $\boldsymbol{n}$ *and* s. Eq. (10) shows that there is a more complex polarization dependence than the simple $\boldsymbol{\varepsilon}_{\lambda'}'^* \cdot \boldsymbol{\varepsilon}_\lambda$ of non-resonant charge scattering. The polarization dependence of the last term in parentheses is similar to that for Templeton scattering [10]. This term is of particular importance in antiferromagnets when considering magneto-optic phenomena on transmission. From equation (A10) the index of refraction depends on the forward scattering amplitude, for which $\boldsymbol{K} = 0$. From (A6) the non-resonant magnetic scattering amplitude vanishes when $\boldsymbol{k} = \boldsymbol{k}'$, so only the resonant term can contribute to these effects. Since for an antiferromagnet $\sum_{ns} \boldsymbol{m}_{ns} = 0$, the only contribution to the index of refraction must come from the terms quadratic in $\boldsymbol{m}_{ns}$, i.e. the terms proportional to C_{2s} in (10). These terms will be non-zero for a simple uniaxial antiferromagnet, but may vanish for more complex magnetic structures. These terms also determine the Cotton-Mouton effect in ferromagnets.

The term linear in $\boldsymbol{m}$ is a purely magnetic phenomenon. Indeed, the antisymmetric part of $C^{\alpha\beta}$ will vanish if time reversal is conserved, so that a magnetic field must be present, a broken magnetic symmetry with magnetic ordering must occur, or a time reversal non-invariant term must be present in the system Hamiltonian. (The latter effects are of fundamental interest, but we will not consider them here.) To see this we introduce the notation $|\bar{a}\rangle$ for the time reversed $|a\rangle$. If, for example, $|a\rangle$ is labeled by a magnetic quantum number m, then $|\bar{a}\rangle = |-m\rangle$. The sum over c and a in eq. (7) can then equally well be taken over $\bar{c}$ and $\bar{a}$. Hence

$$C^{\alpha\beta} = \frac{1}{2}\sum_{ac}\left\{p_a \frac{\langle a|R^\alpha|c\rangle\langle c|R^\beta|a\rangle}{\omega - \omega_{ca} - i\frac{\Gamma}{2\hbar}} + p_{\bar{a}} \frac{\langle \bar{a}|R^\alpha|\bar{c}\rangle\langle \bar{c}|R^\beta|\bar{a}\rangle}{\omega - \omega_{\bar{c}\bar{a}} - i\frac{\Gamma}{2\hbar}}\right\} \tag{11}$$

Further, $\langle\bar{a}|R^\alpha|\bar{c}\rangle = \langle c|R^\alpha|a\rangle$, so

$$C^{\alpha\beta} = \frac{1}{2}\sum_{ac}\left\{p_a \frac{\langle a|R^\alpha|c\rangle\langle c|R^\beta|a\rangle}{\omega - \omega_{ca} - i\frac{\Gamma}{2\hbar}} + p_{\bar{a}} \frac{\langle a|R^\beta|c\rangle\langle c|R^\alpha|a\rangle}{\omega - \omega_{\bar{c}\bar{a}} - i\frac{\Gamma}{2\hbar}}\right\} \tag{12}$$

Writing $p'_a = \dfrac{p_a}{\omega - \omega_{ca} - i\frac{\Gamma}{2\hbar}} \quad ; \quad p'_{\bar{a}} = \dfrac{p_{\bar{a}}}{\omega - \omega_{\bar{c}\bar{a}} - i\frac{\Gamma}{2\hbar}}$,

$$\begin{aligned} C^{\alpha\beta} =& \frac{1}{4}\sum_{ac}\Big\{(p'_a + p'_{\bar{a}})(\langle a|R^\alpha|c\rangle\langle c|R^\beta|a\rangle + \langle a|R^\beta|c\rangle\langle c|R^\alpha|a\rangle) \\ &+(p'_a - p'_{\bar{a}})(\langle a|R^\alpha|c\rangle\langle c|R^\beta|a\rangle - \langle a|R^\beta|c\rangle\langle c|R^\alpha|a\rangle)\Big\}, \end{aligned}$$

and

$$C_-^{\alpha\beta} = \frac{1}{4}\sum_{ac}(p'_a - p'_{\bar{a}})(\langle a|R^\alpha|c\rangle\langle c|R^\beta|a\rangle - \langle a|R^\beta|c\rangle\langle c|R^\alpha|a\rangle) \tag{13}$$

This shows that $C_-^{\alpha\beta} = 0$ unless $p'_a \neq p'_{\bar{a}}$. This will be the case if $p_a \neq p_{\bar{a}}$ (magnetic ordering) or if $\omega_{ac} \neq \omega_{\bar{a}\bar{c}}$ (magnetic field present - Zeeman splitting) or both.

The largest effect occurs when the excited state $|c\rangle$ consists of a core hole together with an additional electron in the valence shell. The sensitivity to the magnetic properties occurs because of the magnetic order of the partially filled shell. The Pauli principle then permits transitions only to unoccupied electronic states, which are orbitals with specific magnetic quantum numbers. To see this most easily consider an atom with one hole in the outer shell (e.g. $Yb^{3+} : (4f)^{13}$). If the atom is magnetically ordered only the state $m_\ell = -\ell$, $m_s = -\frac{1}{2}$ is unoccupied. The excited state will involve an electron filling that hole and leaving a single hole of the same spin $(-\frac{1}{2})$, with $m_\ell = -\ell + 1$ (for the dipole term). This gives a transition that is dependent on the magnetic properties of the atom, even though the transition is electric dipole in character. Because of the role of the Pauli principle this effect was called x-ray resonant exchange scattering in the first theoretical treatment by Hannon, Trammell, Blume, and Gibbs [11]. From the point of view taken here this appears as a subset of anomalous dispersion phenomena (i.e. the antisymmetric part of the tensor).

Further consideration of the size of the effect leads to consideration of the radial integral for the matrix element:

$$\langle a|R^\alpha|c\rangle \propto \int_0^\infty r^2 dr R_{n\ell}(r) r R_{n'\ell'}(r),$$

where $R_{n\ell}(r)$ is the radial wave function for the core electron and $R_{n'\ell'}$ that for the valence electron. This integral will be largest when the overlap of the two functions is large. Since the lowest energy electrons like $1s$ are concentrated around the origin and the valence electron's wave functions are practically zero there the transitions are likely to be weak. We can conclude that transitions in the actinides from the $3d$ levels to the $5f$ shell (the M_{III} and M_{IV} transitions) will have the largest matrix elements and hence the largest effect. Experiments by McWhan *et al* [12] on UAs show a spectacular effect, with an increase of six orders of magnitude in the intensity of the antiferromagnetic Bragg peak as the photon energy passes through the M_{IV} ($3d_{3/2} \rightarrow 5f$) resonance. Figure 2 shows the experimental data. At the peak of the resonance the magnetic scattering intensity is 1% of the charge scattering intensity (i.e. $\sim$ 9 electrons)! The detailed calculation of the resonance matrix elements is best done by using the techniques of j-symbols and the spherical representation of the dipole (or quadrupole) operators. This is done in ref. [11]. The results obtained there are identical to those that would result from the Cartesian representation of the dipole operators given here.

In eq. (9) we considered the form of $C^{\alpha\beta}$ when the only vector in the problem is the magnetic moment $\boldsymbol{m}$ of the atom. We now consider the case of an atom without a magnetic moment in a uniaxial environment. If $\hat{z}_s$ is a unit vector in the direction of that axis for the s^{th} atom in the unit cell,

$$C^{\alpha\beta}_{+s} \propto \hat{z}^{\alpha}_s \hat{z}^{\beta}_s - \frac{1}{3}\delta^{\alpha\beta},$$

which is just the form for Templeton scattering [10].

Since there is no magnetic ordering $C^{\alpha\beta}_{-s} = 0$. The form of A^{dd}_{res} is then

$$A^{dd}_{res} = -\frac{e^2}{mc^2}\frac{m\omega_0^3}{\hbar\omega}\sum_{ns} e^{i\boldsymbol{K}\cdot(\boldsymbol{n}+\boldsymbol{d}_s)-W_s}\Big\{\Big(\boldsymbol{\varepsilon}'^{*}_{\lambda'}\cdot\boldsymbol{\varepsilon}_{\lambda}C_{0s}\Big) + C_{2s}\Big((\boldsymbol{\varepsilon}'^{*}_{\lambda'}\cdot\hat{z}_s)(\boldsymbol{\varepsilon}_{\lambda}\cdot\hat{z}_s) - \frac{1}{3}\boldsymbol{\varepsilon}'^{*}_{\lambda'}\cdot\boldsymbol{\varepsilon}_{\lambda}\Big)\Big\}. \quad (14)$$

In both equations (10) and (14) the anisotropic terms provide the possibility of the change of polarization on scattering, of the observation of magnetic Bragg peaks, and for the explanation of Bragg peaks forbidden by the space group symmetry of the crystal. The latter possibility follows because A^{dd}_{res} depends on the direction of the scattering vector as well as on the orientation of the dyadic $\hat{z}^{\alpha}_s\hat{z}^{\beta}_s$. The two together will not necessarily have the full symmetry of the space group.

It is also of interest to consider the possible forms for $C^{\alpha\beta}$ when a magnetic moment and a crystalline field are present. These are

$$\begin{aligned} C^{\alpha\beta}_{+} &\propto (\hat{z}^{\alpha}\hat{z}^{\beta} - \frac{1}{3}\delta^{\alpha\beta})(a_1 + b_1(\hat{z}\cdot\boldsymbol{m})^2) \\ &+ c_1(m^{\alpha}m^{\beta} - \frac{1}{3}m^2\delta^{\alpha\beta}) \\ &+ d_1(\hat{z}^{\alpha}m^{\beta} + \hat{z}^{\beta}m^{\alpha} - \frac{2}{3}(\hat{z}\cdot\boldsymbol{m})\delta^{\alpha\beta})(\hat{z}\cdot\boldsymbol{m}) \\ C^{\alpha\beta}_{-} &= i\varepsilon^{\alpha\beta\gamma}(a_2 m^{\gamma} + b_2\hat{z}^{\gamma}(\hat{z}\cdot\boldsymbol{m})). \end{aligned} \quad (15)$$

(The constants a_i and b_i have resonant denominators.) As the symmetry of the surroundings are lowered increasingly complex polarization phenomena occur.

QUADRUPOLE TRANSITIONS

We now turn to the quadrupole terms in eq. (5). We have

$$A^{qq}_{res} = -\frac{e^2}{mc^2} \cdot \varepsilon'^{\alpha *}_{\lambda'} \varepsilon^{\beta}_{\lambda} \frac{1}{4} m \frac{\omega_0^3}{\hbar\omega} \sum_{ns} e^{i\mathbf{K}\cdot(\mathbf{n}+\mathbf{d}_s)-W_s} D_s^{\alpha\gamma,\beta\delta} k'^{\gamma} k^{\delta},$$

with

$$D^{\alpha\gamma,\beta\delta} = \sum_a p_a \frac{\langle a|Q^{\alpha\gamma}_{\mathbf{n}s}|c\rangle\langle c|Q^{\beta\delta}_{\mathbf{n}s}|a\rangle}{\omega - \omega_{ca} - i\frac{\Gamma}{2\hbar}}. \tag{16}$$

There are many terms possible even in the simplest cases. We follow the reasoning used in the dipole transitions. The fourth rank tensor $D^{\alpha\gamma,\beta\delta}$ has the following symmetries:

$$D^{\alpha\gamma,\beta\delta} = D^{\gamma\alpha,\beta\delta} = D^{\alpha\gamma,\delta\beta}.$$

We define $D^{\alpha\gamma,\beta\delta} = D_+^{\alpha\gamma,\beta\delta} + D_-^{\alpha\gamma,\beta\delta}$, with $D_\pm^{\alpha\gamma,\beta\delta} = \pm D^{\beta\delta,\alpha\gamma}$. Using the same reasoning that led to eq. (13),

$$D_\pm^{\alpha\gamma,\beta\delta} = \frac{1}{4}\sum_a (p'_a \pm p'_{\bar{a}})\Big(\langle a|Q^{\alpha\gamma}|c\rangle\langle c|Q^{\beta\delta}|a\rangle \pm \langle a|Q^{\beta\delta}|c\rangle\langle c|Q^{\alpha\gamma}|a\rangle\Big). \tag{17}$$

From this we see that $D_-^{\alpha\gamma,\beta\delta}$ will vanish if time reversal is conserved. We first consider the case where the atom has a magnetic moment. The tensors must be constructed from $\delta^{\alpha\beta}$, $\varepsilon^{\alpha\beta\gamma}$, and m^{γ}. The possible forms are

$$\begin{aligned} D_-^{\alpha\gamma,\beta\delta} = {} & a_1\Big\{\varepsilon^{\alpha\beta\sigma}m^{\sigma}\delta^{\gamma\delta} + \varepsilon^{\gamma\delta\sigma}m^{\sigma}\delta^{\alpha\beta} \\ & + \varepsilon^{\alpha\delta\sigma}m^{\sigma}\delta^{\gamma\beta} + \varepsilon^{\gamma\beta\sigma}m^{\sigma}\delta^{\alpha\delta}\Big\} \\ & + b_2\Big\{\varepsilon^{\alpha\beta\gamma}m^{\sigma}m^{\gamma}m^{\delta} + \varepsilon^{\gamma\beta\sigma}m^{\sigma}m^{\alpha}m^{\beta} \\ & + \varepsilon^{\alpha\delta\sigma}m^{\sigma}m^{\gamma}m^{\beta} + \varepsilon^{\gamma\beta\sigma}m^{\sigma}m^{\alpha}m^{\delta}\Big\}, \end{aligned}$$

$$\begin{aligned} D_+^{\alpha\gamma,\beta\delta} = {} & a_2\delta^{\alpha\gamma}\delta^{\beta\delta} + b_2\Big\{\delta^{\alpha\beta}\delta^{\gamma\delta} + \delta^{\alpha\delta}\delta^{\beta\gamma}\Big\} \\ & + c_2\Big\{\delta^{\alpha\beta}m^{\gamma}m^{\delta} + \delta^{\alpha\delta}m^{\gamma}m^{\beta} + m^{\alpha}m^{\beta}\delta^{\gamma\delta} \\ & + m^{\alpha}m^{\delta}\delta^{\gamma\beta}\Big\} + d_2\Big\{m^{\alpha}m^{\gamma}\delta^{\beta\delta} + \delta^{\alpha\gamma}m^{\beta}m^{\delta}\Big\} \\ & + e_2 m^{\alpha}m^{\beta}m^{\gamma}m^{\delta} + f_2\Big\{\varepsilon^{\alpha\beta\sigma}\varepsilon^{\gamma\delta\sigma'}m^{\sigma}m^{\sigma'} \\ & + \varepsilon^{\alpha\delta\sigma}\varepsilon^{\gamma\beta\sigma'}m^{\sigma}m^{\sigma'}\Big\}. \end{aligned} \tag{18}$$

For the case where the magnetic moment is zero but the atom is in a uniaxial crystalline field along the direction $\hat{z}_s$, $D_- = 0$ and the D_+ terms are obtained by substituting $\hat{z}$ for $\boldsymbol{m}$. Writing out the terms in full we find

$$
\begin{aligned}
&\varepsilon'^{\alpha *}_{\lambda'} \varepsilon^{\beta}_{\lambda} D_-^{\alpha\gamma,\beta\delta} k'^{\gamma} k^{\delta} \\
&\quad = a_1 \Big\{ (\boldsymbol{\varepsilon}'^{*}_{\lambda'} \times \boldsymbol{\varepsilon}_{\lambda}) \cdot \boldsymbol{m} (\boldsymbol{k}' \cdot \boldsymbol{k}) + (\boldsymbol{k}' \times \boldsymbol{k}) \cdot \boldsymbol{m} (\boldsymbol{\varepsilon}'^{*}_{\lambda'} \cdot \boldsymbol{\varepsilon}_{\lambda}) \\
&\qquad + (\boldsymbol{\varepsilon}'^{*}_{\lambda'} \times \boldsymbol{k}) \cdot \boldsymbol{m} (\boldsymbol{k}' \cdot \boldsymbol{\varepsilon}_{\lambda}) + (\boldsymbol{k}' \times \boldsymbol{\varepsilon}_{\lambda}) \cdot \boldsymbol{m} (\boldsymbol{k} \cdot \boldsymbol{\varepsilon}'^{*}_{\lambda'}) \Big\} \\
&\quad + b_1 \Big\{ (\boldsymbol{\varepsilon}'^{*}_{\lambda'} \times \boldsymbol{\varepsilon}_{\lambda}) \cdot \boldsymbol{m} (\boldsymbol{k}' \cdot \boldsymbol{m})(\boldsymbol{k} \cdot \boldsymbol{m}) + (\boldsymbol{k}' \times \boldsymbol{k}) \cdot \boldsymbol{m} (\boldsymbol{\varepsilon}'^{*}_{\lambda'} \cdot \boldsymbol{m})(\boldsymbol{\varepsilon}_{\lambda} \cdot \boldsymbol{m}) \\
&\qquad + (\boldsymbol{\varepsilon}'^{*}_{\lambda'} \times \boldsymbol{k}) \cdot \boldsymbol{m} (\boldsymbol{k}' \cdot \boldsymbol{m})(\boldsymbol{\varepsilon}_{\lambda} \cdot \boldsymbol{m}) + (\boldsymbol{k} \times \boldsymbol{\varepsilon}_{\lambda}) \cdot \boldsymbol{m} (\boldsymbol{\varepsilon}'^{*}_{\lambda'} \cdot \boldsymbol{m})(\boldsymbol{k} \cdot \boldsymbol{m}) \Big\},
\end{aligned}
$$

and

$$
\begin{aligned}
&\varepsilon^{\alpha'*}_{\lambda'} \varepsilon^{\beta}_{\lambda} D_+^{\alpha\gamma,\beta\delta} k'^{\gamma} k^{\delta} \\
&\quad = b_2 \Big\{ (\boldsymbol{\varepsilon}'^{*}_{\lambda'} \cdot \boldsymbol{\varepsilon}_{\lambda})(\boldsymbol{k}' \cdot \boldsymbol{k}) + (\boldsymbol{\varepsilon}'^{*}_{\lambda'} \cdot \boldsymbol{k})(\boldsymbol{\varepsilon}_{\lambda} \cdot \boldsymbol{k}') \Big\} \\
&\quad + c_2 \Big\{ (\boldsymbol{\varepsilon}'^{*}_{\lambda'} \cdot \boldsymbol{\varepsilon}_{\lambda})(\boldsymbol{k}' \cdot \boldsymbol{m})(\boldsymbol{k} \cdot \boldsymbol{m}) + (\boldsymbol{\varepsilon}'^{*}_{\lambda'} \cdot \boldsymbol{k})(\boldsymbol{k}' \cdot \boldsymbol{m})(\boldsymbol{\varepsilon}_{\lambda} \cdot \boldsymbol{m}) \\
&\qquad + (\boldsymbol{\varepsilon}'^{*}_{\lambda'} \cdot \boldsymbol{m})(\boldsymbol{\varepsilon}_{\lambda} \cdot \boldsymbol{m})(\boldsymbol{k}' \cdot \boldsymbol{k}) + (\boldsymbol{\varepsilon}_{\lambda} \cdot \boldsymbol{k}')(\boldsymbol{\varepsilon}'^{*}_{\lambda'} \cdot \boldsymbol{m})(\boldsymbol{k} \cdot \boldsymbol{m}) \Big\} \\
&\quad + e_2 \Big\{ (\boldsymbol{\varepsilon}'^{*}_{\lambda'} \cdot \boldsymbol{m})(\boldsymbol{\varepsilon}_{\lambda} \cdot \boldsymbol{m})(\boldsymbol{k}' \cdot \boldsymbol{m})(\boldsymbol{k} \cdot \boldsymbol{m}) \Big\} \\
&\quad + f_2 \Big\{ ((\boldsymbol{\varepsilon}'^{*}_{\lambda'} \times \boldsymbol{\varepsilon}_{\lambda}) \cdot \boldsymbol{m})((\boldsymbol{k}' \times \boldsymbol{k}) \cdot \boldsymbol{m}) + ((\boldsymbol{\varepsilon}'^{*}_{\lambda'} \times \boldsymbol{k}) \cdot \boldsymbol{m})((\boldsymbol{k}' \times \boldsymbol{\varepsilon}_{\lambda}) \cdot \boldsymbol{m}) \Big\}.
\end{aligned} \tag{19}
$$

The a_2 and d_2 terms vanish because of the orthogonality of $\boldsymbol{\varepsilon}'$ and $\boldsymbol{k}'$ as well as that of $\boldsymbol{\varepsilon}$ and $\boldsymbol{k}$.

The linear and cubic terms in D_- give rise to antiferromagnetic Bragg peaks and to satellites of those peaks. The quadratic and quartic terms give second, fourth, and zeroth harmonics of those peaks. For the case of non-magnetic anisotropy the quadrupolar equivalent of Templeton scattering occurs. This can also lead to the appearance of Bragg peaks that are forbidden by the space group symmetry [13].

DIPOLE-QUADRUPOLE CROSS TERMS

Finally, we consider the dipole-quadrupole cross terms. These vanish, as mentioned above, unless the ion is not in a center of symmetry. While they can give rise to magnetic effects, their principal importance arises because they produce optical activity, (non magnetic) circular dichroism, and, in the case of scattering, circularly polarized radiation. From eq. (5),

$$
\begin{aligned}
A^{dq}_{res} &= -\frac{e^2}{mc^2} \sum_{\boldsymbol{n}s} e^{i\boldsymbol{K}\cdot(\boldsymbol{n}+\boldsymbol{d}_s) - W_s} \varepsilon'^{\alpha *}_{\lambda'} \varepsilon^{\beta}_{\lambda} \\
&\quad \times \frac{1}{2} i \frac{m\omega_0^3}{\hbar\omega} \sum_{ac} p'_a \Big\{ \langle a|R^{\alpha}|c\rangle \langle c|Q^{\beta\gamma}|a\rangle k^{\gamma} \\
&\qquad - \langle a|Q^{\alpha\gamma}|c\rangle \langle c|R^{\beta}|a\rangle k'^{\gamma} \Big\},
\end{aligned} \tag{20}
$$

$$
\begin{aligned}
&= -\frac{e^2}{mc^2}\sum_{ns} e^{iK\cdot(n+d_s)-W_s}\varepsilon'^{\alpha *}_{\lambda'}\varepsilon^{\beta}_{\lambda} \\
&\times \frac{1}{4} i \frac{m\omega_0^3}{\hbar\omega}\sum_{ac} p'_a \Big\{ \langle a|R^\alpha|c\rangle\langle c|Q^{\beta\gamma}|a\rangle(k^\gamma - k'^\gamma) \\
&\quad + \langle a|R^\alpha|c\rangle\langle c|Q^{\beta\gamma}|a\rangle(k^\gamma + k'^\gamma) \\
&\quad + \langle a|Q^{\alpha\gamma}|c\rangle\langle c|R^{\beta}|a\rangle(k^\gamma - k'^\gamma) \\
&\quad - \langle a|Q^{\alpha\gamma}|c\rangle\langle c|R^{\beta}|a\rangle(k^\gamma + k'^\gamma) \Big\}.
\end{aligned} \tag{21}
$$

Again using the reasoning that led to eq. (13), we find

$$
\begin{aligned}
A^{dq}_{res} = -\frac{e^2}{mc^2}\sum_{ns} e^{iK\cdot(n+d_s)-W_s}\varepsilon'^{\alpha *}_{\lambda'}\varepsilon^{\beta}_{\lambda}\cdot\frac{i}{8}\frac{m\omega_0^3}{\hbar\omega}\Big\{ G^{\alpha\beta\gamma}_{++}(k^\gamma - k'^\gamma) \\
+ G^{\alpha\beta\gamma}_{--}(k^\gamma - k'^\gamma) + G^{\alpha\beta\gamma}_{-+}(k^\gamma + k'^\gamma) + G^{\alpha\beta\gamma}_{+-}(k^\gamma + k'^\gamma \Big\},
\end{aligned} \tag{22}
$$

where

$$
\begin{aligned}
G^{\alpha\beta\gamma}_{\mu\nu} &= \sum_{ac}(p'_a + \mu p'_{\bar{a}}) \\
&\times \Big\{ \langle a|R^\alpha|c\rangle\langle c|Q^{\beta\gamma}|a\rangle + \nu\langle a|Q^{\alpha\gamma}|c\rangle\langle c|R^{\beta}|a\rangle \Big\}.
\end{aligned} \tag{23}
$$

and $\mu, \nu = \pm 1$. The terms with $\mu = -1$ are not invariant under time reversal, so these are sensitive to magnetic structure. Of special interest are the terms with $\mu = +1$ (time-reversal invariant). In a non magnetic system in the forward direction ($\boldsymbol{k} = \boldsymbol{k}'$) only the term $G^{\alpha\beta\gamma}_{+-}(k^\gamma + k'^\gamma)$ is non-zero. This term is antisymmetric in α and β, and in a homogeneous system it will be proportional to $\varepsilon^{\alpha\beta\gamma}(k^\gamma + k'^\gamma)$. It is therefore responsible for optical activity and dichroism. The term with $\mu = +1$, $\nu = +1$ is proportional to the scattering vector $\boldsymbol{K}$, and is symmetric in α and β. Both $G^{\alpha\beta\gamma}_{++}$ and $G^{\alpha\beta\gamma}_{+-}$ give rise to polarization dependences of scattering involving circular polarization, and they have been reported at this conference in the paper by Templeton.

FORM FACTORS

In order to make contact with the usual notation for form factors we write equation (3) as

$$
A = -\frac{e^2}{mc^2}\varepsilon'^{\alpha *}_{\lambda'}\varepsilon^{\beta}_{\lambda}\sum_{ns} e^{iK\cdot(n+d)-W_s}\left(f^{\alpha\beta}_{ns} - i\frac{\hbar\omega}{mc^2} f^{\alpha\beta}_{0mag,ns} \right), \tag{24}
$$

where (omitting the subscripts $\boldsymbol{ns}$ for clarity)

$$
f^{\alpha\beta} = f_0\delta^{\alpha\beta} + f'^{\alpha\beta} + i f''^{\alpha\beta} \tag{25}
$$

with

$$f_0 = \sum_a p_a \langle a| \sum_i {}^{(ns)} e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i} |a\rangle \equiv f_0(\boldsymbol{K}), \tag{26}$$

the usual charge form factor (i.e. the Fourier transform of the charge density), and

$$f_{0mag}^{\alpha\beta} = \sum_a p_a \langle a| \sum_i {}^{(ns)} e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i} \left\{ -\frac{i(\boldsymbol{K}\times\boldsymbol{p}_i)^\gamma}{\hbar K^2} A^{\alpha\beta\gamma} + \boldsymbol{s}_i^\gamma B^{\alpha\beta\gamma} \right\} |a\rangle \tag{27}$$

the non-resonant magnetic form factor. From eqs. (4) and (5) we see that the "anomalous" form factors $f'^{\alpha\beta} + if''^{\alpha\beta}$ are given by

$$f'^{\alpha\beta} + if''^{\alpha\beta} = m \sum_{ac} p_a \frac{\omega_{ca}^3}{\hbar\omega} \frac{\langle a|(R_{\boldsymbol{n}s}^\alpha - \frac{1}{2}iQ_{\boldsymbol{n}s}^{\alpha\gamma}k'^\gamma)|c\rangle\langle c|(R_{\boldsymbol{n}s}^\beta + \frac{1}{2}iQ_{\boldsymbol{n}s}^{\beta\gamma}k^\gamma)|a\rangle}{\omega - \omega_{ca} - i\frac{\Gamma}{2\hbar}}. \tag{28}$$

Using equations (6), (7), (16), (22), and (23) we find

$$f'^{\alpha\beta} + if''^{\alpha\beta} = \frac{m\omega_0^3}{\hbar\omega} \Big\{ C^{\alpha\beta} + \frac{1}{4} D^{\alpha\gamma,\beta\delta} k'^\gamma k^\delta + \frac{1}{8} i \sum_{\mu\nu} G_{\mu\nu}^{\alpha\beta\gamma}(k^\gamma - \mu\nu k'^\gamma) \Big\}. \tag{29}$$

The anomalous terms contain both magnetic and non magnetic contributions. We see from this form that these terms have only a weak angular dependence. The Debye-Waller factor gives some contribution to such a dependence, but the tensors $\boldsymbol{C}$, $\boldsymbol{D}$, and $\boldsymbol{G}$ are essentially independent of angle. Further contributions come from the polarization factors and from the presence of $\boldsymbol{k}'$ and $\boldsymbol{k}$ in the quadrupole-quadrupole and dipole-quadrupole cross terms. Since the dipole-dipole terms are usually largest we have most commonly

$$f'^{\alpha\beta} + if''^{\alpha\beta} \approx \frac{m\omega_0^3}{\hbar\omega} C^{\alpha\beta},$$

and angular dependence arises from the directional dependence of C together with the polarization factor $\varepsilon_{\lambda'}'^{\alpha *} \varepsilon_\lambda^\beta$. In the usual treatment of anomalous dispersion (before the Templetons' work [10]) only the trace of these tensors was considered.

CONCLUSIONS

The magnetic effects in anomalous dispersion are potentially quite large. They are intimately related to the usual charge dispersive effects. The electric dipole and quadrupole interactions and their cross terms, together with symmetry arguments, give excellent explanations for the polarization dependence of scattering, as well as for forbidden reflections, dichroism, Faraday effect, magnetic scattering, optical activity, etc. We have shown here only the simplest applications of symmetry: time reversal (which distinguishes magnetic and non-magnetic effects), parity (which shows how optical activity arises) and local uniaxial symmetry. More detailed group theoretical analysis can yield explicit forms for the tensors C, D and G.

It is clear from the theory that anomalous dispersion effects are strongly dependent on the resonance structure of the ions in the solid, and, especially near those resonances, are sensitive to the local environment and bonding configuration. This might be considered an annoyance by crystallographers, who would like to have a simple tabulation of anomalous dispersion "corrections" that is broadly usable in experiments. This is unfortunately, from that point of view, not the case. On the other hand, such sensitivity enables experiments which can give otherwise unobtainable information about magnetic and electronic structures. Much work remains to be done, both experimentally and theoretically. The equations are old, but, because of the synchrotron radiation revolution in x-ray sources, the ideas and experiments are new.

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APPENDIX

In reference [4], the interaction between photons and electrons is shown to be

$$\mathcal{H}' = \frac{e^2}{2mc^2}\sum_i \boldsymbol{A}^2(\boldsymbol{r}_i) - \frac{e}{mc}\sum_i \boldsymbol{p}_i \cdot \boldsymbol{A}(\boldsymbol{r}_i)$$
$$-\frac{e\hbar}{mc}\sum_i \boldsymbol{s}_i \quad \nabla \times \boldsymbol{A}(\boldsymbol{r}_i) - \frac{e^2\hbar}{2(mc^2)^2}\sum_i \boldsymbol{s}_i \cdot \left(\dot{\boldsymbol{A}}\,(\boldsymbol{r}_i) \times \boldsymbol{A}(\boldsymbol{r}_i)\right), \qquad \text{(A1)}$$

where $\boldsymbol{A}(\boldsymbol{r}_i)$ is the vector potential of the electromagnetic field at the position $\boldsymbol{r}_i$ of the i^{th} electron. The first two terms are familiar, while the second two represent smaller magnetic terms. Since $\boldsymbol{A}$ is linear in photon creation and annihilation operators, scattering is produced in first-order perturbation theory by terms quadratic in $\boldsymbol{A}$ such as the first and fourth terms in (A1) — (since scattering involves "destruction" of the incident photon and "creation" of the scattered photons). Terms linear in $\boldsymbol{A}$, such as the second and third terms in (A1) give scattering in second order perturbation theory. Using Fermi's golden rule to calculate the matrix elements [4] then yields the coherent scattering amplitude

$$A = -\frac{e^2}{mc^2}\varepsilon_{\lambda'}^{\prime\alpha *}\varepsilon_{\lambda}^{\beta}\sum_a p_a\Bigg\{\langle a|\sum_i e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i}|a\rangle\delta^{\alpha\beta} - i\varepsilon^{\alpha\beta\gamma}\frac{\hbar\omega}{mc^2}\langle a|\sum_i \boldsymbol{s}_i^{\gamma}e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i}|a\rangle$$
$$+\frac{1}{m}\sum_c\left\{\frac{\langle a|O^{\alpha^\dagger}(\boldsymbol{k}')|c\rangle\langle c|O^{\beta}(\boldsymbol{k})|a\rangle}{E_a - E_c + \hbar\omega - i\frac{\Gamma}{2}} + \frac{\langle a|O^{\beta}(\boldsymbol{k})|c\rangle\langle c|O^{\alpha^\dagger}(\boldsymbol{k}')|a\rangle}{E_a - E_c - \hbar\omega}.\right\}\Bigg\} \qquad \text{(A2)}$$

Here $\varepsilon_{\lambda'}^{\prime\alpha}$ and $\varepsilon_{\lambda}^{\beta}$ are, respectively the polarization vectors for the scattered and incident photons, where λ and λ' label two orthogonal polarization basis vectors (e.g. left and right circular, or linear polarization parallel and perpendicular to the scattering plane).

$\varepsilon^{\alpha\beta\gamma}$ is the antisymmetric tensor of third rank; α, β, and γ vary over the cartesian indices x, y, z; p_a is the probability that the incident state of the scatterer $|a\rangle$ is occupied (given by $p_a = e^{-E_a/kT}/Z$, Z the partition function, for a system in thermal equilibrium) and $\boldsymbol{K} = \boldsymbol{k} - \boldsymbol{k}'$ is the scattering vector ($|\boldsymbol{K}| = 4\pi \sin\theta/\lambda$, where 2θ is the scattering angle). The operator $O^\beta(\boldsymbol{k})$ is given by

$$O^\beta(\boldsymbol{k}) = \sum_i e^{i\boldsymbol{k}\cdot\boldsymbol{r}_i}(p_i^\beta - i\hbar(\boldsymbol{k}\times\boldsymbol{s}_i)^\beta), \tag{A3}$$

and Γ is the inverse lifetime of the intermediate state $|c\rangle$. (We have considered only the coherent amplitude, where the final state of the scattering system $|a\rangle$ is the same as the initial state. Inelastic or incoherent scattering is accounted for by allowing the final state $|b\rangle$ to be different from the initial state $|a\rangle$ of the scatterer, and for the frequency ω' of the scattered photon to be different from that of the incident photon ω.)

Considering the last two terms in (A2), we note that for photons with energy $\hbar\omega \gg E_c - E_a$ the summation over $|c\rangle$ can be carried out by closure, and the last two terms will reduce to

$$\frac{1}{\hbar\omega}\langle a|[O^{\alpha^\dagger}(\boldsymbol{k}'), O^\beta(\boldsymbol{k})]|a\rangle. \tag{A4}$$

This commutator, as shown in reference [4], gives, together with the second term in (A2), the nonresonant magnetic scattering amplitude [1–5]. We obtain these terms by writing

$$\begin{aligned}\frac{1}{E_a - E_c + \hbar\omega - i\frac{\Gamma}{2}} &= \left(\frac{1}{E_a - E_c + \hbar\omega - i\frac{\Gamma}{2}} - \frac{1}{\hbar\omega}\right) + \frac{1}{\hbar\omega}\\ &\approx -\frac{E_a - E_c}{\hbar\omega}\cdot\frac{1}{E_a - E_c + \hbar\omega - i\frac{\Gamma}{2}} + \frac{1}{\hbar\omega},\end{aligned}$$

and

$$\begin{aligned}\frac{1}{E_a - E_c - \hbar\omega} &= \left(\frac{1}{E_a - E_c - \hbar\omega} + \frac{1}{\hbar\omega}\right) - \frac{1}{\hbar\omega}\\ &= +\frac{E_a - E_c}{\hbar\omega}\,\frac{1}{E_a - E_c - \hbar\omega} - \frac{1}{\hbar\omega}.\end{aligned}$$

(We have neglected $i\frac{\Gamma}{2}$ in the numerator, as it is negligible compared to $E_c - E_a$.) Substituting in (A2) we obtain the commutator in (A4) and the terms with energy denominators multiplied by factors $\frac{E_c - E_a}{\hbar\omega}$. Eq. (A2) becomes

$$A = -\frac{e^2}{mc^2}\varepsilon'^{\alpha*}_{\lambda'}\varepsilon^{\beta}_{\lambda}\sum_a p_a\left\{\langle a|\sum_i e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i}|a\rangle\delta^{\alpha\beta}\right.$$
$$-i\frac{\hbar\omega}{mc^2}\langle a|\sum_i e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i}\left(-i\frac{(\boldsymbol{K}\times\boldsymbol{p}_i)^\gamma}{\hbar\boldsymbol{K}^2}A^{\alpha\beta\gamma}+\boldsymbol{s}_i^\gamma B^{\alpha\beta\gamma}\right)|a\rangle$$
$$-\frac{1}{m}\sum_c\left(\frac{E_a-E_c}{\hbar\omega}\right)\frac{\langle a|O^{\alpha^\dagger}(\boldsymbol{k}')|c\rangle\langle c|O^\beta(\boldsymbol{k})|a\rangle}{E_a-E_c+\hbar\omega-i\frac{\Gamma}{2}}$$
$$\left.+\frac{1}{m}\sum_c\left(\frac{E_a-E_c}{\hbar\omega}\right)\frac{\langle a|O^\beta(\boldsymbol{k})|c\rangle\langle c|O^{\alpha^\dagger}(\boldsymbol{k}')|a\rangle}{E_a-E_c-\hbar\omega}\right\}. \qquad \text{(A5)}$$

The commutator has been combined, as mentioned above, to give the second term in (A5), the non-resonant magnetic scattering amplitude. The polarization factors $A^{\alpha\beta\gamma}$ and $B^{\alpha\beta\gamma}$ are obtained from straightforward algebra. They are

$$A^{\alpha\beta\gamma} = -2(1-\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{k}}')\varepsilon^{\alpha\beta\gamma},$$
$$B^{\alpha\beta\gamma} = \varepsilon^{\alpha\beta\gamma} - \varepsilon^{\alpha\delta\gamma}\hat{k}'^{\delta}\hat{k}'^{\beta} + \varepsilon^{\beta\delta\gamma}\hat{k}^{\delta}\hat{k}^{\alpha}$$
$$-\frac{1}{2}\varepsilon^{\alpha\beta\delta}(\hat{k}'^{\delta}\hat{k}^{\gamma}+\hat{k}^{\delta}\hat{k}'^{\gamma}) + \frac{1}{2}(\hat{\boldsymbol{k}}\times\hat{\boldsymbol{k}}')^{\alpha}\delta^{\beta\gamma}$$
$$+\frac{1}{2}(\hat{\boldsymbol{k}}\times\hat{\boldsymbol{k}}')^{\beta}\delta^{\alpha\gamma} \qquad \text{(A6)}$$

In (A6) $\hat{\boldsymbol{k}}$ and $\hat{\boldsymbol{k}}'$ are unit vectors in the direction of the incident and scattered photons, respectively. The terms multiplying $A^{\alpha\beta\gamma}$ give scattering from the orbital magnetization density of the scatterer, while $B^{\alpha\beta\gamma}$ multiplies the spin density terms. Equation (A5) is the complete expression for the scattering amplitude. The first term gives the standard charge scattering, the second the magnetic scattering, and the third and fourth terms give the resonant and non-resonant anomalous dispersion effects. The latter can be conveniently combined in a form that is useful far from resonance, but that corresponds to the neglect of the last, non-resonant term when $\hbar\omega \approx E_c - E_a$. We write

$$-\frac{1}{m}\sum_c\left(\frac{E_a-E_c}{\hbar\omega}\right)\left\{\frac{\langle a|O^{\alpha^\dagger}(\boldsymbol{k}')|c\rangle\langle c|O^\beta(\boldsymbol{k})|a\rangle}{E_a-E_c+\hbar\omega-i\frac{\Gamma}{2}}\right.$$
$$\left.-\frac{\langle a|O^\beta(\boldsymbol{k})|c\rangle\langle c|O^{\alpha^\dagger}(\boldsymbol{k}')|a\rangle}{E_a-E_c-\hbar\omega+i\frac{\Gamma}{2}}\right\}$$
$$= -\frac{1}{2m}\sum_c\left(\frac{E_a-E_c}{\hbar\omega}\right)\left\{\frac{\langle a|O^{\alpha^\dagger}(\boldsymbol{k}')|c\rangle\langle c|O^\beta(\boldsymbol{k})|a\rangle+\langle a|O^\beta(\boldsymbol{k})|c\rangle\langle c|O^{\alpha^\dagger}(\boldsymbol{k}')|a\rangle}{E_a-E_c+\hbar\omega-i\frac{\Gamma}{2}}\right.$$
$$+\frac{\langle a|O^{\alpha^\dagger}(\boldsymbol{k}')|c\rangle\langle c|O^\beta(\boldsymbol{k})|a\rangle-\langle a|O^\beta(\boldsymbol{k})|c\rangle\langle c|O^{\alpha^\dagger}(\boldsymbol{k}')|a\rangle}{E_a-E_c+\hbar\omega-i\frac{\Gamma}{2}}$$
$$+\frac{\langle a|O^{\alpha^\dagger}(\boldsymbol{k}')|c\rangle\langle c|O^\beta(\boldsymbol{k})|a\rangle-\langle a|O^\beta(\boldsymbol{k})|c\rangle\langle c|O^{\alpha^\dagger}(\boldsymbol{k}')|a\rangle}{E_a-E_c-\hbar\omega+i\frac{\Gamma}{2}}$$
$$\left.-\frac{\langle a|O^{\alpha^\dagger}(\boldsymbol{k}')|c\rangle\langle c|O^\beta(\boldsymbol{k})|a\rangle+\langle a|O^\beta(\boldsymbol{k})|c\rangle\langle c|O^{\alpha^\dagger}(\boldsymbol{k}')|a\rangle}{E_a-E_c-\hbar\omega+i\frac{\Gamma}{2}}\right\}. \qquad \text{(A7)}$$

(Note that we have restored the lifetime $i\frac{\Gamma}{2}$ of the intermediate state $|c\rangle$ in the denominator of the non-resonant term. It is negligible, but in combining the resonant and non-resonant terms it is more symmetrical to include it.) In (A7) we see that both resonant and non-resonant terms have elements symmetric and antisymmetric in α and β. This separation, as shown less generally in equation (13), gives time reversal invariant and non-invariant terms, respectively.

Since

$$\frac{1}{E_a - E_c + \hbar\omega - i\frac{\Gamma}{2}} + \frac{1}{E_a - E_c - \hbar\omega + i\frac{\Gamma}{2}} = \frac{2(E_a - E_c)}{(E_a - E_c)^2 - (\hbar\omega - i\frac{\Gamma}{2})^2}$$

and

$$\frac{1}{E_a - E_c + \hbar\omega - i\frac{\Gamma}{2}} - \frac{1}{E_a - E_c - \hbar\omega + i\frac{\Gamma}{2}} \approx \frac{-2\hbar\omega}{(E_a - E_c)^2 - (\hbar\omega - i\frac{\Gamma}{2})^2},$$

we find for the scattering amplitude

$$\begin{aligned} A = -\frac{e^2}{mc^2}\epsilon'^{\alpha *}_{\lambda'}\epsilon^{\beta}_{\lambda}\sum_a p_a \Bigg\{ &\langle a|\sum_i e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i}|a\rangle\delta^{\alpha\beta} \\ &-i\frac{\hbar\omega}{mc^2}\langle a|\sum_i e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i}\left(-i\frac{(\boldsymbol{K}\times\boldsymbol{p}_i)^{\gamma}}{\hbar K^2}A^{\alpha\beta\gamma} + \boldsymbol{s}_i^{\gamma}B^{\alpha\beta\gamma}\right)|a\rangle \\ &-\frac{1}{m}\sum_c \frac{((E_a - E_c)/\hbar\omega)}{(E_a - E_c)^2 - (\hbar\omega - i\frac{\Gamma}{2})^2} \\ &\times\Big[-\hbar\omega\left(\langle a|O^{\alpha^\dagger}(\boldsymbol{k}')|c\rangle\langle c|O^{\beta}(\boldsymbol{k})|a\rangle + \langle a|O^{\beta}(\boldsymbol{k})|c\rangle\langle c|O^{\alpha^\dagger}(\boldsymbol{k}')|a\rangle\right) \\ &+(E_a - E_c)\left(\langle a|O^{\alpha^\dagger}(\boldsymbol{k}')|c\rangle\langle c|O^{\beta}(\boldsymbol{k})|a\rangle - \langle a|O^{\beta}(\boldsymbol{k})|c\rangle\langle c|O^{\alpha^\dagger}(\boldsymbol{k}')|a\rangle\right)\Big]\Bigg\}. \end{aligned} \tag{A8}$$

When $E_a - E_c + \hbar\omega \approx 0$ the energy dependent terms reduce to the expressions in which the non-resonant parts are neglected. Equation (A8) has no additional approximations beyond those used to derive equation (A2). It is useful for our purposes since the parts antisymmetric in α and β (time reversal non invariant/magnetic) and symmetric (time reversal invariant) are explicitly separated. High and low energy limits of these terms can also be evaluated directly.

The relationship between A in eq. (A5) and the scattering cross-section is

$$\left.\frac{d\sigma}{d\Omega}\right)_{\lambda'\lambda} = |A(\boldsymbol{k}'\lambda', \boldsymbol{k}\lambda)|^2 \tag{A9}$$

where we have written explicitly the dependence of A on the properties of the incident and scattered photons. This cross-section gives the expression for the "kinematic" theory of Bragg scattering. The relationship between A and the index of refraction, which is needed for the calculation of dichroism, the Faraday effect, and other electro- and magneto-optic phenomena, is

$$n_{\lambda'\lambda} = \delta_{\lambda'\lambda} + \frac{2\pi}{k^2} \cdot \frac{1}{V} A(\boldsymbol{k}\lambda', \boldsymbol{k}\lambda), \tag{A10}$$

where V is the volume of the sample. Note that the forward scattering amplitude enters this expression. $n_{\lambda'\lambda}$ is a 2×2 matrix in this case, with real and imaginary parts which do not necessarily commute with one another. The calculation of polarization phenomena in this case is discussed in [14]. Examination of eq. (A5) shows the relationship between this 2×2 index of refraction (whose indices refer to the two polarization vectors) and the usual 3×3 matrix whose indices are the spatial ones. If we rewrite (A5) to define $\mathcal{A}(\boldsymbol{k}'\alpha, \boldsymbol{k}\beta)$, the 3×3 scattering amplitude,

$$A(\boldsymbol{k}'\lambda', \boldsymbol{k}\lambda) \equiv \varepsilon'^{\alpha^*}_{\lambda'} \varepsilon^{\beta}_{\lambda} \mathcal{A}(\boldsymbol{k}'\alpha, \boldsymbol{k}\beta), \tag{A11}$$

then

$$n^{\alpha\beta} = \delta^{\alpha\beta} + \frac{2\pi}{k^2} \frac{1}{V} \mathcal{A}(\boldsymbol{k}\alpha, \boldsymbol{k}\beta). \tag{A12}$$

is the 3×3 index of refraction. The polarization vectors $\varepsilon'^{\alpha}_{\lambda'}$ and $\varepsilon^{\beta}_{\lambda}$ serve as the transformation matrices which project the three dimensional physical space into the two dimensional space labelled by the orthogonal polarization indices λ' and λ:

$$n_{\lambda'\lambda} \equiv \varepsilon'^{\alpha^*}_{\lambda'} \varepsilon^{\beta}_{\lambda} n^{\alpha\beta}. \tag{A13}$$

The calculation of polarization phenomena is generally easier in this two dimensional space, where the Poincaré sphere representation can be used [14].

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FIGURES

Figure 1. Electronic states of the Ho^{3+} ion.

Figure 2. Experimental data showing the six order of magnitude variation in intensity of the $(0, 0, \frac{5}{2})$ magnetic Bragg pack in UAs. The solid line represents a fit to the data without the factor ω_0/ω of eq. (1). Inclusion of that factor improves the fit at high ω. From reference [12].

HOLMIUM

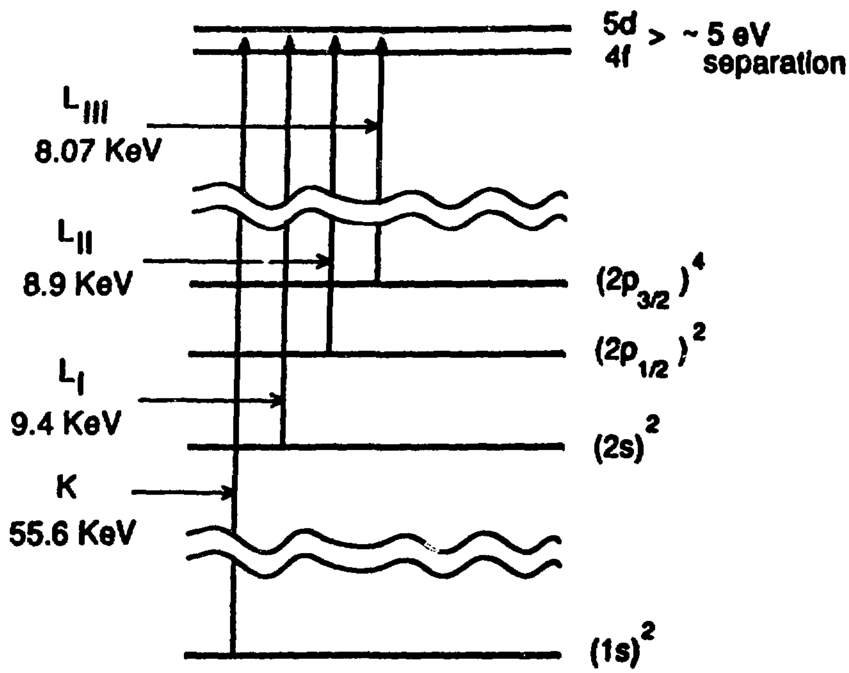
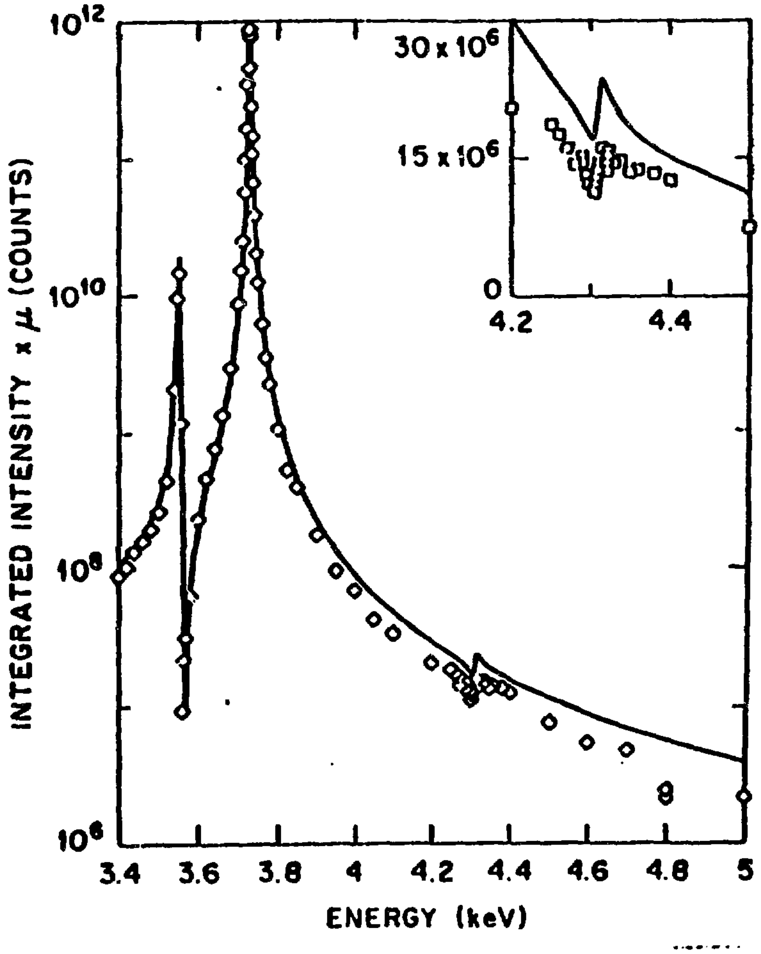


Figure 1



10^{12}
10^{10}
10^{8}
10^{6}
INTEGRATED INTENSITY x μ (COUNTS)
3.4
3.6
3.8
4
4.2
4.4
4.6
4.8
5
ENERGY (keV)
30×10^6
15×10^6
0
4.2
4.4

Figure 2