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Martin BLUME
Brookhaven National Laboratory,
Upton, New York, 11973, U.S.A.

These are preliminary lecture notes, intended only for distribution to participants.

Magnetic scattering of x rays[a)] (invited)

M. Blume
Brookhaven National Laboratory, Upton, New York 11973

The scattering of x rays is used to determine the electric charge distribution in matter. Since x rays are *electromagnetic* radiation, we should expect that they will be sensitive not only to the charge distribution, but also to the magnetization density. That this is indeed the case has been pointed out and studied experimentally. In this paper the magnetic scattering is discussed in a way which allows consideration of the effects of electron binding. The cross section, compared with that for neutron scattering from magnetically ordered materials, is reduced by $(\hbar\omega/mc^2)^2$ (about 5×10^{-4}). With a synchrotron radiation source, however, this factor can be made up, and magnetic x-ray Bragg peaks can be collected in the same time as neutron peaks. Special effects of interest include high momentum resolution, polarization phenomena which separate spin and orbital densities, and resonance effects which give a large enhancement of the x-ray cross section and which may make the study of surface magnetism possible.

I. INTRODUCTION

Neutrons have long been the probe of choice in studying the magnetic structure (static and dynamic) of condensed matter, while x rays have provided detailed information on crystal structure through interaction with the electronic charge distribution. Since x rays are part of the *electromagnetic* spectrum, however, we should expect that they will be sensitive to magnetic as well as to charge distributions. Indeed, this sensitivity has long been used in analyzing polarization effects in Compton scattering.[1] The cross section for the scattering of photons by free charges, including magnetic effects, was derived by Low[2] and by Gell-Mann and Goldberger[3] by taking the nonrelativistic limit of the Compton cross section. A similar calculation was carried out by Platzman and Tzoar,[4] who first pointed out the possibility of using these effects in the study of magnetization densities in solids in a manner comparable to that done with neutron scattering. Subsequently, de Bergevin and Brunel[5] discussed polarization phenomena and orbital magnetic scattering and carried out several experiments demonstrating the existence of the effects predicted by Platzman and Tzoar.

In this paper the cross section for x-ray scattering, including magnetic terms, is derived in a way which allows the effects of electron binding to be accounted for. By starting with the nonrelativistic Hamiltonian for electrons [to order $(v/c)^2$] and the quantized electromagnetic field, we produce a general formula for the cross section including virtually all scattering phenomena in appropriate limits (in the "kinematic" or Born approximation), including Thomson, Rayleigh, Bragg, thermal diffuse, Raman and magnetic scattering, and anomalous dispersion. In the limit of photon energy large compared to electron binding energy, we recover the Platzman–Tzoar expression. The results show new resonant magnetic scattering effects when the photon energy is comparable to the inner electron excitation or binding energies. These magnetic effects are related to anomalous dispersion phenomena, but they have a different polarization dependence and vanish in the absence of magnetic order.[6]

The cross section for magnetic x-ray scattering is smaller than that for neutron scattering (and x-ray charge scattering) by $(\hbar\omega/mc^2)^2$. It is thus difficult to observe these effects against a background of charge scattering, although interference between the two can be used to extract the magnetic cross section. Because of the high intensity of synchrotron radiation sources, it is possible to make up the factor $(\hbar\omega/mc^2)^2$ so that magnetic x-ray peaks can be collected in a time comparable to that for neutron peaks. X rays can then be used, because of the higher resolution possible for them, to study long period modulated magnetic structures and antiferromagnets in which the charge and magnetic peaks do not coincide. X rays are also useful in distinguishing orbital and spin scattering, which have different polarization dependence, unlike the neutron case.

The principal results derived are Eqs. (13) and (15), which give the cross sections necessary for calculating magnetic scattering effects. We consider here elastic scattering, but the formulas are valid for inelastic phenomena as well.

II. CROSS SECTIONS

We start with the Hamiltonian for electrons in a quantized electromagnetic field

$$\begin{aligned}\mathscr{H} = {} & \sum_j \frac{1}{2m}\left(\mathbf{P}_j - \frac{e}{c}\mathbf{A}(\mathbf{r}_j)\right)^2 \\ & + \sum_{ij} V(r_{ij}) - \frac{e\hbar}{2mc}\sum_j \mathbf{s}_j\cdot\nabla\times\mathbf{A}(\mathbf{r}_j) \\ & - \frac{e\hbar}{2(mc)^2}\sum_j \mathbf{s}_j\cdot\mathbf{E}(\mathbf{r}_j)\times\left(\mathbf{P}_j - \frac{e}{c}\mathbf{A}(\mathbf{r}_j)\right) \qquad (1) \\ & + \sum_{k\lambda}\hbar\omega_k\left(c^+(\mathbf{k}\lambda)C(\mathbf{k}\lambda) + \tfrac{1}{2}\right).\end{aligned}$$

This contains the radiation field, the electrons, and interaction terms. The vector potential $\mathbf{A}(\mathbf{r})$ is linear in photon creation and annihilation operators $c^+(\mathbf{k}\lambda)$ and $c(\mathbf{k}\lambda)$ so that scattering occurs in second order for terms linear in $\mathbf{A}$ and in first order for quadratic terms.

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In the spin-orbit term in Eq. (1),

$$\mathbf{E} = -\nabla\phi - \frac{1}{c}\dot{\mathbf{A}},$$

where ϕ is the Coulomb potential. Since the spin-orbit term is already of order $(v/c)^2$, we will omit linear terms in **A** and keep only the quadratic ones and those independent of **A**, so that

$$-\frac{e\hbar}{2(mc)^2}\sum_j \mathbf{s}_j\cdot\mathbf{E}(\mathbf{r}_j)\times\left(\mathbf{P}_j - \frac{e}{c}A(\mathbf{r}_j)\right) \tag{2}$$

$$\rightarrow -\frac{e\hbar}{2(mc)^2}\left(\sum_j \mathbf{s}_j\cdot(-\nabla\varphi_j\times\mathbf{P}_j) + \sum_j \mathbf{s}_j\frac{e}{c^2}[\dot{\mathbf{A}}(\mathbf{r}_j)\times\mathbf{A}(\mathbf{r}_j)]\right).$$

The first term is the ordinary spin-orbit coupling term for electrons, while the second gives spin dependent scattering. We can now write

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_R + \mathscr{H}', \tag{3}$$

with

$$\mathscr{H}_0 = \sum_j \frac{1}{2m}\mathbf{P}_j^2 + \sum_{ij} V(r_{ij}) + \frac{e\hbar}{2(mc)^2}\sum_j \mathbf{s}_j\cdot(\nabla\varphi_j\times\mathbf{P}_j), \tag{4}$$

$$\mathscr{H}_R = \sum_{k\lambda}\hbar\omega_k(C^+(\mathbf{k}\lambda)C(\mathbf{k}\lambda) + \tfrac{1}{2}), \tag{5}$$

$$\mathscr{H}' = \underbrace{\frac{e^2}{2mc^2}\sum_j \mathbf{A}^2(r_j)}_{\mathscr{H}'_1} \underbrace{- \frac{e}{mc}\sum_j \mathbf{A}(\mathbf{r}_j)\cdot\mathbf{P}_j}_{\mathscr{H}'_2} \underbrace{- \frac{e\hbar}{mc}\sum_j \mathbf{s}_j\cdot[\nabla\times\mathbf{A}(\mathbf{r}_j)]}_{\mathscr{H}'_3} \underbrace{- \frac{e\hbar}{2(mc)^2}\frac{e^2}{c^2}\sum_j \mathbf{s}_j\cdot[\dot{\mathbf{A}}(r_j)\times\mathbf{A}(\mathbf{r}_j)]}_{\mathscr{H}'_4} \tag{6}$$

$$\equiv \mathscr{H}'_1 + \mathscr{H}'_2 + \mathscr{H}'_3 + \mathscr{H}'_4. \tag{7}$$

$\mathscr{H}'_1$ and $\mathscr{H}'_4$ are quadratic in **A**, while $\mathscr{H}'_2$ and $\mathscr{H}'_3$ are linear. The vector potential **A** is expanded as

$$\mathbf{A}(\mathbf{r}) = \sum_{q\sigma}\left(\frac{2\pi\hbar c^2}{V\omega_q}\right)^{1/2} \times[\epsilon(\mathbf{q}\sigma)c(\mathbf{q}\sigma)e^{i\mathbf{q}\cdot\mathbf{r}} + \epsilon^*(\mathbf{q}\sigma)c^+(\mathbf{q}\sigma)e^{-i\mathbf{q}\cdot\mathbf{r}}]. \tag{8}$$

V is a quantization volume, which drops out of any physical expression. The index $\sigma(=1,2)$ labels the two polarizations of each wave **q**, and $\epsilon(\mathbf{q}\sigma)$ is the corresponding unit polarization vector. Because of the transversality of the waves,

$$q\cdot\epsilon(q\sigma) = 0.$$

Scattering cross sections are calculated by assuming that initially the solid is in a quantum state $|a\rangle$ which is an eigenstate of $\mathscr{H}_0$ with energy E_a, and that there is a single photon present. We then calculate the probability of a transition induced by $\mathscr{H}'$ to a state $|b\rangle$ with photon $\mathbf{k}'\lambda'$. The transition probability/unit time is given by the "golden rule" (to second order)

$$w = \frac{2\pi}{\hbar}\left|\langle f|\mathscr{H}'|i\rangle + \sum_n \frac{\langle f|\mathscr{H}'|n\rangle\langle n|\mathscr{H}'|i\rangle}{E_i - E_n}\right|^2 \times\delta(E_i - E_f), \tag{9}$$

$$|i\rangle\equiv|a;\mathbf{k}\lambda\rangle; \quad |f\rangle\equiv|b;\mathbf{k}'\lambda'\rangle,$$

$$E_i = E_a + \hbar\omega_k, \quad E_f = E_b + \hbar\omega_{k'}.$$

Only $\mathscr{H}'_1$ and $\mathscr{H}'_4$ contribute to the first-order term, and only $\mathscr{H}'_2$ and $\mathscr{H}'_3$ to second order.

Hence

$$w = \frac{2\pi}{\hbar}\left|\langle b;\mathbf{k}'\lambda'|\mathscr{H}'_1 + \mathscr{H}'_4|a;\mathbf{k}\lambda\rangle + \sum_n \frac{\langle b;\mathbf{k}'\lambda'|\mathscr{H}'_2 + \mathscr{H}'_3|n\rangle\langle n|\mathscr{H}'_2 + \mathscr{H}'_3|a;k\lambda\rangle}{E_a + \hbar\omega_k - E_n}\right|^2 \times\delta(E_a - E_b + \hbar\omega_k - \hbar\omega_{k'}). \tag{10}$$

Assuming $\omega_{k'}\sim\omega_k$ (i.e., that only low-lying excitations of the solid will be considered),

$$\langle b;\mathbf{k}'\lambda'|\mathscr{H}'_1 + \mathscr{H}'_4|a;\mathbf{k}\lambda\rangle = \frac{2\pi\hbar c^2}{V\omega}\frac{e^2}{mc^2} \times\left\{\left\langle b\left|\sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}\right|a\right\rangle\epsilon'\cdot\epsilon\right\} - i\frac{\hbar\omega}{mc^2}\left\langle b\left|\sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}\mathbf{s}_j\right|a\right\rangle\cdot\epsilon_1\times\epsilon\Big\}, \tag{11}$$

where $\epsilon\equiv\epsilon(\mathbf{k}\lambda)$, $\epsilon'\equiv\epsilon^*(\mathbf{k}'\lambda')$, and $\mathbf{K}=\mathbf{k}-\mathbf{k}'$

The first term gives the usual Thomson scattering expression, which depends on the Fourier transform of the electron density $\Sigma_j e^{i\mathbf{K}\cdot\mathbf{r}_j}$. The second term, which is smaller than the first by $\hbar\omega/mc^2$ ($mc^2\sim0.511$ MeV, so $\hbar\omega/mc^2\sim0.02$ for 10-keV x rays) depends on the spin density Fourier transform

$$\sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}\mathbf{s}_j.$$

In the limit of high-energy photons, the terms in $\mathscr{H}'_2$ and $\mathscr{H}'_3$ will give additional contributions of this sort, as will be seen.

In the second-order terms, the intermediate states $|n\rangle$ fall in two classes: those in which the initial photon has been annihilated first, and those in which the final photon has first been created.

Calculating the photon parts of these matrix elements and combining with Eq. (11), the cross section is obtained from the transition probability by multiplying w by the density of final states and dividing by the incident flux:

$$\frac{d^2_\sigma}{d\Omega'dE'} = W\cdot\rho(E_f)/I_0,$$

$$\rho(E_f) = \frac{V}{(2\pi)^3}\frac{\omega_{k'}^2}{\hbar c^3}, \quad I_0 = \frac{c}{V}, \tag{12}$$

so that

$$\left(\frac{d^2\sigma}{d\Omega' dE'}\right)_{\substack{a\to b\\ \lambda\to\lambda'}} = \left(\frac{e^2}{mc^2}\right)^2 \Bigg| \left\langle b\left|\sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}\right|a\right\rangle \boldsymbol{\epsilon}'\cdot\boldsymbol{\epsilon} - i\frac{\hbar\omega}{mc^2}\left\langle b\left|\sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}\mathbf{s}_j\right|a\right\rangle\cdot\boldsymbol{\epsilon}'\times\boldsymbol{\epsilon}$$

$$+\frac{\hbar^2}{m}\sum_c\sum_{ij}\left(\frac{\left\langle b\left|\left(\frac{\boldsymbol{\epsilon}'\cdot\mathbf{P}_i}{\hbar}-i(\mathbf{k}'\times\boldsymbol{\epsilon}')\cdot\mathbf{s}_i\right)e^{-i\mathbf{k}'\cdot\mathbf{r}_i}\right|c\right\rangle\left\langle c\left|\left(\frac{\boldsymbol{\epsilon}\cdot\mathbf{P}_j}{\hbar}+i(\mathbf{k}\times\boldsymbol{\epsilon})\cdot s_j\right)e^{i\mathbf{k}\cdot\mathbf{r}_j}\right|a\right\rangle}{E_a-E_c+\hbar\omega_k-i\Gamma_c/2}\right.$$

$$\left.+\frac{\left\langle b\left|\left(\frac{\boldsymbol{\epsilon}\cdot\mathbf{P}_j}{\hbar}+i(\mathbf{k}\times\boldsymbol{\epsilon})\cdot\mathbf{s}_j\right)e^{i\mathbf{k}\cdot\mathbf{r}_j}\right|c\right\rangle\left\langle c\left|\left(\frac{\boldsymbol{\epsilon}'\cdot\mathbf{P}_i}{\hbar}-i(\mathbf{k}'\times\boldsymbol{\epsilon}')\cdot\mathbf{s}_i\right)e^{-i\mathbf{k}'\cdot\mathbf{r}_i}\right|a\right\rangle}{E_a-E_c-\hbar\omega_{k'}}\right)\Bigg|^2 \delta(E_a-E_b+\hbar\omega_k-\hbar\omega_{k'}). \tag{13}$$

Equation (13) accounts for most x-ray scattering phenomena to order $(\hbar\omega/mc^2)^2$.

The first (Thomson) term gives the usual expression for Bragg scattering when $|b\rangle = |a\rangle$ and the periodicity of the lattice is accounted for. Anomalous dispersion effects occur when $\hbar\omega_k \sim E_a - E_c$ for some state $|c\rangle$, so that an energy denominator vanishes in Eq. (13). We have added a term $i\Gamma_c/2$ to the denominators in Eq. (13) to take into account the level width, which is important only very close to resonance. Equation (13) also includes spin-dependent resonance terms which arise because of the $s\cdot\nabla\times\mathbf{A}$ term in $\mathscr{H}'$.

To derive purely magnetic scattering we assume $\omega_{k'} \sim \omega_k \gg (E_a - E_c)/\hbar$. Neglecting the latter terms in the denominators of the last two terms, these reduce to

$$\frac{\hbar^2}{m}\frac{1}{\hbar\omega}\sum_{ij}\left\langle b\left|\left[\left(\frac{\epsilon'\cdot P_i}{\hbar}-i(\mathbf{k}'\times\boldsymbol{\epsilon}')\cdot\mathbf{s}_i\right),\right.\right.\right.$$
$$\left.\left. e_j^{i\mathbf{k}'\cdot\mathbf{r}_i}\left(\frac{\boldsymbol{\epsilon}\cdot\mathbf{P}_j}{\hbar}+i(\mathbf{k}\times\boldsymbol{\epsilon})\cdot\mathbf{s}_j\right)e^{i\mathbf{k}'\cdot\mathbf{r}_j}\right]\right|a\right\rangle, \tag{14}$$

where we have used closure to carry out the sum over c. The commutators in Eq. (14) are straightforward but tedious. Evaluating them gives

$$-i\frac{\hbar\omega}{mc^2}\left(\left\langle b\left|\sum_j e^{i\mathbf{k}\cdot\mathbf{r}_j} i\frac{\mathbf{K}\times\mathbf{P}_j}{\hbar k^2}(\boldsymbol{\epsilon}'\times\boldsymbol{\epsilon})\right|a\right\rangle\right.$$
$$+\left\langle b\left|\sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}\mathbf{s}_j\right|a\right\rangle\cdot(-(\hat{\mathbf{k}}'\times\boldsymbol{\epsilon}')\times(\hat{\mathbf{k}}\times\boldsymbol{\epsilon})$$
$$\left.+(\hat{\mathbf{k}}'\times\epsilon')(\hat{\mathbf{k}}'\cdot\boldsymbol{\epsilon})-(\hat{\mathbf{k}}\times\boldsymbol{\epsilon})(\hat{\mathbf{k}}\cdot\boldsymbol{\epsilon}'))\right),$$

and combining this with the other terms in Eq. (13) gives

$$\left(\frac{d^2\sigma}{d\Omega' dE'}\right)_{\substack{a\to b\\ \lambda\to\lambda'}} = \left(\frac{e^2}{mc^2}\right)^2\Bigg|\left\langle b\left|\sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}\right|a\right\rangle\boldsymbol{\epsilon}'\cdot\boldsymbol{\epsilon}$$
$$-i\frac{\hbar\omega}{mc^2}\left\langle b\left|\sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}\left(i\frac{\mathbf{K}\times\mathbf{P}_j}{\hbar k^2}\cdot\mathbf{A}+\mathbf{s}_j\cdot\mathbf{B}\right)\right|a\right\rangle\Bigg|^2$$
$$\times\delta(E_a-E_b+\hbar\omega_k-\hbar\omega_{k'}), \tag{15}$$

where

$$\mathbf{A} = \boldsymbol{\epsilon}'\times\boldsymbol{\epsilon}$$

and

$$\mathbf{B} = \boldsymbol{\epsilon}'\times\boldsymbol{\epsilon} + (\hat{k}'\times\boldsymbol{\epsilon}')(\hat{k}\cdot\boldsymbol{\epsilon}) - (\hat{k}\times\boldsymbol{\epsilon})(\hat{k}\cdot\boldsymbol{\epsilon}')$$
$$-(\hat{k}'\times\boldsymbol{\epsilon})\times(\hat{k}\times\boldsymbol{\epsilon}) \quad .$$

Equation (15) gives the cross section for scattering from magnetization densities. The magnetic terms are smaller by $\hbar\omega/mc^2$ in amplitudes than the charge terms. An *interference* can occur which will be of this same order. Because of the factor i in front of the magnetic term, this interference will occur only if the polarization factors are complex (*circular* polarization) or if the structure is noncentrosymmetric. The pure charge scattering is larger than the pure magnetic scattering by a significant factor:

$$\frac{\sigma_{\text{mag}}}{\sigma_{\text{charge}}} \simeq \left(\frac{\hbar\omega}{mc^2}\right)^2\frac{N_m^2}{N^2}\langle\mathbf{s}\rangle^2\frac{f_m^2}{f^2},$$

where N_m is the number of magnetic electrons/atom, N the number of electrons/atom, and f_m and f are the magnetic and charge form factors.

For Fe and 10-keV photons,

$$\frac{\sigma_{\text{mag}}}{\sigma_{\text{charge}}} \sim 4\times10^{-6}\langle s\rangle^2.$$

Also, the magnetic form factor f of an atom falls off more rapidly than the charge form factor because the magnetization density is more diffuse spatially than is the charge density. This reduces the ratio even further. Finally, the factor $\langle S\rangle$, which goes to zero at the Curie temperature, is unity only at low temperatures. By comparison the cross section for magnetic *neutron* scattering is

$$\frac{d^2\sigma}{d\Omega' dE'} = \left(\frac{-1.91e^2}{mc^2}\right)^2\frac{k'}{k}\Bigg|\Bigg\langle b\Bigg|$$
$$\times\sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}\left(-\frac{i}{\hbar K}\hat{K}\times\mathbf{P}_j+\hat{K}\times(\mathbf{s}_j\times\hat{K})\right)\Bigg|a\Bigg\rangle\Bigg|^2$$
$$\times\delta\left(E_a-E_b+\frac{\hbar^2k^2}{2m_0}-\frac{\hbar^2k'^2}{2m_0}\right). \tag{17}$$

The ratio of *magnetic* terms for x rays and neutrons is approximately

$$\frac{I_0^x\sigma_{\text{mag}}^x}{I_0^n\sigma_{\text{mag}}^n} \approx \frac{1}{4}\left(\frac{\hbar\omega}{mc^2}\right)^2\frac{I_0^x}{I_0^n} \approx \frac{1}{4}\times10^{-4}\frac{I_0^x}{I_0^n}.$$

Neutron sources can give $\sim 10^8$ neutrons/sec on a sample. An x-ray source which gives $\sim 10^{12}$ photons sec (monochromatic) will give comparable x-ray and neutron peaks.

The x-ray *pure* magnetic scattering should be observed in structures (like antiferromagnets or spirals) in which the Bragg peaks do *not* occur at the same point in $\mathbf{K}$ space as the much larger charge scattering. Note too that Eq. (15) shows a different polarization factor for spin and orbital terms, providing the possibility of distinguishing spin and orbit magnetization densities.

Finally, we consider the possibility of a resonance effect—where $\hbar\omega \sim E_c - E_a$ in Eq. (13). These resonances are the source of anomalous dispersion. Here we consider the case where the core levels are exchange-split by magnetization of the outer electrons. The spin-dependent terms become

$$\frac{\hbar^2 k^2}{m}\sum_{ij}\sum_{c}\frac{\langle b|(\hat{k}'\times\epsilon')\cdot s_i e^{-ik'\cdot r_i}|c\rangle\langle c|(\hat{k}\times\epsilon)\cdot s_j e^{ik\cdot r_j}|a\rangle}{E_a - E_c + \hbar\omega - i\frac{\Gamma c}{2}}.$$

For $\hbar\omega \sim E_c - E_a$, this is of order

$$i\frac{\hbar\omega}{mc^2}2\frac{\hbar\omega}{\Gamma_c}\sum_{ij}\langle b|e^{-ik'\cdot r_i}|c\rangle\langle c|e^{ik\cdot r_j}|a\rangle.$$

The factor $\hbar\omega/\Gamma c$ can be as large as 10^4. The experiment requires $\gamma_{\text{photon}} < \Gamma_c < \Delta$, where γ_{photon} is the width of the incident photon and Δ is the core-level exchange splitting. Circular polarization is also in general required to observe antiferromagnetic peaks.

In summary, there are many interesting effects which can be studied in the magnetic scattering of photons. This technique can complement in some cases the neutron scattering measurements.

Among the experiments are measurement to study

(1) long period modulated structures;

(2) differences of spin and orbital magnetization density;

(3) resonance effects, i.e., spin-dependent anomalous dispersion, which can give greater intensity and will give Bragg peaks at points in K space different from the charge peaks;

(4) surfaces using the above resonance methods; and

(5) interference between the magnetic and charge scattering with circular polarization.

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[1]A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiments* (van Nostrand, New York, 1935).

[2]F. E. Low, Phys. Rev. 96, 1428 (1954).

[3]M. Gell-Mann and M. L. Goldberger, Phys. Rev. 96, 1433 (1954).

[4]P. M. Platzman and N. Tzoar, Phys. Rev. B 2, 3556 (1970).

[5]F. de Bergevin and M. Brunel, Acta Cryst. A 37, 314, 325 (1981).

[6]M. Blume, Proceedings of the New Rings Workshop, Stanford, 1983; I. B. Khriplovich and O. L. Zhizhimov (preprint).

[7]L. L. Foldy and S. Wouthuysen, Phys. Rev. 78, 29 (1950).

[8]J. J. Sakurai, *Advanced Quantum Mechanics* (Addison-Wesley, Reading, MA, 1967).

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Polarization dependence of magnetic x-ray scattering

M. Blume and Doon Gibbs
Brookhaven National Laboratory, Upton, New York 11973
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We calculate the polarization dependence of the x-ray scattering cross section, including magnetic terms, using the Poincaré representation for the polarization. General expressions are given for the polarization dependence of the cross section of the pure magnetic scattering and of the interference between charge and magnetic scattering, and for the polarization of the scattered beam in both cases. These expressions are compared to the equivalent results for magnetic neutron scattering. The general results are then specialized to several typical cases, including the scattering of linearly and circularly polarized radiation from spiral, uniaxially modulated, and ferromagnetic structures. It is shown that detailed magnetic-structure determinations are possible using synchrotron radiation. It is further demonstrated that the orbital- and spin-angular-momentum contributions of both ferromagnets and antiferromagnets may be separately measured in a variety of simple geometries. It is found that, although the efficiency is very low, linearly polarized radiation can be completely converted to circular polarization by scattering from a magnetic spiral. Finally, it is shown that, in addition to the interference between charge and magnetic scattering, there is an interference involving the spin- and orbital-angular-momentum scattering, which can couple moments in different spatial directions.

I. INTRODUCTION

In the last several years magnetic x-ray experiments using synchrotron radiation have been performed on a steadily growing number of magnetic systems. These experiments have included high-resolution studies of the pure magnetic scattering in antiferromagnets[1–3] as well as of the interference between charge and magnetic scattering in bulk and thin-film ferromagnets.[4–6] Spin-dependent Compton- (Refs. 7 and 8) and resonance-magnetic-scattering[9] studies have been performed on a variety of ferromagnets. The high brightness of synchrotron radiation sources has been an important factor in the success of many of these experiments. It has now become apparent that the polarization dependence of the magnetic cross section can also be exploited in even more detailed studies. First, the use of the polarization dependence provides a natural technique for determining magnetic structures by x-ray scattering. Beyond this, there are novel possibilities which arise from the well-defined polarization characteristics of synchrotron radiation. For example, using the high degree of linear polarization of the incident beam it has been possible in synchrotron experiments to distinguish between charge peaks, arising from lattice modulations, and magnetic peaks, in a spiral magnetic structure.[2,10] This distinction was crucial to the interpretation of the diffraction pattern in recent studies of rare-earth metals. Furthermore, it has been suggested that by analyzing the polarization of the scattered beam, it should be possible to separately measure the spin and orbital contributions to the cross section.[11] This separation is not directly possible by neutron-scattering techniques and is important to a fundamental understanding of the electronic properties of magnetic materials. Along these lines, we note the elegant experiments of Brunel *et al.*[5] in which the scattering of circularly polarized synchrotron radiation was explicitly observed in a powdered ferrite.

In this paper we calculate the polarization dependence of the x-ray scattering cross section, including magnetic terms, using the Poincaré representation for the polarization. General expressions are given for the polarization dependence of the cross section of the pure magnetic scattering and of the interference between charge and magnetic scattering, and for the polarization of the scattered beam in both cases. These expressions are compared to the equivalent results for magnetic neutron scattering. The general results are then specialized to several typical cases, including the scattering of linearly and circularly polarized radiation from spiral, uniaxially modulated, and ferromagnetic structures. It is shown that detailed magnetic-structure determinations are possible using synchrotron radiation by measuring the polarization dependence of the magnetic and interference cross sections, and by analyzing the polarization of the magnetically scattered beam. It is further demonstrated that the orbital- and spin-angular-momentum contributions of both ferromagnets and antiferromagnets may be separately measured in a variety of simple geometries. It is found that, although the efficiency is very low ($<\sim 10^{-6}$), linearly polarized radiation can be completely converted to circular polarization by scattering from a magnetic spiral. Finally, we note that, in addition to the interference between charge and magnetic scattering, there is an interference involving the spin- and orbital-angular-momentum scattering which can couple moments in different spatial directions.

Although particular features of the polarization dependence of the cross section have already appeared in earlier papers,[12,1,4,5,11] the general case, explicitly including the orbital angular momentum and the final polarization, has not been previously published. The present results are surprisingly simple and will be important for their utility in suggesting and in analyzing the results of synchrotron experiments. The general results for the x-ray cross section are summarized in Eqs. (6), (7), and (9). This expression is expanded using the Poincaré representation in Eqs. (11), (12), (14), and (16). General expressions for the final polarization of the magnetic scattering are given in Eq. (13).

II. CROSS SECTION

The cross section for magnetic scattering of photons by free charges and atoms has been discussed by a number of authors.[13,14,12,4,5,11] In the following we reproduce the expression of Blume[11] obtained by a nonrelativistic calculation of the cross section using perturbation theory. In the limit of high photon energy the cross section for elastic scattering is

$$\frac{d^2\sigma}{d\Omega' dE'}\bigg|_{\lambda\to\lambda', a\to b} = \left[\frac{e^2}{mc^2}\right]^2 \left| \left\langle b\left|\sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}\right|a\right\rangle \hat{\epsilon}\cdot\hat{\epsilon}' - \frac{i\hbar\omega}{mc^2}\left\langle b\left|\sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}\left[\frac{i\mathbf{K}\times\mathbf{p}_j}{\hbar k^2}\cdot\mathbf{A}+\mathbf{s}_j\cdot\mathbf{B}\right]\right|a\right\rangle\right|^2 \delta(E_a-E_b-(\hbar\omega_k'-\hbar\omega_k)) \,, \quad (1)$$

where $\mathbf{A}=\hat{\epsilon}'\times\hat{\epsilon}$ and

$$\mathbf{B}=\hat{\epsilon}'\times\hat{\epsilon}+(\hat{\mathbf{k}}'\times\hat{\epsilon}')(\hat{\mathbf{k}}'\cdot\hat{\epsilon})-(\hat{\mathbf{k}}\times\hat{\epsilon})(\hat{\mathbf{k}}\cdot\hat{\epsilon}') -(\hat{\mathbf{k}}'\times\hat{\epsilon}')\times(\hat{\mathbf{k}}\times\hat{\epsilon}) \,.$$

Here the sum is taken over all electrons j, $\mathbf{K}=\mathbf{k}-\mathbf{k}'$ is the momentum transfer, $\hbar\omega$ ($\hbar\omega'$) is the incident (scattered) photon energy, a (b) is the initial (final) state of the scatterer, $\hat{\epsilon}$ ($\hat{\epsilon}'$) is the initial (scattered) polarization, and $\mathbf{p}_j$ is the electronic momentum. The geometry and convections used here are illustrated in Fig. 1. The modulus of the first term on the right-hand side of the equation gives the usual Thomson cross section for charge scattering and depends on the Fourier transform of the charge density. The modulus of the second term, which is reduced from the first by $(\hbar\omega/mc^2)^2$, describes the pure magnetic scattering and depends on the Fourier transforms of the spin and orbital magnetization densities. In addition, there is an interference term proportional to $(i\hbar\omega/cm^2)$, involving the products of charge and magnetic densities. We first develop an expression for the orbital momentum.

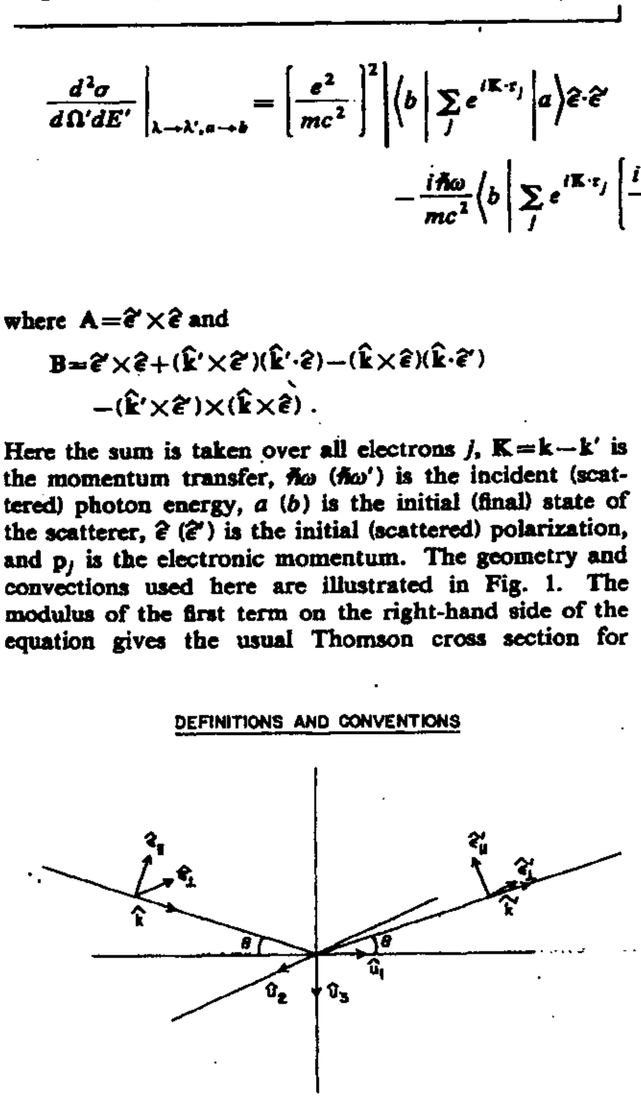

FIG. 1. The definitions and conventions used in this paper. $\hat{\mathbf{k}}$ and $\hat{\mathbf{k}}'$ are the incident and scattered wavevectors and 2θ is the scattering angle. $\hat{\epsilon}_\perp$ and $\hat{\epsilon}_\parallel$ are the components of the polarization perpendicular and parallel to the diffraction plane (spanned by $\hat{\mathbf{k}}$ and $\hat{\mathbf{k}}'$). The $\hat{\mathbf{U}}_i$'s define a basis for the magnetic structure which is expressed in terms of the incident and scattered wavevectors: $\hat{\mathbf{U}}_1=(\hat{\mathbf{k}}+\hat{\mathbf{k}}')/2\cos\theta$, $\hat{\mathbf{U}}_2=\hat{\mathbf{k}}\times\hat{\mathbf{k}}'/\sin 2\theta$, $\hat{\mathbf{U}}_3=(\hat{\mathbf{k}}-\hat{\mathbf{k}}')/2\sin\theta$. By these conventions we also have $\hat{\epsilon}_\perp=-\hat{\mathbf{U}}_2$, $\hat{\epsilon}'_\perp=-\hat{\mathbf{U}}_2$, $\hat{\epsilon}_\parallel=\sin\theta\,\hat{\mathbf{U}}_1-\cos\theta\,\hat{\mathbf{U}}_3$, and $\hat{\epsilon}'_\parallel=-(\sin\theta\,\hat{\mathbf{U}}_1+\cos\theta\,\hat{\mathbf{U}}_3)$.

Rewriting the orbital term:

$$\sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}\frac{i(\mathbf{K}\times\mathbf{p}_j)}{k^2}\cdot\mathbf{A}\to\sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}\left[\frac{-i}{K}\hat{\mathbf{K}}\times\mathbf{p}_j\right]\cdot\mathbf{A}' \,,$$

where $\mathbf{A}'=-(K^2/k^2)\mathbf{A}=-4(\sin^2\theta)(\hat{\epsilon}'\times\hat{\epsilon})$ and 2θ is the scattering angle. This expression is analogous to that encountered in neutron scattering and for elastic scattering may be rewritten as[15–18]

$$-\left\langle a\left|\sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}\frac{(i\hat{\mathbf{K}}\times\mathbf{p}_j)}{K}\right|a\right\rangle\to\tfrac{1}{2}\hat{\mathbf{K}}\times[\mathbf{L}(\mathbf{K})\times\hat{\mathbf{K}}] \,,$$

where $\mathbf{L}(\mathbf{K})$ is the Fourier transform of the atomic-orbital magnetization density.[15–17] Explicitly,[15]

$$\mathbf{L}(\mathbf{K})=\frac{1}{2}\langle a\mid\sum_j[f(\mathbf{K}\cdot\mathbf{r}_j)\mathbf{l}_j+\mathbf{l}_j f(\mathbf{K}\cdot\mathbf{r}_j)]\mid a\rangle \,,$$

where

$$f(x)=2\sum_{n=0}^{\infty}\frac{(ix)^n}{(n+2)n!} \,.$$

As a consequence of the vector product the contribution of the orbital term in the direction of the momentum transfer $\mathbf{K}$ is zero, just as with neutron scattering. Through the use of simple vector identities,

$$\hat{\mathbf{K}}\times(\mathbf{L}\times\hat{\mathbf{K}})\cdot\mathbf{A}'=\mathbf{L}\cdot[\mathbf{A}'-(\mathbf{A}\cdot\mathbf{K})\hat{\mathbf{K}}]\equiv\mathbf{L}\cdot\mathbf{A}'' \quad (2)$$

with

$$\mathbf{A}''=\mathbf{A}'-(\mathbf{A}'\cdot\hat{\mathbf{K}})\hat{\mathbf{K}}$$
$$=2(1-\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}')(\hat{\epsilon}'\times\hat{\epsilon})$$
$$-(\hat{\mathbf{k}}\times\hat{\epsilon})(\hat{\mathbf{k}}\cdot\hat{\epsilon}')+(\hat{\mathbf{k}}'\times\hat{\epsilon}')(\hat{\mathbf{k}}'\cdot\hat{\epsilon}) .$$

Defining the Fourier transform of the spin density,

$$\mathbf{S}(\mathbf{K})=\left\langle a\left|\sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}\mathbf{s}_j\right|a\right\rangle ,$$

the magnetization-dependent part $\langle M_m\rangle$ of the x-ray cross section may be written explicitly in terms of $\mathbf{L}(\mathbf{K})$ and $\mathbf{S}(\mathbf{K})$:

$$\langle M_m\rangle=\tfrac{1}{2}\mathbf{L}(\mathbf{K})\cdot\mathbf{A}''+\mathbf{S}(\mathbf{K})\cdot\mathbf{B} . \tag{3}$$

$\mathbf{A}''$ and $\mathbf{B}$ are given in Eqs. (1) and (2). It is clear that the orbital and spin contributions to the x-ray cross section are different and so they may be distinguished by analyzing the polarization of the scattered beam. This difference does not appear in neutron scattering, where the interaction is purely magnetic in origin. Explicitly, the expression for neutron magnetic scattering is[11]

$$\langle M_n\rangle=\hat{\mathbf{K}}\times\{[\tfrac{1}{2}\mathbf{L}(\mathbf{K})+\mathbf{S}(\mathbf{K})]\times\hat{\mathbf{K}}\}\cdot\sigma$$
$$\equiv[\tfrac{1}{2}\mathbf{L}(\mathbf{K})+\mathbf{S}(\mathbf{K})]\cdot\mathbf{C} ,$$

where σ is the neutron spin operator and $\mathbf{C}=[\hat{\mathbf{K}}\times(\sigma\times\hat{\mathbf{K}})]$. It is seen that the polarization dependence of the spin magnetization density is identical to that for the orbital magnetization density. The difference in the cross sections for x-ray scattering and neutron scattering arises because the x-ray interacts both with the charge (through the electric field and its gradients) and with the magnetic moment (through the magnetic fields and their gradients). Thus, the Lorentz force, for example, affects only the orbital magnetic moment and not the spin, to first order in $(\hbar\omega/mc^2)$.

From the point of view of performing synchrotron experiments it is convenient to express the vectors $\mathbf{A}''$ and $\mathbf{B}$ as 2×2 matrices in a basis whose components are parallel and perpendicular to the diffraction plane (see Fig. 1). Then

$$\mathbf{A}''=\begin{bmatrix}A''_{\perp\perp} & A''_{\perp\parallel}\\ A''_{\parallel\perp} & A''_{\parallel\parallel}\end{bmatrix}=\frac{K^2}{2k^2}\begin{bmatrix}0 & -(\hat{\mathbf{k}}+\hat{\mathbf{k}}')\\ \hat{\mathbf{k}}+\hat{\mathbf{k}}' & 2\hat{\mathbf{k}}\times\hat{\mathbf{k}}'\end{bmatrix} , \tag{4a}$$

$$\mathbf{B}=\begin{bmatrix}B_{\perp\perp} & B_{\perp\parallel}\\ B_{\parallel\perp} & B_{\parallel\parallel}\end{bmatrix}=\begin{bmatrix}\hat{\mathbf{k}}\times\hat{\mathbf{k}}' & -\hat{\mathbf{k}}'(1-\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}')\\ \hat{\mathbf{k}}(1-\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}') & \hat{\mathbf{k}}\times\hat{\mathbf{k}}'\end{bmatrix} . \tag{4b}$$

This representation of the matrix $\mathbf{B}$ has been given by de Bergevin and Brunel.[1,4] $\langle M_m\rangle$ may now be written as

$$\langle M_m\rangle=\begin{bmatrix}\langle M_m\rangle_{\perp\perp} & \langle M_m\rangle_{\perp\parallel}\\ \langle M_m\rangle_{\parallel\perp} & \langle M_m\rangle_{\parallel\parallel}\end{bmatrix}=\begin{bmatrix}\mathbf{S}\cdot(\hat{\mathbf{k}}\times\hat{\mathbf{k}}') & -\frac{K^2}{2k^2}\left[\left[\frac{\mathbf{L}(\mathbf{K})}{2}+\mathbf{S}(\mathbf{K})\right]\cdot\hat{\mathbf{k}}'+\frac{\mathbf{L}(\mathbf{K})}{2}\cdot\hat{\mathbf{k}}\right]\\ \frac{K^2}{2k^2}\left[\left[\frac{\mathbf{L}}{2}\mathbf{L}(\mathbf{K})+\mathbf{S}(\mathbf{K})\right]\cdot\hat{\mathbf{k}}+\frac{\mathbf{L}(\mathbf{K})}{2}\cdot\hat{\mathbf{k}}'\right] & \left[\frac{K^2}{2k^2}\mathbf{L}(\mathbf{K})+\mathbf{S}(\mathbf{K})\right]\cdot(\hat{\mathbf{k}}\times\hat{\mathbf{k}}')\end{bmatrix} . \tag{5}$$

The diagonal matrix element involve magnetization density oriented only in the direction perpendicular to the diffraction plane, while the off-diagonal matrix elements involve magnetization density oriented only within the diffraction plane. Further, $\langle M_m\rangle_{\perp\perp}$ is independent of $\mathbf{L}(\mathbf{K})$. For general magnetic structures this same expression holds with $\mathbf{L}(\mathbf{K})$ and $\mathbf{S}(\mathbf{K})$ representing the complex structure factors. Expressing the component of the magnetic structure in the basis defined in Fig. 1 we have

$$\langle M_m\rangle=\begin{bmatrix}(\sin 2\theta)S_2 & -2(\sin^2\theta)[(\cos\theta)(L_1+S_1)-(\sin\theta)S_3]\\ 2(\sin^2\theta)[(\cos\theta)(L_1+S_1)+(\sin\theta)S_3] & (\sin 2\theta)[2(\sin^2\theta)L_2+S_2]\end{bmatrix} , \tag{6}$$

where 2θ is the scattering angle and we have used $\frac{1}{2}(K/k)^2=2\sin^2\theta$. In this basis we may also write the interaction matrix describing the charge scattering:

$$\langle M_c\rangle=\rho(\mathbf{K})\begin{bmatrix}1 & 0\\ 0 & \cos 2\theta\end{bmatrix} , \tag{7}$$

where $\rho(\mathbf{K})$ is the Fourier transform of the electronic charge density.

III. POINCARÉ REPRESENTATION

Having general expressions for the matrices $\langle M_m\rangle$ and $\langle M_c\rangle$, it is now possible to calculate the cross section and the final polarization for arbitrary incident polarization and for any magnetic structure. It is convenient to introduce the Poincaré representation for the polarization and the density matrix for the incident beam. The Poincaré representation is particularly useful as it applies to both completely and partially polarized incident radiation and involves only variables which are measured in experiments. A general discussion of these techniques has been given by Fano.[18] A discussion of their application to neutron scattering and to the transmission of x-rays through matter has been given by Blume and Kistner.[17] The first application of the Poincaré representation to magnetic x-ray scattering was by de Bergevin and Brunel.[1]

We write the expression for elastic scattering by explicitly introducing the initial λ and final λ' polarizations and taking the expectation value of M in the initial and final state $|a\rangle$ of the scatterer:

$$\frac{d\sigma}{d\Omega'}=\left[\frac{e^2}{mc^2}\right]^2\sum_{\lambda,\lambda'}p_\lambda\left|\langle\lambda'|\langle M_c\rangle|\lambda\rangle-\frac{i\hbar\omega}{mc^2}\langle\lambda'|\langle M_m\rangle|\lambda\rangle\right|^2, \quad (8)$$

where

$$\langle\lambda'|\langle M_c\rangle|\lambda\rangle=\left\langle a\left|\sum e^{i\mathbf{K}\cdot\mathbf{r}_j}\right|a\right\rangle\hat{\epsilon}_\lambda\cdot\hat{\epsilon}_{\lambda'}$$

and

$$\langle\lambda'|\langle M_m\rangle|\lambda\rangle=\tfrac{1}{2}\mathbf{L}(\mathbf{K})\cdot\mathbf{A}''_{\lambda'\lambda}+\mathbf{S}(\mathbf{K})\cdot\mathbf{B}_{\lambda'\lambda}\,.$$

Here p_λ is the probability for incident polarization λ. We next define the (2×2) density matrix ρ for the incident beam by

$$\rho=\sum_\lambda|\lambda\rangle p_\lambda\langle\lambda|\,.$$

Evaluating, we obtain the general expression for the equilibrium differential cross section for elastic scattering:

$$\frac{d\sigma}{d\Omega}=\left[\frac{e^2}{mc^2}\right]^2\mathrm{tr}\left[\left\langle M_c-\frac{i\hbar\omega}{mc^2}M_m\right\rangle\rho\left\langle M_c-\frac{i\hbar\omega}{mc^2}M_m\right\rangle^\dagger\right]$$
$$=\left[\frac{e}{mc^2}\right]^2\mathrm{tr}\left[\langle M_c\rangle\rho\langle M_c^\dagger\rangle-\frac{i\hbar\omega}{mc^2}(\langle M_m\rangle\rho\langle M_c^\dagger\rangle-\langle M_c\rangle\rho\langle M_m^\dagger\rangle)+\left[\frac{\hbar\omega}{mc^2}\right]^2\langle M_m\rangle\rho\langle M_m^\dagger\rangle\right]. \quad (9)$$

$\langle M^\dagger\rangle$ is the Hermitian conjugate of $\langle M\rangle$.

Following Fano,[18] we now develop the expression for the density matrix. Because the density matrix is the averaged outer product of a two-dimensional vector, it is Hermitian, and consequently may be expressed in terms of the unit matrix and the Pauli matrices:

$$\rho=\tfrac{1}{2}(1+\mathbf{P}\cdot\sigma)\quad\text{where}\quad\begin{cases}\mathbf{P}=(P_\xi,P_\eta,P_\zeta),\\ \sigma=(\sigma_\xi,\sigma_\eta,\sigma_\zeta).\end{cases}$$

Here σ represents the Pauli matrices, I_0 is the total intensity, and P_ξ, P_η, and P_ζ give the Poincaré-Stokes representation of the polarization. We write the components of the Poincaré vector $\mathbf{P}$ using Greek symbols to emphasize that it is not a vector in real space. In the usual Cartesian coordinate system we have

$$\rho=\frac{1}{2}\begin{bmatrix}1+P_\zeta & P_\xi-iP_\eta\\ P_\xi+iP_\eta & 1-P_\zeta\end{bmatrix},$$

where $\sigma_\xi=\begin{pmatrix}0&1\\1&0\end{pmatrix}$, $\sigma_\eta=\begin{pmatrix}0&-i\\i&0\end{pmatrix}$, and $\sigma_\zeta=\begin{pmatrix}1&0\\0&-1\end{pmatrix}$. Taking $\hat{\epsilon}_\perp$ and $\hat{\epsilon}_\parallel$ as two orthogonal unit vectors perpendicular to the beam direction defined in Fig. 1 (with $\mathbf{E}=E_1\hat{\epsilon}_\perp+E_2\hat{\epsilon}_\parallel$), the components of $\mathbf{P}$ are defined as follows. Let I_1 be the difference between the light intensity with linear polarization parallel to a vector oriented 45° to $\hat{\epsilon}_\perp$ and the intensity with linear polarization parallel to a vector oriented 45° to $\hat{\epsilon}_\parallel$. Then

$$P_\xi=\frac{I_1}{I_0}=\frac{|E_1+E_2|^2-|E_1-E_2|^2}{4(E_1|^2+|E_2|^2)}=\frac{\mathrm{Re}(E_1^*E_2)}{|E_1|^2+|E_2|^2}\,.$$

Let I_2 be the difference between the light intensity with left circular polarization and the intensity with right circular polarization. Then

$$P_\eta=\frac{I_2}{I_0}=\frac{|E_1+iE_2|^2-|E_1-iE_2|^2}{4(|E_1|^2+|E_2|^2)}=\frac{\mathrm{Im}(E_1^*E_2)}{|E_1|^2+|E_2|^2}\,.$$

Let I_3 be the difference between the light intensity with linear polarization parallel to $\hat{\epsilon}_\perp$ and the intensity with polarization parallel to $\hat{\epsilon}_\parallel$. Then

$$P_\zeta=\frac{I_3}{I_0}=\frac{|E_1|^2-|E_2|^2}{|E_1|^2+|E_2|^2}\,.$$

It follows that $P_\xi=+1$ (-1) represent linear polarization at angles $+45°$ $(-45°)$ to the $\hat{\mathbf{U}}_3$ axis, $P_\eta=+1$ (-1) represent left (right) circular polarization, and $P_\zeta=+1$ (-1) represent linear polarization along the $\hat{\mathbf{U}}_2$ $(\hat{\mathbf{U}}_3)$ axis, respectively (see Fig. 1). If $|\mathbf{P}|=1$, the beam is completely polarized; if $|\mathbf{P}|\leq1$, the beam is partially polarized; and if $|\mathbf{P}|=0$, the beam is unpolarized. The vector $\mathbf{P}$ may simply be thought of as a vector in an abstract space which is rotated upon scattering, as shown in Fig. 2.

Once the Poincaré vector $\mathbf{P}$ and the total intensity I_0 are specified, the polarization is completely characterized in terms of measurable intensities. To calculate the density matrix and final polarization after scattering we will require that[18]

$$\mathbf{P}=\mathrm{tr}(\sigma\rho)\,, \quad (10a)$$

$$\rho'=M\rho M^\dagger\,, \quad (10b)$$

$$\frac{d\sigma}{d\Omega}=\left[\frac{e^2}{mc^2}\right]^2\mathrm{tr}(\rho')\,, \quad (10c)$$

$$\mathbf{P}'=\frac{\mathrm{tr}(\sigma\rho')}{\mathrm{tr}(\rho')}\,. \quad (10d)$$

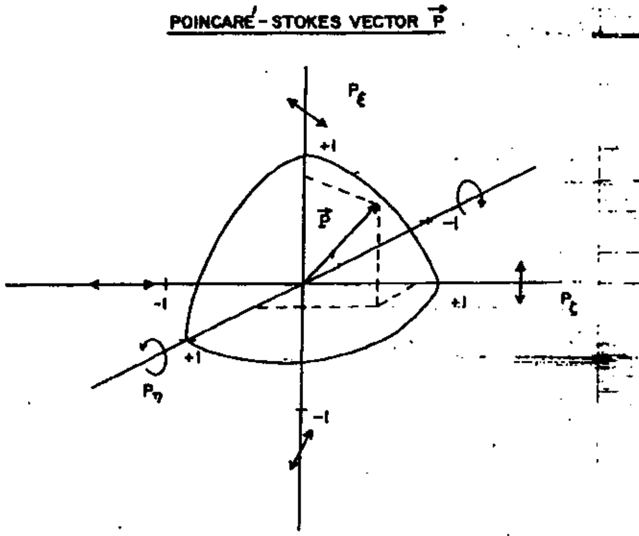

FIG. 2. The Poincaré sphere. The polarization is completely characterized by the values of the Poincaré coefficients P_ξ, P_η, P_ζ, and by the total intensity I_0. By definition, $|\mathbf{P}| \le 1$.

IV. RESULTS

In this section we calculate the general expressions for the differential cross section and the final polarization for each of the terms in Eq. (8), assuming arbitrary incident polarization $\mathbf{P}=(P_\xi,P_\eta,P_\zeta)$. For the purpose of discussion, the terms multiplying P_ξ will be referred to as the 45°-linear component, the terms multiplying P_η will be referred to as the circular component, and the terms multiplying P_ζ will be referred to as the linear component. The terms not associated with a Poincaré coefficient are referred to as the unpolarized component.

A. Charge scattering

This case is straightforward and gives the expected results. From Eq. (7) and (10) we write

$$\frac{d\sigma}{d\Omega}=\left[\frac{e^2}{mc^2}\right]^2 \mathrm{tr}\langle M_c\rangle\rho\langle M_c^\dagger\rangle$$

$$=\left[\frac{e^2}{mc^2}\right]^2 \tfrac{1}{2}|\rho(\mathbf{K})|^2[1+\cos^2 2\theta+P_\zeta(1-\cos^2 2\theta)], \tag{11}$$

independent of P_ξ and P_η. The components of the final polarization $\mathbf{P}'$ may be found using Eq. (10d):

$$P'_\xi=\frac{2(\cos 2\theta)P_\xi}{1+\cos^2 2\theta+P_\zeta(1-\cos^2 2\theta)},$$

$$P'_\eta=\frac{2(\cos 2\theta)P_\eta}{1+\cos^2 2\theta+P_\zeta(1-\cos^2 2\theta)},$$

$$P'_\zeta=\frac{1-\cos^2 2\theta+P_\zeta(1+\cos^2 2\theta)}{1+\cos^2 2\theta+P_\zeta(1-\cos^2 2\theta)}.$$

B. Pure magnetic scattering

From Eq. (9) we write

$$\frac{d\sigma}{d\Omega}=\left[\frac{e^2}{mc^2}\right]^2\left[\frac{\hbar\omega}{mc^2}\right]^2 \mathrm{tr}\{\langle M_m\rangle\rho\langle M_m^\dagger\rangle\}$$

$$\to\left[\frac{e^2}{mc^2}\right]^2\left[\frac{\hbar\omega}{mc^2}\right]^2 \tfrac{1}{2}\{(1+P_\zeta)(|m_{11}|^2+|m_{21}|^2)+(1-P_\zeta)(|m_{12}|^2+|m_{22}|^2)$$

$$+2\,\mathrm{Re}[(P_\xi+iP_\eta)(m_{11}^*m_{12}+m_{21}^*m_{22})]\}, \tag{12}$$

where we have left the result in terms of $m_{i,j}$, the elements of $\langle M_m\rangle$. This form permits several general conclusions to be drawn below, and makes writing the cross section for magnetic structures and orientations not considered in the examples straightforward. Similarly, we expand Eq. (10d) to obtain

$$\frac{d\sigma}{d\Omega}P'_\xi=\left[\frac{e^2}{mc^2}\right]^2\left[\frac{\hbar\omega}{mc^2}\right]^2\{(1+P_\zeta)\mathrm{Re}(m_{11}^*m_{21})+(1-P_\zeta)\mathrm{Re}(m_{12}^*m_{22})+\mathrm{Re}[(P_\xi+iP_\eta)(m_{11}^*m_{22}+m_{21}^*m_{12})]\},$$

$$\frac{d\sigma}{d\Omega}P'_\eta=\left[\frac{e^2}{mc^2}\right]^2\left[\frac{\hbar\omega}{mc^2}\right]^2\{(1+P_\zeta)\mathrm{Im}(m_{11}^*m_{21})+(1-P_\zeta)\mathrm{Im}(m_{12}^*m_{22})+\mathrm{Im}[(P_\xi+iP_\eta)(m_{11}^*m_{22}-m_{21}^*m_{12})]\}, \tag{13}$$

$$\frac{d\sigma}{d\Omega}P'_\zeta=\frac{1}{2}\left[\frac{e^2}{mc^2}\right]^2\left[\frac{\hbar\omega}{mc^2}\right]^2\{(1+P_\zeta)(|m_{11}|^2-|m_{21}|^2)+(1-P_\zeta)(|m_{12}|^2-|m_{22}|^2)$$

$$+2\,\mathrm{Re}[(P_\xi+iP_\eta)(m_{11}^*m_{12}-m_{21}^*m_{22})]\}.$$

In each of the expressions above the linear and unpolarized components and the circular and 45°-linear components display a simple symmetry, involving the same products of matrix elements. If $\langle M_m \rangle$ is diagonal, then there are no contributions to the cross section from the 45°-linear or the circular components. If $\langle M_m \rangle$ is nondiagonal, there are again no contributions from the 45°-linear or circular components. Similarly, if $\langle M_m \rangle$ is diagonal or nondiagonal and $P_\xi = P_\eta = 0$ then $P'_\xi = P'_\eta = 0$.

A feature of the cross section which is special to magnetic x-ray scattering is the existence of an interference between the spin and orbital angular momentum, which may couple moments in different spatial directions. These terms arise in each of the matrix element products above, except $|m_{11}|^2$. To illustrate, we write the general expression for the magnetic cross section by substituting Eq. (6) for $\langle M_m \rangle$ in Eq. (12):

$$\frac{d\sigma}{d\Omega} = \frac{1}{2}\left[\frac{e^2}{mc^2}\right]^2\left[\frac{\hbar\omega}{mc^2}\right]^2 [(1+P_\zeta)\{(\sin^2 2\theta)[\,|S_2|^2 + (\sin^2\theta)\,|L_1+S_1|^2] + 4(\sin^6\theta)\,|S_3|^2$$

$$+4(\sin 2\theta)(\sin^4\theta)[(L'_1+S'_1)S'_3 + (L''_1+S''_1)S''_3]\}$$

$$+(1-P_\zeta)\{(\sin^2 2\theta)[\,|2(\sin^2\theta)L_2+S_2|^2 + (\sin^2\theta)\,|L_1+S_1|^2] + 4(\sin^6\theta)\,|S_3|^2$$

$$-4(\sin 2\theta)(\sin^4\theta)[(L'_1+S'_1)S'_3 + (L''_1+S''_1)S''_3]\}$$

$$-8P_\eta(\sin 2\theta)(\sin^2\theta)((\cos\theta)\{(L'_1+S'_1)[(\sin^2\theta)L''_2+S''_2] - (L''_1+S''_1)[(\sin^2\theta)L'_2+S'_2]\}$$

$$+(\sin^3\theta)(S'_3L''_2 - S''_3L'_2))$$

$$+8P_\xi(\sin 2\theta)(\sin^2\theta)((\sin^2\theta)(\cos\theta)[(L'_1+S'_1)L'_2 + (L''_1+S''_1)L''_2]$$

$$+(\sin\theta)\{S'_3[(\sin^2\theta)L'_2+S'_2] + S''_3[(\sin^2\theta)L''_2+S''_2]\})] \,. \qquad (14)$$

In this expression prime and double prime refer to the real and imaginary parts, respectively, of the generally complex structure factors **L** and **S**. Unprimed variables L_j and S_j refer to the jth components of the complex structure factors, $L_j = L'_j + iL''_j$ and $S_j = S'_j + S''_j$, with i and j labeling different symmetry directions in the U basis (see Fig. 1). When $i \neq j$ and $P \neq 0$ terms of the form L_iS_j, L_iL_j, and S_iS_j occur. In many materials the components associated with different symmetry directions are equal, so that $S_iS_j \to |S_i|^2$. The magnetic structure of erbium,[2] however, is an example where for intermediate temperatures the c axis and basal plane magnetic structures are distinct—thereby giving rise to just this sort of interference in the pure magnetic scattering. It may also be seen from this expression that for **L** and **S** purely real or imaginary, the cross section is independent of the circular component. For a structure factor whose spatial direction is parallel to a U-basis vector, the cross section is independent of both the circular and 45°-linear components.

C. Interference scattering

From Eq. (8) we write

$$\left.\frac{d\sigma}{d\Omega}\right|_I = -\left[\frac{i\hbar\omega}{mc^2}\right]\left[\frac{e^2}{mc^2}\right]^2 \mathrm{tr}(\langle M_m\rangle\rho\langle M_c^\dagger\rangle - \langle M_c\rangle\rho\langle M_m^\dagger\rangle)$$

$$= \left[\frac{e^2}{mc^2}\right]^2 \frac{\hbar\omega}{mc^2}[\mathrm{Im}(\rho^* m_{11} + \rho^* m_{22}\cos 2\theta) + P_\zeta \mathrm{Im}(\rho^* m_{11} - \rho^* m_{22}\cos 2\theta) + P_\xi \mathrm{Im}(\rho^* m_{12} + \rho^* m_{21}\cos 2\theta)$$

$$+P_\eta \mathrm{Re}(\rho^* m_{12} - \rho^* m_{21}\cos 2\theta)] \,, \qquad (15)$$

where we have substituted for $\langle M_c \rangle$ using Eq. (7) and $m_{i,j}$ represent the elements of $\langle M_m \rangle$. When $\langle M_m \rangle$ is diagonal the interference term is independent of the circular and the 45°-linear components. When $\langle M_m \rangle$ is off diagonal, the only coupling is to the circular and the 45°-linear components.

Substituting for $\langle M_m \rangle$ from Eq. (6),

$$\left.\frac{d\sigma}{d\Omega}\right|_I = \left[\frac{e^2}{mc^2}\right]^2 \frac{\hbar\omega}{mc^2}\Big((\sin 2\theta)(1+P_\zeta)(\rho' S_2'' - \rho'' S_2')$$
$$+(\sin 2\theta)(\cos 2\theta)(1-P_\zeta)\{\rho'[2(\sin^2\theta)L_2''+S_2'']-\rho''[2(\sin^2\theta)L_2'+S_2']\}$$
$$-P_\eta(\sin\theta)\{(1+\cos 2\theta)(\sin 2\theta)[\rho'(L_1'+S_1')-\rho''(L_1''+S_1'')]-(1-\cos 2\theta)^2(\rho' S_3'-\rho'' S_2'')\}$$
$$-P_\xi(\sin\theta)\{(1-\cos 2\theta)(\sin 2\theta)[\rho'(L_1''+S_1'')-\rho''(L_1'+S_1')]$$
$$-(1+\cos 2\theta)(1-\cos 2\theta)(\rho' S_3''-\rho'' S_3')\}\Big) . \tag{16}$$

In this expression ρ' and ρ'' refer to the real and imaginary parts of the charge form factor, respectively. When $\mathbf{P}=0$ the only contributions to the interference term come from magnetization density oriented perpendicular to the diffraction plane. The interference term is considerably simplified for centrosymmetric systems (when $L_j''=S_j''=0$). Then,

$$\left.\frac{d\sigma}{d\Omega}\right|_I = -\left[\frac{e^2}{mc^2}\right]^2 \frac{\hbar\omega}{mc^2}\{(\sin 2\theta)(1+P_\zeta)\rho'' S_2'' + (\sin 2\theta)(\cos 2\theta)(1-P_\zeta)\rho''[2(\sin^2\theta)L_2+S_2]$$
$$+4(\sin^2\theta)P_\eta[(\cos^3\theta)\rho'(L_1+S_1)-(\sin^3\theta)\rho' S_3]$$
$$-4(\sin^2\theta)P_\xi[(\sin^2\theta)(\cos\theta)\rho''(L_1+S_1)-(\sin\theta)(\cos^2\theta)\rho'' S_2]\} . \tag{17}$$

It is seen in this case that the circular component couples to the real part of the electronic form factor, while both linear components couple to the imaginary part of the electronic form factor.

V. EXAMPLES

We now apply the general formulas obtained above to several simple examples of magnetic structures. We recall in this regard that synchrotron radiation is predominantly linearly polarized within the median plane of the storage ring ($P_\zeta=\pm 1$, depending on the orientation of the diffraction plane) and elliptically polarized above and below the median plane[19] ($P_\eta, P_\zeta \neq 0$). The detailed polarization dependence of the incident beam depends on a number of machine parameters including beam size, magnet geometry, electron energy, etc.

A. Ferromagnets

In ferromagnets the magnetic and charge scattering are coincident in reciprocal space. Since the magnetic scattering is typically reduced from the charge scattering by $> \sim 10^{-6}$ it is difficult to measure the magnetic scattering from ferromagnets directly. One method to over come this limitation is to introduce a magnetic field and measure the flipping ratio, thereby isolating the interference term in the cross section.[4,6] As will be seen, it is also possible to isolate the interference term by "flipping" the incident polarization.[5] In addition, because the magnetic scattering also flips the incident polarization (for some geometries), it is in principle possible to measure the pure magnetic scattering from a ferromagnet by analyzing the polarization of the scattered beam. Experiments performed to analyze the polarization of the magnetically scattered beam are described in references 10 and 20. In the Appendix we develop a formalism for these experimental schemes by introducing the D matrix for detection efficiency. For written simplicity we assume below that the spin- and orbital-angular-momentum densities are collinear.

(i) If $\mathbf{L}$ and $\mathbf{S}$ are perpendicular to the diffraction plane (parallel to $\hat{U}_2$), then

$$\langle M_m \rangle = \sin(2\theta)\begin{bmatrix} S & 0 \\ 0 & 2(\sin^2\theta)L+S \end{bmatrix}$$

and the interference term is

$$\left.\frac{d\sigma}{d\Omega}\right|_I = \left[\frac{e^2}{mc^2}\right]^2 \left[-\frac{\hbar\omega}{mc^2}\right](\sin 2\theta)\big((1+P_\zeta)(\rho' S''-\rho'' S')$$
$$+(1-P_\zeta)(\cos 2\theta)\{\rho'[2(\sin^2\theta)L''+S'']-\rho''[2(\sin^2\theta)L'+S']\}\big) ,$$

independent of P_ξ and P_η. In this case the real and imaginary parts of the charge form factor multiply the imaginary and real parts of the magnetic structure factor, respectively. The interference cross sections for purely circular and 45°-linear incident polarizations are identical and equal to the result for $\mathbf{P}=0$. Note that for purely linear incident polarization ($P_\zeta=\pm 1$) it is possible to separate L and S by alternately scattering in the horizontal and vertical planes. For centrosymmetric systems with $P_\zeta=1$ we recover the simple result[4,6]

$$\left.\frac{d\sigma}{d\Omega}\right|_I=\left[\frac{e^2}{mc^2}\right]^2\left[\frac{-2\hbar\omega}{mc^2}\right](\sin 2\theta)\rho'' S \ .$$

The magnetic scattering for L and S along $\hat{\mathbf{U}}_2$ is

$$\left.\frac{d\sigma}{d\Omega}\right|_m=\left[\frac{e^2}{mc^2}\right]^2\left[\frac{\hbar\omega}{mc^2}\right]^2\frac{1}{2}(\sin^2 2\theta)[(1+P_\zeta)|S|^2+(1-P_\zeta)|2(\sin^2\theta)L+S|^2] \ ,$$

independent of P_ξ and P_η. The final polarizations are

$$P'_\xi=(P_\xi\{S'[2(\sin^2\theta)L'+S']+S''[2(\sin^2\theta)L''+S'']\}$$
$$-P_\eta\{S'[2(\sin^2\theta)L''+S'']-S''[2(\sin^2\theta)L'+S']\})/\tfrac{1}{2}[(1+P_\zeta)|S|^2+(1-P_\zeta)|2(\sin^2\theta)L+S|^2] \ ,$$

$$P'_\eta=(-P_\xi\{S''[2(\sin^2\theta)L'+S']-S'[2(\sin^2\theta)L''+S'']\}$$
$$+P_\eta\{S'[2(\sin^2\theta)L'+S']+S''[2(\sin^2\theta)L''+S'']\})/\tfrac{1}{2}[(1+P_\zeta)|S|^2+(1-P_\zeta)|2(\sin^2\theta)L+S|^2] \ ,$$

$$P'_\zeta=\frac{(1+P_\zeta)|S|^2-(1-P_\zeta)|2(\sin^2\theta)L+S|^2}{(1+P_\zeta)|S|^2+(1-P_\zeta)|2(\sin^2\theta)L+S|^2} \ .$$

For noncentrosymmetric systems the magnetic scattering mixes the 45°-linear and circular components. Note also that for $\mathbf{L}=0$,

$$\frac{d\sigma}{d\Omega}=\left[\frac{e^2}{mc^2}\right]^2\left[\frac{\hbar\omega}{mc^2}\right]^2(\sin^2 2\theta)|S|^2, \quad \mathbf{P}'=\mathbf{P} \ .$$

Thus, in this configuration it is the orbital magnetization density which introduces the polarization dependence into the magnetic cross section. Finally, we point out that for unpolarized incident radiation ($\mathbf{P}=0$) and $\mathbf{L}=0$, the magnetic scattering is also unpolarized, $\mathbf{P}'=0$.

(ii) If L and S are in the diffraction plane and parallel to $\hat{\mathbf{U}}_1$, then

$$\langle M_m\rangle=-i(\sin 2\theta)(\sin\theta)(L+S)\sigma_\eta \ ,$$

where σ_η is the Pauli matrix defined above. Setting $P_\xi=0$, the interference term is

$$\left.\frac{d\sigma}{d\Omega}\right|_I=\left[\frac{e^2}{mc^2}\right]\left[\frac{-\hbar\omega}{mc^2}\right](\sin^2 2\theta)(\cos\theta)P_\eta$$
$$\times[\rho'(L'+S')-\rho''(L''+S'')] \ .$$

In contrast to the last example, the interference scattering now depends on the product of the real parts of the charge and magnetic structure factors, on the product of the imaginary parts of the charge and magnetic structure factors, on the degree of circular polarization, and on the sum (L+S). Because of the linear dependence on P_η it is possible to isolate the interference term by taking the difference in intensities above and below the median plane of the storage ring (as well as by measuring flipping ratios in a magnetic field) as has been demonstrated in a powdered ferrite.[5]

The magnetic scattering is given by

$$\left.\frac{d\sigma}{d\Omega}\right|_m=\left[\frac{e^2}{mc^2}\right]\left[\frac{\hbar\omega}{mc^2}\right]^2\sin^2 2\theta\sin^2\theta\,|\mathbf{L}+\mathbf{S}|^2 \ ,$$

independent of incident polarization. The final polarization is

$$\mathbf{P}'=(P_\xi,-P_\eta,-P_\zeta) \ .$$

The magnetic scattering flips the linear and 45°-linear components, but not the circular component.[21] This suggests that for purely linear incident polarization $P_\zeta=1$ the magnetic scattering may be directly measured by analyzing the rotated linear component.

(iii) If L and S are in the diffraction plane[10,22] parallel to $-\hat{\mathbf{U}}_3$, then

$$\langle M_m\rangle=2(\sin^3\theta)S\sigma_\xi \ ,$$

where σ_ξ is the Pauli matrix defined above. The magnetic scattering is

$$\left.\frac{d\sigma}{d\Omega}\right|_m=\left[\frac{e^2}{mc^2}\right]^2\left[\frac{\hbar\omega}{mc^2}\right]^2 4|S|^2\sin^6\theta \ ,$$

independent of the incident polarization and orbital-angular-momentum density. In contrast to neutron scattering, the cross section for magnetic x-ray scattering is nonzero when the momentum transfer and the magnetization are collinear. The final polarization is

$$\mathbf{P}'=(P_\xi,-P_\eta,-P_\zeta) \ .$$

The magnetic scattering flips the initial circular and linear polarizations, again suggesting the possibility of measuring it directly by analyzing the polarization of the scattered beam. Setting $P_\xi=0$, the interference term is

$$\left.\frac{d\sigma}{d\Omega}\right|_I=\left[\frac{e^2}{mc^2}\right]^2\left[\frac{\hbar\omega}{mc^2}\right]4(\sin^3\theta)P_\eta(\rho'S'-\rho''S'') .$$

The interference term is again linear in P_η and independent of the orbital-angular-momentum density.

We remark that, in principle, the spin and orbital magnetic-moment contributions to the cross section may each be separately measured in ferromagnets. For example, in cases (ii) and (iii) above (and assuming a centrosymmetric system), by rotating the moments from $\hat{U}_1$ to $\hat{U}_3$, and measuring flipping ratios in each direction, the interference scattering is first proportional to $L+S$ and then to S. The directions $\hat{U}_1$ and $\hat{U}_3$ are particularly convenient as the ratio R of the two cross sections is also simple,

$$R=\frac{(\sin\theta)^3}{\cos\theta}\frac{S}{L+S} .$$

Similarly, by analyzing the final polarization for two directions of the moment, the pure magnetic scattering may also be used to separate L and S. Provided the incident polarization is well characterized, these same techniques apply to the directions $\hat{U}_1$ and $\hat{U}_2$.

It is also worth commenting that the angular and polarization dependence of the magnetic and interference scattering and the final polarization of the scattered beam may all be used to determine unknown ferromagnetic structures. For example, the existence of interference or magnetic scattering at chemical Bragg positions for linearly polarized incident radiation requires a component of the moment parallel to $\hat{U}_2$. Similarly, the existence of magnetic or interference scattering for circularly polarized incident radiation requires that magnetization density lie in the $\hat{U}_1$-$\hat{U}_3$ plane. These directions may be distinguished by studying the angular dependence of the cross section for several different reflections or by analyzing the final polarization. A general technique for determining unknown magnetic structures by x-ray scattering is to study the angular dependence of the magnetic or interference cross sections, Eq. (14) and (16), for rotations of the sample about the momentum transfer. Although these last remarks have been made in a discussion of ferromagnetic structures, similar statements are possible for antiferromagnetic structures, and particularly for uniaxially modulated structures.

B. Antiferromagnets

In the following we make an analogy to the rare-earth elements and write the structure factors for $\mathbf{L}(\mathbf{K})$ and $\mathbf{S}(\mathbf{K})$ in terms of a single quantum $\mathbf{J}=\mathbf{L}+\mathbf{S}$. Thus,

$$\mathbf{L}(\mathbf{K})=\phi_l(\mathbf{K})\sum_{n\ \text{atoms}}^{\text{unit cell}}\mathbf{J}_n(0)e^{i\mathbf{K}\cdot\mathbf{n}}$$

and

$$\mathbf{S}(\mathbf{K})=\phi_s(\mathbf{K})\sum_{n\ \text{atoms}}^{\text{unit cell}}\mathbf{J}_n(0)e^{i\mathbf{K}\cdot\mathbf{n}} ,$$

where

$$\phi_l(\mathbf{K})=\frac{\frac{1}{2}\left\langle a\left|\mathbf{J}\cdot\sum_j^{\text{atom}}[\mathbf{L}_j(0)f(\mathbf{K}\cdot\mathbf{r}_j)+f(\mathbf{K}\cdot\mathbf{r}_j)\mathbf{L}_j(0)]\right|a\right\rangle}{(\frac{1}{2}\mathbf{L}\cdot\mathbf{J}+\mathbf{S}\cdot\mathbf{J})} ,$$

$$\phi_s(\mathbf{K})=\frac{\left\langle a\left|\mathbf{J}\cdot\sum_j^{\text{atom}}\mathbf{s}_je^{i\mathbf{K}\cdot\mathbf{r}_j}\right|a\right\rangle}{(\frac{1}{2}\mathbf{L}\cdot\mathbf{J}+\mathbf{S}\cdot\mathbf{J})},\quad \mathbf{J}_n=J\sum_l g_l(\tau\cdot\mathbf{n})\hat{\mathbf{U}}_n(i) .$$

In these expressions $\mathbf{n}$ is the vector giving the position of the nth atom in a magnetic unit cell, τ is the modulation wavevector, g_l gives the lth component of the magnetization in the $\hat{U}$ basis, and $\hat{\mathbf{U}}_n(i)$ specifies the direction of the ith component of the magnetization of the nth atom. $\phi_s(\mathbf{K})$ and $\phi_l(\mathbf{K})$ are the ionic form factors for the spin- and orbital-angular-momentum densities, respectively.[15,22]

(i) For uniaxially modulated systems, $\mathbf{J}_n=Jg(\tau\cdot\mathbf{n})\hat{\mathbf{U}}_l$ (g periodic) and all the results derived above for ferromagnets apply by introducing the prefactor

$$\left|\sum g(\tau\cdot\mathbf{n})e^{i(\mathbf{K}-\tau)\cdot\mathbf{n}}\right|^2J^2$$

and by making the replacements $S_l\to\phi_s$ and $L_l\to\phi_l$. In contrast to the case for ferromagnets, the magnetic scattering is now located at positions distinct from the charge scattering and so may be directly measured. It follows, of course, that the interference scattering is zero. By measuring the cross section of the magnetic scattering for suitable orientations of the moments (for example, by rotation of the sample about the momentum transfer or by use of a magnetic field), detailed magnetic-structure determinations and separation of the orbital and spin form factors are possible in a manner analogous to that in ferromagnets.

(ii) The final example we consider is that of a simple basal plane spiral with modulation wavevector τ oriented along $\hat{U}_3$, $\tau=\tau\hat{U}_3$. In that case we have

$$\mathbf{J}_n=[\cos(\tau\cdot\mathbf{n})\hat{\mathbf{x}}+\sin(\tau\cdot\mathbf{n})\hat{\mathbf{y}}]$$

$$=\frac{J}{2}(\hat{\mathbf{U}}_+e^{-i\tau\cdot\mathbf{n}}+\hat{\mathbf{U}}_-e^{i\tau\cdot\mathbf{n}}) ,$$

where $\hat{U}_+=\hat{U}_1+i\hat{U}_2$ and $\hat{U}_-=\hat{U}_1-i\hat{U}_2$. Then $M_m\to M_m^++M_m^-$, giving magnetic scattering at satellites split symmetrically about each chemical Bragg peak along the direction of $\hat{U}_3$. Thus

$$\langle M_m^\pm\rangle=\frac{J}{2}\sum_n^{\text{cell}}e^{i(\mathbf{K}\mp\tau)\cdot\mathbf{n}}(\sin2\theta)\times\begin{bmatrix}\pm i\phi_s & -\sin\theta(\phi_l+\phi_s)\\(\sin\theta)(\phi_l+\phi_s) & \pm i[2(\sin^2\theta)\phi_l+\phi_s]\end{bmatrix} .$$

For simplicity we specialize to the case of linear polarization with $P_\xi=1$ and assume ϕ_s and ϕ_l are real. Then the magnetic scattering may be written

$$\frac{d\sigma}{d\Omega}\bigg|_m=\left[\frac{e^2}{mc^2}\right]^2\left[\frac{\hbar\omega}{mc^2}\right]^2\left|\sum_n e^{i(\mathbf{K}\mp\tau)\cdot\mathbf{n}}\right|^2\left|\frac{J}{2}\right|^2 \times(\sin^2 2\theta)(|\phi_s|^2+|\phi_l+\phi_s|^2\sin^2\theta)$$

and the final polarization is

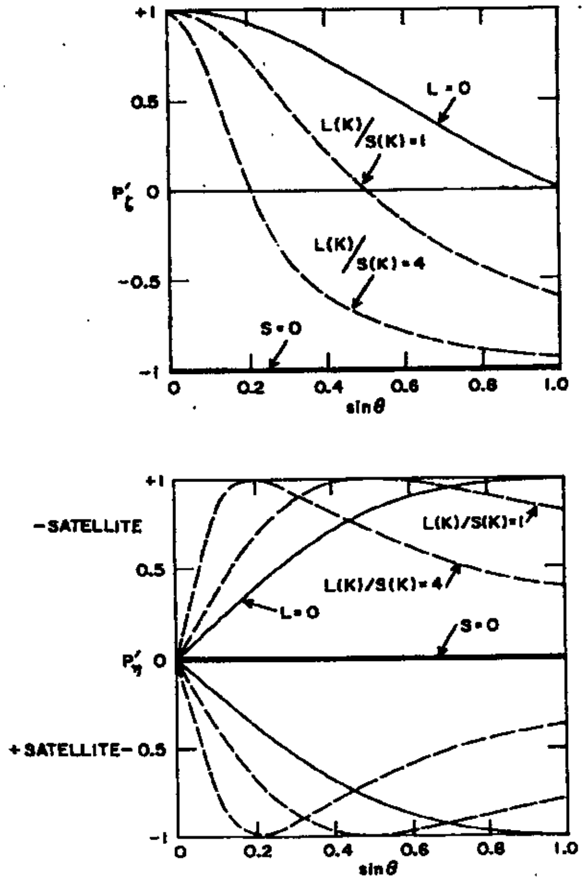

FIG. 3. K dependence of the scattered linear and circular Poincaré coefficients for linearly polarized radiation ($P_\xi=1$) incident upon a magnetic spiral. Upper: When L=0, then $P'_\zeta=[(1-\sin^2\theta)/(1+\sin^2\theta)]$ is positive definite and decreases from 1 to 0 with increasing momentum transfer K. When S=0 (and $\theta>0$), then $P'_\zeta=-1$. The dashed lines illustrate the general behavior for two simple cases when the ratio of orbital to spin form factor is constant. Lower: When L=0 the scattered circular Poincaré coefficient for the positive satellite is negative definite and decreases from 0 to −1 $[P'_\eta=-2\sin\theta/(1+\sin^2\theta)]$. When S=0, then $P'_\eta=0$. The behavior for the negative satellite mirrors that for the positive satellite. For nonzero spin there is always a value of θ for which the scattered beam may be totally circular.

$$P'_\xi=0\ ,$$

$$P'_\eta=\frac{\mp 2(\sin\theta)\phi_s(\phi_l+\phi_s)}{|\phi_s|^2+|\phi_l+\phi_s|^2\sin^2\theta}\ ,$$

$$P'_\zeta=\frac{|\phi_s|^2-|\phi_l+\phi_s|^2\sin^2\theta}{|\phi_s|^2+|\phi_l+\phi_s|^2\sin^2\theta}\ .$$

From this result it is apparent that the term in the cross section proportional to $|\phi_s|^2$ is the probability for polarization parallel to $\hat{\epsilon}_\perp$ in Fig. 1, while the term proportional to $|\phi_l+\phi_s|^2\sin^2\theta$ is that for polarization parallel to $\hat{\epsilon}_\parallel$. Thus, by analyzing the degree of linear polarization in the scattered beam it is possible to separately measure the real form factors $\phi_l(\mathbf{K})$ and $\phi_s(\mathbf{K})$ in a magnetic spiral[20] (see Fig. 3). Provided there is a single spiral domain of well-defined helicity, then the circular components of the positive and negative satellites will have opposite helicity, as shown in Fig. 3. It follows that by adding a circularly polarized component to the incident beam and measuring the degree of linear polarization for the two satellites, the helicity of the spiral may be determined (see Fig. 4). Finally, note that if

$$\sin^2\theta=\frac{|\phi_s(\mathbf{K})|^2}{|\phi_l(\mathbf{K})+\phi_s(\mathbf{K})|^2}\ ,$$

then the scattering is totally circular. Although the efficiency is very low ($<10^{-6}$), it is therefore possible to completely convert linearly polarized radiation to circu-

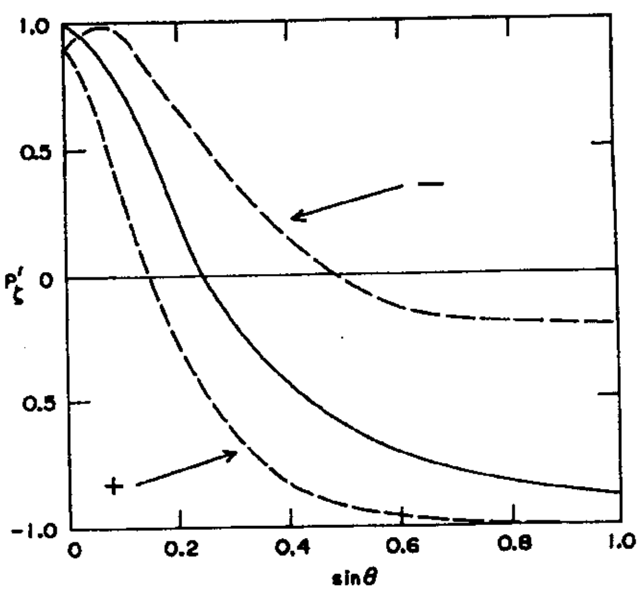

FIG. 4. Linear Poincaré coefficient for scattering from a magnetic spiral for the case $L(K)/S(K)=3$. The solid line shows P'_ζ for incident Poincaré vector $P_\xi=1$ and $P_\eta=0$. There is no difference between positive and negative satellites. The dashed lines illustrate the change when a small component of circular polarization is introduced in the incident beam ($P_\xi=0.90$ and $P_\eta=0.43$).

lar by scattering from a magnetic spiral. From theoretical calculations of the form factors for ϕ_l and ϕ_s,[22] it turns out that this condition is approximately satisfied for the $(0\,0\,2\frac{1}{4})$ satellite of holmium with ~ 10 keV incident photon energy.

VI. SUMMARY

In this paper we have derived general expressions for the polarization dependence of magnetic x-ray scattering for high photon energies and indicated a variety of directions for new kinds of synchrotron experiments. The extension of this work into the resonant regime, when the photon energy is near an excitation energy of the solid, will likely produce novel effects and remains to be carried out. Finally, it is worth mentioning that while polarization-dependent magnetic x-ray scattering experiments are possible with present-day synchrotron sources, reliable intensity measurements of the sort required for some of these experiments are still difficult. This class of experiment will clearly benefit from the next generation of synchrotron sources, and particularly by the development of beamlines or insertion devices with tunable polarization characteristics.

Note added in proof. After completion of this manuscript, we received a copy of this work by S. Lovesy [J. Phys. C (in press)].

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APPENDIX: D MATRIX FOR DETECTION EFFICIENCY

Quantitative polarization analysis may be included in the formalism by defining a matrix D which represents the detection efficiency and polarization sensitivity of the detector assembly:

$$\frac{d\sigma}{d\Omega}=\left[\frac{e^2}{mc^2}\right]^2 \mathrm{tr}(DM\rho M^\dagger)\ .$$

In this formalism an open detector has the D matrix

$$D_1=e_1 1\ ,$$

where e_1 is the quantum efficiency for the detector. A simple analyzing crystal diffracting within the scattering plane has the D matrix

$$D_2=e_2\begin{bmatrix}1 & 0\\ 0 & \cos^2 2\theta\end{bmatrix}$$

$$=\frac{e_2}{2}(1+\cos^2 2\theta)1+\frac{e_2}{2}(1-\cos^2 2\theta)\sigma_\zeta\ ,$$

where e_2 is the analyzer reflectivity and 2θ its Bragg angle. The D matrix for a linear polarization analyzer oriented at ϕ° to the scattering plane[10,20] is

$$D_3=e_3\begin{bmatrix}\cos^2\phi & 0\\ 0 & \sin^2\phi\end{bmatrix}=\frac{e_3}{2}[1+\cos(2\phi)\sigma_\zeta]\ ,$$

where e_3 is the analyzer crystal reflectivity. Operationally, the D matrix for the linear polarization analyzer simply multiplies m_{11} and m_{12} by $\cos\phi$ and multiplies m_{22} and m_{21} by $\sin\phi$.

[1] M. Brunel and F. de Bergevin, Acta Crystallogr. Sect. A 37, 324 (1981).
[2] D. Gibbs, D. E. Moncton, K. L. D'Amico, J. Bohr, B. Grier, Phys. Rev. Lett. 55, 234 (1985); D. Gibbs, J. Bohr, J. D. Axe, D. E. Moncton, and K. L. D'Amico, Phys. Rev. B 34, 8182 (1986); J. Bohr, D. Gibbs, D. E. Moncton, and K. L. D'Amico Physica A 140, 349 (1986).
[3] A. Goldman, K. Mohanty, G. Shirane, P. Horn, R. L. Greene, C. Peters, J. Thurston, and R. J. Birgeneau, Phys. Rev. B 36, 5609 (1987).
[4] F. de Bergevin and M. Brunel, Acta Crystallogr. Sect. A 37, 314 (1981).
[5] P. M. Brunel, G. Patraff, F. de Bergevin, F. Rousseau, and M. Lemonnier, Acta Cryallogr. Sect. A 39, 84 (1983).
[6] C. Vettier, D. B. McWhan, E. M. Gyorgy, J. Kwo, B. M. Buntschuh, and B. W. Batterman, Phys. Rev. Lett. 56, 757 (1986).
[7] M. J. Cooper, D. Laundy, D. A. Cardwell, D. N. Timms, R. S. Holt, and G. Clark, Phys. Rev. B 34, 5984 (1986).
[8] D. Mills (unpublished).
[9] K. Namikawa, M. Ando, T. Nakajima, and H. Kawata, J. Phys. Soc. Jpn. 54, 4099 (1985).
[10] D. E. Moncton, D. Gibbs, and J. Bohr, Nucl. Instrum. Methods A26, 839 (1986).
[11] M. Blume, J. Appl. Phys. 57, 3615 (1985).
[12] P. Platzmann and N. Tzoar, Phys. Rev. B 2, 3556 (1970).
[13] F. E. Low, Phys. Rev. 96, 1428 (1954).
[14] M. Gell-Mann and M. L. Goldberger, Phys. Rev. 96, 1433 (1954).
[15] G. T. Trammel, Phys. Rev. 92, 1387 (1953).
[16] O. Steinsvoll, G. Shirane, R. Nathans, M. Blume, H. A. Alperin, and S. J. Pickart, Phys. Rev. 161, 499 (1967).
[17] M. Blume, Phys. Rev. 130, 1670 (1963); M. Blume and O. C. Kistner, *ibid.* 171, 417 (1968).
[18] U. Fano, Rev. Mod. Phys. 29, 74 (1957).
[19] Greene, G. K. in *Proceedings of 1976 Spectra and Optics of Synchrotron Radiation* (National Technical Information Service, Springfield, Virginia, 1976).
[20] D. Gibbs, D. Harshman, D. McWhan, D. Mills, and C. Vettier (unpublished).
[21] Whenever $M_m \alpha\sigma_i$ (σ_i a Pauli matrix), then $P_j'=-P_j$ $(i\neq j)$ and $P_i'=P_i$. This follows from the commutation properties governing the Pauli matrices.
[22] M. Blume, A. J. Freeman, and R. E. Watson, J. Chem. Phys. 37, 1242 (1962); 41, 1878 (1964).

X-Ray Resonance Exchange Scattering

J. P. Hannon and G. T. Trammell
Physics Department, Rice University, Houston, Texas 77251
and
M. Blume and Doon Gibbs
Brookhaven National Laboratory, Upton, New York 11973
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Large resonant magnetization-sensitive x-ray scattering is predicted to occur in the vicinity of L_{II}, L_{III}, and M_{II}–M_V absorption edges in the rare-earth and actinide elements, and at the K and L edges in the transition elements. These "magnetic" resonances result from electric multipole transitions, with the sensitivity to the magnetization arising from exchange. For some transitions, the magnetic scattering will be comparable to the charge scattering. The general features of the observed L_{III} resonance in Ho are discussed.

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In the course of investigating the magnetic spiral structure of a holmium crystal using the x-ray magnetic scattering of synchrotron radiation, Gibbs *et al.*[1] observed a large resonant enhancement (by a factor of 50) in the magnetic satellite intensities when the energy of the incident x rays was tuned through the L_{III} absorption edge. Second-, third-, and fourth-harmonic satellites were also observed at resonance. A complex polarization dependence was found, with the resonance peaks for the σ-σ and σ-π components of the magnetic scattering being separated by about 6 eV for the first two harmonics, and occurring at the same resonance energy for the third and fourth harmonics.

This behavior (resonant increase, additional harmonics, polarization dependence) can be understood on the basis of electric quadrupole ($E2$) transitions to $4f$ levels and electric dipole ($E1$) transitions to $5d$ levels. It is noteworthy that this "magnetic" scattering results from *electric* multipole transitions. This is due to the exclusion principle allowing only transitions to unoccupied orbitals, resulting in an "exchange interaction" which is sensitive to the magnetization of the f and d bands.

To get a strong resonant enhancement, the scattering must involve a low-order electric multipole transition ($E1$ or $E2$) between a core level and either an unfilled atomic shell, or a narrow band.[2] In the latter case, the atomiclike nature of the transition is increased because the core hole gives an additional binding of the excited level.

For the rare earths, enhanced magnetic resonance scattering will occur at the L_{II}, L_{III}, M_{II}, and M_{III} absorption edges, involving the $E2$ transitions to the tightly bound $4f$ shell, and the $E1$ transitions to the $5d$ band. Although the latter transition is $E1$, the strength of the magnetic scattering depends on the induced polarization and exchange splitting of the band, resulting in a contribution of comparable magnitude to the $E2$ transition to the $4f$ shell. At the M_{IV} and M_V edges, the very strong $E1$ transition to the $4f$ shell will give a resonant magnetic scattering amplitude on the order of $100r_0$! The resonances at the K and L_I edges will be relatively weak, involving $E3/M2$ transitions to the $4f$ shell, and $E2$ transitions to the $5d$ band. The L_{II} and L_{III} resonances lie in the 1–2-Å region, well suited for diffraction studies of magnetism in crystals. The strong $E1$ resonances at the M_{IV} and M_V edges lie in the 5–10-Å region, but can still be used for diffraction studies of the long-range antiferromagnetic spirals, and for grazing incidence studies of surface magnetism, and they will give rise to very strong magneto-optical effects in reflection and transmission in magnetic samples.

Similar magnetization-sensitive electric multipole resonances should be useful for the study of the magnetic properties of the transition elements and the actinide series. These large resonant enhancements should also be important for the study of two-dimensional magnetic ordering, with possible applications to high-T_c superconductors.

The coherent elastic-scattering amplitude for nonresonant magnetic x-ray scattering from a magnetic ion is given by[3-7]

$$f^{(\mathrm{mag})} = i r_0 (\hbar\omega/mc^2) f_D [\tfrac{1}{2}\mathbf{L}(K)\cdot\mathbf{A} + \mathbf{S}(K)\cdot\mathbf{B}],$$

where $\mathbf{L}(K)$ and $\mathbf{S}(K)$ are the atomic orbital and spin magnetization densities, $\mathbf{A}$ and $\mathbf{B}$ are polarization vectors determined by $\mathbf{k}_0, \mathbf{e}_0, \mathbf{k}_f, \mathbf{e}_f$, and f_D is the Debye-Waller factor. The x-ray magnetic scattering is considerably weaker than the charge scattering, with magnitudes typically $\approx 0.01 r_0$. The total coherent elastic-scattering amplitude is $f \approx f_0 + f' + if'' + f^{(\mathrm{mag})}$, where $f_0 \propto -Zr_0$ is the usual Thomson contribution, and $f' + if''$ is the contribution from dispersive and absorptive processes. The resonant scattering processes we consider below contribute to $f' + if''$.

For an electric 2^L-pole resonance (EL) in a magnetic ion, the contribution to the coherent scattering amplitude is given by[2,8,9]

$$f_{EL}^{(\mathrm{xres})}(\mathbf{k}_f\mathbf{e}_f;\mathbf{k}_0\mathbf{e}_0)=4\pi\lambda f_D\sum_{M=-L}^{L}[\mathbf{e}_f^*\cdot\mathbf{Y}_{LM}^{(e)}(\hat{\mathbf{k}}_f)\mathbf{Y}_{LM}^{(e)*}(\hat{\mathbf{k}}_0)\cdot\mathbf{e}_0]F_{LM}^{(e)}(\omega), \tag{1}$$

where

$$F_{LM}^{(e)}(\omega)=\sum_{\alpha,\eta}\left[\frac{p_\alpha p_\alpha(\eta)\Gamma_x(\alpha M\eta;EL)/\Gamma(\eta)}{x(\alpha,\eta)-i}\right].$$

$|\alpha)$ is the initial ground state of the ion, and $|\eta)=|\alpha(h\mu_h)^{-1}(n\mu_n)^{+1})$ is the excited state with an electron excited to the level $(n\mu_n)$ leaving a hole in the core level $(h\mu_h)$, where μ_n and μ_h are the appropriate spin and angular momentum indices. The excited states $(n\mu_n)$ are more tightly bound than the corresponding states in the unexcited ion due to the potential of the core hole. p_α gives the statistical probabilities for the various possible initial state $|\alpha)$, and $p_\alpha(\eta)$ gives the probability that the $(n\mu_n)$ state is unoccupied in $|\alpha)$. $p_\alpha(\eta)$ is determined by the overlap integrals of the "old" orbitals which are occupied in the initial state $|\alpha)$ with the orbital $(n\mu_n)$ which is a "new" level in the presence of the $(h\mu_h)$ core hole, a familiar procedure in shakeoff calculations. Γ_x is given to lowest order in kr by[9]

$$\Gamma_x(\alpha M\eta;EL)=8\pi\left[\frac{e^2}{\lambda}\right]\left[\frac{L+1}{L}\right]\left|(\alpha|\sum_l j_L(kr_l)Y_{LM}(\hat{\mathbf{r}}_l)|\eta)\right|^2, \tag{2}$$

where j_L is the spherical bessel function of order L. Summed over M, Γ_x gives the *partial* width for *EL radiative decay* from $|\eta)\rightarrow|\alpha)$. $\Gamma(\eta)$ is the *total width* for the excited state $|\eta)$, which is determined by *all* radiative (from any shell) and nonradiative (Auger, Coster-Kronig) deexcitations of $|\eta)$. $\Gamma(\eta)$ is typically ≈ 1–10 eV, so that the scattering will be fast $\approx 10^{-16}$ s, accounting for the presence of the Debye-Waller factor in Eq. (1).[8] In the resonance denominator, $x(\alpha,\eta)=[\epsilon(\eta)-\epsilon(\alpha)-\hbar\omega]/[\Gamma(\eta)/2]$ gives the deviation from resonance in units of $\Gamma(\eta)/2$. The polarization dependence is determined by the vector spherical harmonics $\mathbf{Y}_{LM}^{(e)}$ for an EL transition,[10] and the relevant factors which appear in Eq. (2) can be expressed as products of the components of $\mathbf{k}$ and $\mathbf{e}$,

$$\mathbf{e}\cdot\mathbf{Y}_{LM}^{(e)}(\hat{\mathbf{k}})=\left[\frac{4\pi(2L+1)}{3(L+1)}\right]^{1/2}\sum_{\mu=-1}^{1}C(1\,L-1\,L;\mu\,M-\mu)Y_{L-1,M-\mu}(\hat{\mathbf{k}})Y_{1\mu}(\hat{\mathbf{e}}).$$

For the *electric dipole transitions* ($E1$), we have

$$[\mathbf{e}_f^*\cdot\mathbf{Y}_{1\pm1}^{(e)}(\hat{\mathbf{k}}_f)\mathbf{Y}_{1\pm1}^{(e)*}(\hat{\mathbf{k}}_0\cdot\mathbf{e}_0]=\left[\frac{3}{16\pi}\right][\mathbf{e}_f^*\cdot\mathbf{e}_0\mp i(\mathbf{e}_f^*\times\mathbf{e}_0)\cdot\hat{\mathbf{z}}_J-(\mathbf{e}_f^*\cdot\hat{\mathbf{z}}_J)(\mathbf{e}_0\cdot\hat{\mathbf{z}}_J)],$$

$$[\mathbf{e}_f^*\cdot\mathbf{Y}_{10}^{(e)}(\hat{\mathbf{k}}_f)\mathbf{Y}_{10}^{(e)*}(\hat{\mathbf{k}}_0)\cdot\mathbf{e}_0]=\left[\frac{3}{8\pi}\right][(\mathbf{e}_f^*\cdot\hat{\mathbf{z}}_J)(\mathbf{e}_0\cdot\hat{\mathbf{z}}_J)],$$

giving the scattering amplitude

$$f_{E1}^{(\mathrm{xres})}=\tfrac{3}{4}\lambda\{\mathbf{e}_f^*\cdot\mathbf{e}_0[F_{11}^{(e)}+F_{1-1}^{(e)}]-i(\mathbf{e}_f^*\times\mathbf{e}_0)\cdot\hat{\mathbf{z}}_J[F_{11}^{(e)}-F_{1-1}^{(e)}]+(\mathbf{e}_f^*\cdot\hat{\mathbf{z}}_J)(\mathbf{e}_0\cdot\hat{\mathbf{z}}_J)[2F_{10}^{(e)}-F_{11}^{(e)}-F_{1-1}^{(e)}]\}, \tag{3}$$

where $\mathbf{z}_J$ is the direction of the quantization axis defined by the local moment of the ion. Thus there are only three distinct polarization responses for $E1$ scattering[9]: The first term, $\mathbf{e}_f^*\cdot\mathbf{e}_0$, is independent of the direction of the magnetic moment. The second term, $-i(\mathbf{e}_f^*\times\mathbf{e}_0)\cdot\mathbf{z}_J$, depends linearly on the direction of the magnetic moment, and will give first-harmonic satellites in an antiferromagnet. If we use the linear σ,π polarizations as basis (which are perpendicular and parallel to the $\mathbf{k}_0$-$\mathbf{k}_f$ scattering plane, respectively), incident σ_0 scatters only to π_f, while incident π_0 scatters to both σ_f and π_f. The third contribution, $(\mathbf{e}_f^*\cdot\mathbf{z}_J)(\mathbf{e}_0\cdot\mathbf{z}_J)$, depends quadratically on the moment direction, and will give second-harmonic satellites in a spiral antiferromagnet (and also a contribution to the zeroth harmonic). This term scatters either σ_0 or π_0 to both σ_f and π_f. The appearance of first- and second-harmonic magnetic satellites is a characteristic signature of a dipole transition ($E1$ or $M1$).

Two simplified examples illustrate the main ideas: First, if the ground state of the ion has a single hole in the $4f$ shell, then by Hund's-rule, in the fully aligned case, the empty orbital is $m_l=-3$, $m_s=-\frac{1}{2}$, which is also a state of good $j=\frac{7}{2}$, $m_j=-\frac{7}{2}$. Then in Eq. (1), $p_\alpha=1$ for the Hund's-rule ground state $|\alpha)$, and $p_\alpha(m_l,m_s)=1$ for $(m_l,m_s)=(-3,\downarrow)$, and zero otherwise. (Here we ignore the question of overlap integrals discussed below, but this should be less important for the highly localized $4f$ orbitals.) Then at the M_V edge, only $M=-1$ is allowed, the transition being $|3d_{5/2},m_j=-\frac{5}{2})\leftrightarrow|4f_{7/2},m_j=-\frac{7}{2})$. This corresponds to a circularly polarized electric dipole oscillator, with left-hand circulation about $+\mathbf{z}_J$. As a consequence, $F_{11}=F_{10}=0$ in Eq. (3), and $F_{1-1}=[\Gamma_x(\alpha,-1,\eta;E1)/\Gamma(\eta)]/[x-i]$ as given by Eqs. (1) and (2). All three polarization terms then contribute with equal amplitude to $f_{E1}^{(\mathrm{xres})}$ in Eq. (3), and so the magnetic scattering will be as large as the charge scattering. Fluorescence yield calculations[11] indicate that $(\Gamma_x/\Gamma)\approx 10^{-2}$ for the rare earths, so that magnetic resonance scattering amplitudes $\approx 100r_0$ should be possible for these soft x-ray resonances, giving very strong magneto-optical effects in both reflection and transmission.

As a second example, consider the L_{III}-edge resonance $2p_{3/2}\leftrightarrow 5d$, treating the "impurity" $5d$ states in the presence of the core hole as atomic levels $|5d,m_l,m_s\rangle$, with an exchange splitting Δ between the (lower energy) $|5d,m_l,\uparrow\rangle$ orbitals and the $|5d,m_l,\downarrow\rangle$ orbitals induced by the $4f$ moment. For such a system, the probability $p_a(5d,m_l,m_s)$ that the impurity orbital $|5d,m_l,m_s\rangle$ is empty would be determined by the overlap integrals of the occupied orbitals in the ground state $|\alpha\rangle$ with the impurity orbital. For simplicity, we will assume that $p_a(5d,m_l,m_s)\equiv p(m_s)$ independent of m_l. The partial radiative width is then

$$\Gamma_x((2p_{3/2}m_j)M(5d,m_l,m_s))=C^2(1,\tfrac{1}{2},\tfrac{3}{2};m_l-M,m_s,m_j)C^2(1,1,2;m_l-M,m_s,m_l)|\chi|^2,$$

where $|\chi|^2=\frac{24}{5}ke^2|(2p_{3/2}||kr||5d)|^2$, and the scattering amplitude becomes

$$f_{EL}^{(\mathrm{xres})}=F[\mathbf{e}_f^*\cdot\mathbf{e}_0 n_h+i(\mathbf{e}_f^*\times\mathbf{e}_0)\cdot\mathbf{z}_J P/4], \quad (4)$$

where $P=[n_e(\uparrow)-(\Delta/\Gamma)n_h$, $n_e(\uparrow)=5[p(\downarrow)-p(\uparrow)]$ is the net number of spin-up *electrons* in the $5d$ band, $n_h=5[p(\downarrow)+p(\uparrow)]$ is the number of *holes* in the $5d$ band, and $F=\lambda|\chi|^2]/3\Gamma(x-i)$. We have assumed that $\Delta\ll\Gamma$, giving an unresolved resonance doublet, and x is the deviation from the central frequency. There is no quadratic magnetic contribution $(\mathbf{e}_f^*\cdot\mathbf{z}_J)(\mathbf{e}_0\cdot\mathbf{z}_J)$ because of the assumed m_l independence of $p_a(5d,m_l,m_s)$. The linear magnetic contribution is seen to arise from both the spin polarization of a partially occupied band, and from the exchange splitting of the empty states, with the sign and magnitude of the "polarization factor" P depending on the relative magnitude of the two contributions. As an order-of-magnitude estimate for Ho, taking $\Delta\approx 0.3$ eV, $n_e(\uparrow)\approx 0.3$, $Fn_h\approx 30r_0/(x-i)$, $\Gamma\approx 10$ eV, and $n_h\approx 8$, gives $P\approx +0.07$; and a linear magnetic scattering contribution of $\approx +0.06r_0 i(\mathbf{e}_f^*\times\mathbf{e}_0\cdot\mathbf{z}_J)/(x-i)$.

For electric quadrupole transitions ($E2$), $f_{E2}^{(\mathrm{xres})}$ will contain thirteen distinct terms—order (0):

$$(\mathbf{k}_f\cdot\mathbf{k}_0)(\mathbf{e}_f^*\cdot\mathbf{e}_0),$$

order (1):

$$i(\mathbf{k}_f\cdot\mathbf{k}_0)(\mathbf{e}_f^*\times\mathbf{e}_0)\cdot\mathbf{z}_J+[\mathbf{k}_f\leftrightarrow\mathbf{e}_f,\mathbf{k}_0\leftrightarrow\mathbf{e}_0],$$

order (2):

$$(\mathbf{k}_f\cdot\mathbf{k}_0)(\mathbf{e}_f^*\cdot\mathbf{z}_J)(\mathbf{e}_0\cdot\mathbf{z}_J)+[\mathbf{k}_f\leftrightarrow\mathbf{e}_f]+[\mathbf{k}_0\leftrightarrow\mathbf{e}_0]+[\mathbf{k}_f\leftrightarrow\mathbf{e}_f,\mathbf{k}_0\leftrightarrow\mathbf{e}_0]+i(\mathbf{k}_f\times\mathbf{k}_0)\cdot\mathbf{z}_J(\mathbf{e}_f^*\times\mathbf{e}_0)\cdot\mathbf{z}_J,$$

order (3):

$$i(\mathbf{k}_f\cdot\mathbf{z}_J)(\mathbf{k}_0\cdot\mathbf{z}_J)(\mathbf{e}_f^*\times\mathbf{e}_0)\cdot\mathbf{z}_J+[\mathbf{k}_f\leftrightarrow\mathbf{e}_f]+[\mathbf{k}_0\leftrightarrow\mathbf{e}_0]+[\mathbf{k}_f\leftrightarrow\mathbf{e}_f,\mathbf{k}_0\leftrightarrow\mathbf{e}_0],$$

order (4):

$$(\mathbf{k}_f\cdot\mathbf{z}_J)(\mathbf{k}_0\cdot\mathbf{z}_J)(\mathbf{e}_f^*\cdot\mathbf{z}_J)(\mathbf{e}_0\cdot\mathbf{z}_J).$$

The relevant coefficients with which these terms contribute for each M will be given elsewhere. In a spiral antiferromagnet, each order will give rise to a separate magnetic satellite. The appearance of four harmonic satellites is a characteristic signature of a quadrupole resonance ($E2$ or $M2$). The polarization dependences of the four $E2$ magnetic contributions will generally allow all the possible combinations of $\sigma\leftrightarrow\sigma$, $\sigma\leftrightarrow\pi$, and $\pi\leftrightarrow\pi$ scattering. (In contrast, the first-order $E1$ harmonic only allows $\sigma\leftrightarrow\pi$ and $\pi\leftrightarrow\pi$ scattering.)

These ideas give a simple explanation for the complex resonance spectra obtained at the L_{III} edge in Ho (Ref. 1): The double-peak structure is the superposition of resonance arising from different transitions. The lower resonance several eV below the edge is the $E2$ transition $2p_{3/2}\leftrightarrow 4f$, giving rise to four harmonics, which were predicted and observed. The appearance of only two harmonics at the high-energy resonance, and the absence of $\sigma\leftrightarrow\sigma$ scattering in the first harmonic, identify this as an $E1$ resonance, presumably the $2p_{3/2}\leftrightarrow 5d$ transition. In Fig. 1, we give theoretical curves for the four harmonics. These curves are a combination of calculation and parametrization, carried out under the simplest approximations. The purposes here is qualitative illustration, and not a detailed fit to the data. We have calculated $f_{E2}^{(\mathrm{xres})}$ using nonrelativistic Hartree-Fock wave functions assuming a Hund's-rule ground state for the Ho ion, with four empty atomic orbitals $|4f,m_l,\downarrow\rangle$, $m_l=-3$ to 0. For $\sigma\leftrightarrow\sigma$ scattering, the calculated peak resonance-nonresonance ratio $f_{E2}^{(\mathrm{xres})}/f^{(\mathrm{mag})}=4.3i$ for the first harmonic, giving a 19/1 intensity ratio, in reasonable agreement with the observations. $f^{(\mathrm{mag})}$ only contributes to the first harmonic, interfering with $f_{E2}^{(\mathrm{xres})}$ for $\sigma\leftrightarrow\sigma$ scattering, giving a pronounced symmetry of the first-harmonic $\sigma\leftrightarrow\sigma$ resonance curve, with constructive interference predicted on the high-frequency side of resonance, as observed. The calculation of $f_{E1}^{(\mathrm{xres})}$ is more complicated. The $5d$ states are more extensive than the highly localized $4f$ orbitals, and it is necessary to include banding (or "hopping"), crystal-field mixing of the m_l

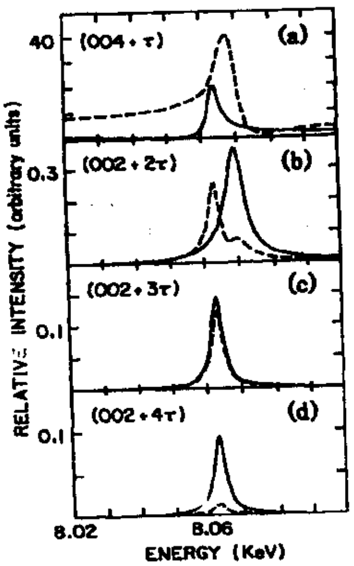

FIG. 1. Relative scattered intensities (theoretical) vs x-ray energy for the L_{III} edge in Ho: (a) $(004+\tau)$, (b) $(002+2\tau)$, (c) $(002+3\tau)$, and (d) $(002+4\tau)$. The solid lines give the $\sigma\leftrightarrow\sigma$ scattering, and the dashed lines give $\sigma\leftrightarrow\pi$.

orbitals, and exchange splitting. In addition, band occupation and induced polarization must be determined, as discussed above. These calculations are underway, but regardless of the detailed nature of the states, the parametric form for the polarization dependence is given by Eq. (3). In Fig. 1(a), the magnitude of $F_{11}-F_{1-1}$ was chosen to give a 2/1 ratio for the peak $E1$ and $E2$ intensities, and the sign was chosen to give constructive interference with $f^{(\mathrm{mag})}$ on the low-frequency side of resonance, to agree with experiment. As shown in Eq. (3), either sign is possible. The present choice of sign and magnitude corresponds to $P(\mathrm{Ho}) \approx +0.11$, in reasonable agreement with the previous simple estimate of $+0.07$. In Fig. 1(b), the magnitude of $2F_{10}-F_{11}-F_{1-1}$ was chosen to give a 4/3 ratio for the peak $E1$ and $E2$ intensities. The dominant $E1$ contribution is predicted to be $\sigma\leftrightarrow\sigma$, but with a small $\sigma\leftrightarrow\pi$ contribution which interferes with the $E2$ resonance which is predicted to be almost entirely $\sigma\leftrightarrow\pi$ for the (002) reflection, in good agreement with the observations. The $E1$ contribution to the second harmonic indicates that there is a nonsphericity in the $5d$ polarization. The third and fourth harmonics arise entirely from the $E2$ resonance, and both $\sigma\leftrightarrow\sigma$ and $\sigma\leftrightarrow\pi$ contributions are predicted, in agreement with experiment.

The theory gives excellent qualitative and reasonable quantitative agreement with the observations even with these simple approximations. More sophisticated calculations will be required to give accurate fits to the data. The sensitivity of the measurements to the details of the magnetic properties, and the large enhancement of the magnetic scattering, promise to make this new spectroscopy an important new probe for magnetic studies.

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[1]D. Gibbs, D. R. Harshman, E. D. Isaacs, D. B. McWhan, D. Mills, and C. Vettier, preceding Letter [Phys. Rev. Lett. 61, 1241 (1988)].

[2]For the transitions of interest here, with $E1$ or $E2$ allowed, the magnetic multipole contributions are smaller by a factor of $(\hbar\omega/mc^2)$. These will be discussed elsewhere.

[3]M. Blume, J. Appl. Phys. 57, 3615 (1985).

[4]P. M. Platzman and N. Tzoar, Phys. Rev. B 2, 3556 (1970).

[5]F. DeBergevin and M. Brunel, Acta Crystallogr. A 37, 314 (1981).

[6]M. Blume and Doon Gibbs, Phys. Rev. B 37, 1779 (1988).

[7]A review of nonresonant magnetic x-ray scattering is given by S. W. Lovesey, J. Phys. C 20, 5625 (1987).

[8]This problem is closely related to resonance γ-ray scattering. See, e.g., G. T. Trammell and J. P. Hannon, Phys. Rev. 126, 1045 (1962), and 186, 306 (1969).

[9]In Eqs. (1) and (2), we have made the simplifying assumption that only a single value of M is allowed in the transition $|a\rangle\leftrightarrow|\eta\rangle$. The generalization when this does not hold (due to crystal effects) will be discussed elsewhere.

[10]V. B. Berestetskii, E. M. Lifshitz, and L. P. Pitaevskii, *Relativistic Quantum Theory* (Pergamon, New York, 1971).

[11]M. H. Chen, B. Craesmann, and H. Mark, Phys. Rev. A 21, 449 (1980).

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X-Ray Resonance Exchange Scattering. J. P. HANNON, G. T. TRAMMELL, M. BLUME, and DOON GIBBS [Phys. Rev. Lett. **61**, 1245 (1988)]

The factor P appearing in Eq. (4) should be $P=\{n_e(\uparrow)-[\Delta/\Gamma(x-i)]n_h\}$. Because of the additional frequency factor, $(x-i)^{-1}$, the exchange splitting Δ and the induced moment $n_e(\uparrow)$ can be separately determined. This correction was pointed out to us by M. Altarelli.

In Eq. (2), $Y_{LM}(\hat{\mathbf{r}}_l)$ should be $Y_{LM}(\hat{\mathbf{r}}_l)^*$.

In the first equation on p. 1247, $C^2(1,1,2;m_l-M,m_s,m_l)$ should be $C^2(1,1,2;m_l-M,M,m_l)$, and the factor $\frac{24}{5}$ in $|\chi|^2$ should be $\frac{8}{15}$.

In the seventh line from the bottom of p. 1247, "symmetry" should be "asymmetry."

Possible Observation of Light Neutral Bosons in Nuclear Emulsions. F. W. N. DE BOER and R. VAN DANTZIG [Phys. Rev. Lett. **61**, 1274 (1988)].

The vertical scale in Fig. 2 (and in Fig. 8 of Ref. 10) has to be divided by a factor of 2.

In the dashed curve in Fig. 2 obscuration has been taken into account but not the finite grain density.

Spectrum of $J^P=2^+$ Mesons. S. K. BOSE and E. C. G. SUDARSHAN [Phys. Rev. Lett. **62**, 1445 (1989)].

The terms P^*3 and Q^*3 that appear under the integral sign of Eq. (3) should correctly read as $(P^*)^3$ and $(Q^*)^3$, respectively.

Two-Photon Absorption of Nonclassical Light. J. GEA-BANACLOCHE [Phys. Rev. Lett. **62**, 1603 (1989)].

In Fig. 1, the dashed line is for *amplitude*-squeezed light and the dash-dotted line is for *phase*-squeezed light, contrary to what the figure caption reads.

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Magnetic effects in anomalous dispersion

M. Blume

Brookhaven National Laboratory, Upton, NY 11973, USA

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 general or magnetic scattering properties the theory is also applicable to "forward scattering" properties such as the Faraday effect and circular dichroism.

1. INTRODUCTION

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.

2. THEORY

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

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

where $O^\beta(\boldsymbol{k}) = \sum_i e^{i\boldsymbol{k}\cdot\boldsymbol{r}_i}(p_i^\beta - i\hbar(\boldsymbol{k}\times\boldsymbol{s}_i)^\beta)$, and the remainder of the notation used in Eq. (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 $i\hbar\omega/mc^2$, 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 Eq. (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

$$\boldsymbol{r}_j = \boldsymbol{n} + \boldsymbol{d}_s + \boldsymbol{r}_j', \quad (2)$$

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

$$A = -\frac{e^2}{mc^2}\varepsilon'^{\alpha *}_{\lambda'}\varepsilon^{\beta}_{\lambda}\sum_{n,s} e^{i\boldsymbol{K}\cdot(\boldsymbol{n}+\boldsymbol{d}_s)-W_s}\sum_a p_a \Bigg\{ \langle a|\sum_i{}^{(n,s)} e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i}|a\rangle \delta^{\alpha\beta}$$
$$-i\frac{\hbar\omega}{mc^2}\langle a|\sum_i{}^{(n,s)} e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i}\left\{\frac{-i(\boldsymbol{K}\times\boldsymbol{p}_i)^{\gamma}}{\hbar K^2}A^{\alpha\beta\gamma} + s_i^{\gamma}B^{\alpha\beta\gamma}\right\}|a\rangle$$
$$+m\sum_c\left(\frac{(E_c-E_a)^3}{\hbar^3\omega}\right)\frac{\langle a|\sum_i^{(n,s)} r_i^{\alpha}(1-\frac{1}{2}i\boldsymbol{k}'\cdot\boldsymbol{r}_i)|c\rangle\langle c|\sum_j^{(n,s)} r_j^{\beta}(1+\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}_j)|a\rangle}{E_a - E_c + \hbar\omega - i\frac{\Gamma}{2}}\Bigg\} \quad (3)$$

with $\sum^{(n,s)}$ indicating a summation over electrons in the ion at $\boldsymbol{n}+\boldsymbol{d}_s$. 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

$$R^{\alpha}_{ns} = \sum_i{}^{(n,s)} r_i^{\alpha} \quad , \quad Q^{\alpha\delta}_{ns} = \sum_i{}^{(n,s)} r_i^{\alpha} r_i^{\delta},$$

the resonance term in Eq. (3) becomes

$$A_{res} = -\frac{e^2}{mc^2}\sum_{n,s} e^{i\boldsymbol{K}\cdot(\boldsymbol{n}+\boldsymbol{d}_s)-W_s}\varepsilon'^{\alpha *}_{\lambda'}\varepsilon^{\beta}_{\lambda}$$
$$\times\frac{m}{\hbar}\sum_{ca} p_a\frac{\omega^3_{ca}}{\omega}\frac{\langle a|(R^{\alpha}_{ns} - \frac{1}{2}iQ^{\alpha\delta}_{ns}k'^{\delta})|c\rangle\langle c|(R^{\beta}_{ns} + \frac{1}{2}iQ^{\beta\gamma}_{ns}k^{\gamma})|a\rangle}{\omega - \omega_{ca} - i\frac{\Gamma}{2\hbar}} \quad (4)$$

This expression is the usual one (except for the factor ω_{ca}/ω) for the calculation of anomalous dispersion up to electric quadrupole emission and absorption. We can write

$$A_{res} = -\frac{e^2}{mc^2}\sum_{ns} e^{i\boldsymbol{K}\cdot(\boldsymbol{n}+\boldsymbol{d}_s)-W_s}\varepsilon'^{\alpha *}_{\lambda'}\varepsilon^{\beta}_{\lambda}$$
$$\times\frac{m}{\hbar}\sum_{ca} p_a\frac{\omega^3_{ca}}{\omega}\Bigg\{\frac{\langle a|R^{\alpha}_{ns}|c\rangle\langle c|R^{\beta}_{ns}|a\rangle}{\omega - \omega_{ca} - i\frac{\Gamma}{2\hbar}}$$
$$+\frac{1}{2}i\left[\frac{\langle a|R^{\alpha}_{ns}|c\rangle\langle c|Q^{\beta\gamma}_{ns}k^{\gamma}|a\rangle - \langle a|Q^{\alpha\gamma}_{ns}k'^{\gamma}|c\rangle\langle c|R^{\beta}_{ns}|a\rangle}{\omega - \omega_{ca} - i\frac{\Gamma}{2\hbar}}\right]$$
$$+\frac{1}{4}\frac{\langle a|Q^{\alpha\delta}_{ns}k'^{\delta}|c\rangle\langle c|Q^{\beta\gamma}_{ns}k^{\gamma}|a\rangle}{\omega - \omega_{ca} - i\frac{\Gamma}{2\hbar}}\Bigg\}. \quad (5)$$

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

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 $\mathbf{n}$ of the unit cell: $R_{\mathbf{n}s}^{\alpha} = R_s^{\alpha}$ and $Q_{\mathbf{n}s}^{\alpha\delta} = Q_s^{\alpha\delta}$. 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_{res}^{dq} 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.

2.1 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

$$A_{res}^{dd} = -\frac{e^2}{mc^2}\sum_{\mathbf{n}s} e^{i\mathbf{K}\cdot(\mathbf{n}+\mathbf{d}_s)-W_s}\varepsilon_{\lambda'}^{\prime\alpha *}\varepsilon_{\lambda}^{\beta}\, C_s^{\alpha\beta}\cdot\frac{m\omega_0^3}{\hbar\omega}, \tag{6}$$

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

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

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 Fig. 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.

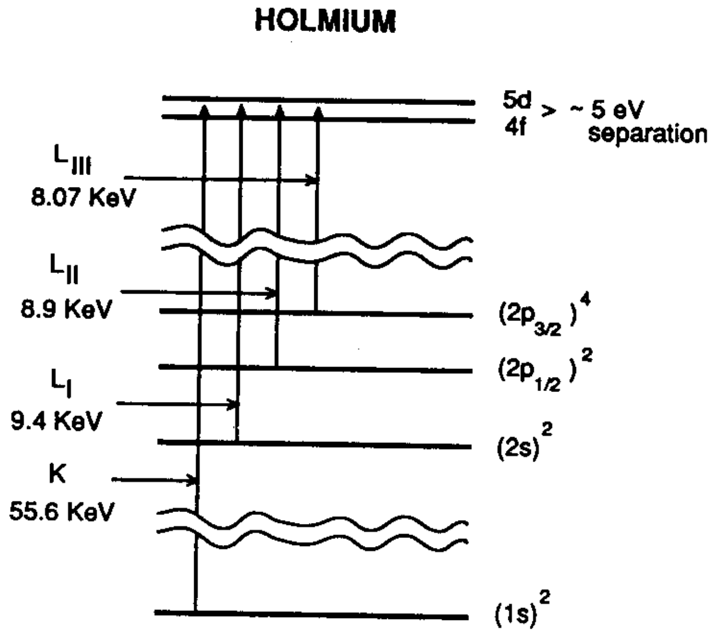

Figure 1. Electronic states of the Ho^{3+} ion.

Returning to Eq. (7) we may consider the decomposition of $C_s^{\alpha\beta}$, 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)

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

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. Equation (10) shows that there is a more complex polarization dependence than the simple $\boldsymbol{\varepsilon}_{\lambda'}^{\prime *} \cdot \boldsymbol{\varepsilon}_\lambda$ 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 Eq. (A10) the index of refraction depends on the forward scattering amplitude, for which $\boldsymbol{K} = 0$. From Eq. (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 Eq. (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

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

With $p_a' = \dfrac{p_a}{\omega - \omega_{ca} - i\frac{\Gamma}{2\hbar}}$; $p_{\bar{a}}' = \dfrac{p_{\bar{a}}}{\omega - \omega_{\bar{c}\bar{a}} - i\frac{\Gamma}{2\hbar}}$, then

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

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. ~ 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.

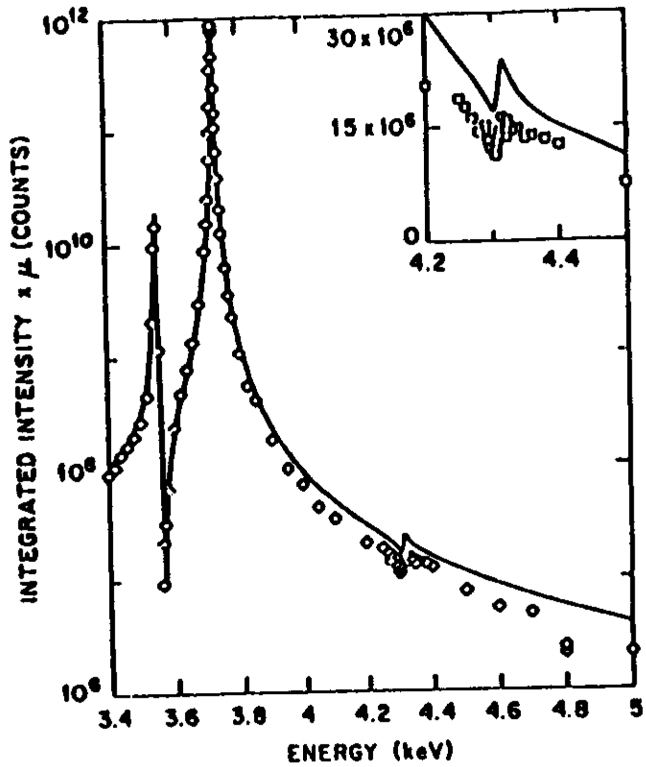

Figure 2. Experimental data showing the six order of magnitude variation in intensity of the $(0, 0, \frac{5}{2})$ magnetic Bragg peak in UAs. The solid line represents a fit to the data without the factor ω_0/ω of Eq. (1). Inclusion of that factor improves the fit at high ω. From reference [12].

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

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

In both Eqs. (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

$$C^{\alpha\beta}_+ \propto (\hat{z}^\alpha\hat{z}^\beta - \frac{1}{3}\delta^{\alpha\beta})(a_1 + b_1(\hat{z}\cdot m)^2)$$
$$+c_1(m^\alpha m^\beta - \frac{1}{3}m^2\delta^{\alpha\beta})$$
$$+d_1(\hat{z}^\alpha m^\beta + \hat{z}^\beta m^\alpha - \frac{2}{3}(\hat{z}\cdot m)\delta^{\alpha\beta})(\hat{z}\cdot m),$$

and

$$C^{\alpha\beta}_- = i\varepsilon^{\alpha\beta\gamma}(a_2 m^\gamma + b_2\hat{z}^\gamma(\hat{z}\cdot m)). \quad (15)$$

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

2.2 Quadrupole Transitions

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

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

with

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

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

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

and

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

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

2.3 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),

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

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

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

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

where

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

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. It is therefore capable of producing 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 observation of an effect produced by $G^{\alpha\beta\gamma}_{++}$ has been reported in this book by Templeton.

2.4 Form Factors

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

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

where (omitting the subscripts ns for clarity)

$$f^{\alpha\beta} = f_0\delta^{\alpha\beta} + f'^{\alpha\beta} + if''^{\alpha\beta} \quad (25)$$

with

$$f_0 = \sum_a p_a\langle a|\sum_i{}^{(ns)} e^{iK\cdot r_i}|a\rangle \equiv f_0(\boldsymbol{K}), \quad (26)$$

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

$$f^{\alpha\beta}_{0mag} = \sum_a p_a\langle a|\sum_i{}^{(ns)} e^{iK\cdot r_i}\left\{-\frac{i(\boldsymbol{K}\times \boldsymbol{p}_i)^\gamma}{\hbar K^2}A^{\alpha\beta\gamma} + s_i^\gamma B^{\alpha\beta\gamma}\right\}|a\rangle \quad (27)$$

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

$$f'^{\alpha\beta} + if''^{\alpha\beta} = m\sum_{ac} p_a\frac{\omega^3_{ca}}{\hbar\omega}\frac{\langle a|(R^\alpha_{ns} - \frac{1}{2}iQ^{\alpha\gamma}_{ns}k'^\gamma)|c\rangle\langle c|(R^\beta_{ns} + \frac{1}{2}iQ^{\beta\gamma}_{ns}k^\gamma)|a\rangle}{\omega - \omega_{ca} - i\frac{\Gamma}{2\hbar}}. \quad (28)$$

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

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

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 C, D, and 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

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

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

3. 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

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

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 Eq. (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 Eq. (A1) give scattering in second order perturbation theory. The use of Fermi's golden rule to calculate the matrix elements [4] then yields the coherent scattering amplitude

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

Here $\varepsilon'^{\alpha}_{\lambda'}$ and $\varepsilon^{\beta}_{\lambda}$ 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 Eq. (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 Eq. (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 Eq. (A2) we obtain the commutator in Eq. (A4) and the terms with energy denominators multiplied by factors $\frac{E_c - E_a}{\hbar\omega}$. Equation (A2) becomes

$$\begin{aligned}A = -\frac{e^2}{mc^2}\varepsilon_{\lambda'}^{\prime\alpha^*}\varepsilon_{\lambda}^{\beta}\sum_a p_a \Bigg\{ &\langle a|\sum_i e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i}|a\rangle\delta^{\alpha\beta}\\ &-i\frac{\hbar\omega}{mc^2}\langle a|\sum_i e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i}\left(-i\frac{(\boldsymbol{K}\times\boldsymbol{p}_i)^\gamma}{\hbar K^2}A^{\alpha\beta\gamma} + s_i^\gamma B^{\alpha\beta\gamma}\right)|a\rangle\\ &-\frac{1}{m}\sum_c\left(\frac{E_a - E_c}{\hbar\omega}\right)\frac{\langle a|O^{\alpha^\dagger}(\boldsymbol{k}')|c\rangle\langle c|O^{\beta}(\boldsymbol{k})|a\rangle}{E_a - E_c + \hbar\omega - i\frac{\Gamma}{2}}\\ &+\frac{1}{m}\sum_c\left(\frac{E_a - E_c}{\hbar\omega}\right)\frac{\langle a|O^{\beta}(\boldsymbol{k})|c\rangle\langle c|O^{\alpha^\dagger}(\boldsymbol{k}')|a\rangle}{E_a - E_c - \hbar\omega}\Bigg\}.\end{aligned} \tag{A5}$$

The commutator has been combined, as mentioned above, to give the second term in Eq. (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

$$\begin{aligned}A^{\alpha\beta\gamma} &= -2(1 - \hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{k}}')\varepsilon^{\alpha\beta\gamma},\\ B^{\alpha\beta\gamma} &= \varepsilon^{\alpha\beta\gamma} - \varepsilon^{\alpha\delta\gamma}\hat{k}'^{\delta}\hat{k}'^{\beta} + \varepsilon^{\beta\delta\gamma}\hat{k}^{\delta}\hat{k}^{\alpha}\\ &\quad -\frac{1}{2}\varepsilon^{\alpha\beta\delta}(\hat{k}'^{\delta}\hat{k}^{\gamma} + \hat{k}^{\delta}\hat{k}'^{\gamma}) + \frac{1}{2}(\hat{\boldsymbol{k}}\times\hat{\boldsymbol{k}}')^{\alpha}\delta^{\beta\gamma}\\ &\quad +\frac{1}{2}(\hat{\boldsymbol{k}}\times\hat{\boldsymbol{k}}')^{\beta}\delta^{\alpha\gamma}\end{aligned} \tag{A6}$$

In Eq. (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

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

(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 Eq. (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 Eq. (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

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

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 Eq. (A2). 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

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

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

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

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 Eq. (A5) to define $\mathcal{A}(\boldsymbol{k}'\alpha, \boldsymbol{k}\beta)$, the 3×3 scattering amplitude,

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

then

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

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:

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

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

REFERENCES

1. P.M. Platzman and N. Tzoar, Phy. Rev. B2 (1970) 3556.
2. F. de Bergevin and M. Brunel, Phys. Lett. A39 (1972) 141; F. de Bergevin and M. Brunel, Acta Cryst. A37 (1981) 314.
3. D. Gibbs, D.E. Moncton, K.L. d'Amico, J. Bohr, and B.H. Grier, Phys. Rev. Lett. 55 (1985) 234.
4. M. Blume, Proceedings of the New Rings Workshop, SSRL Report 83/02, p. 126 (1983); J. Appl. Phys. 57 (1985) 3615.
5. O.L. Zhizhimov and I.B. Khriplovich, Zh. Eksp. Teor. Fiz. 87 (1984) 547 [Sov. Phys—JETP 60 (1984) 313].
6. K. Namikawa, M. Ando, T. Nakajima, and H. Kawata, J. Phys. Soc. Japan 54 (1985) 4099.
7. There is an additional factor $\frac{E_a - E_c}{\hbar\omega}$ in the dispersive terms that does not appear in the usual expressions. This results from the extraction of the non-resonant magnetic scattering from the high frequency limit of the perturbation series, as shown in the appendix. The factor is not important near resonance but may be of significance when $(E_c - E_a)/\hbar\omega \neq 1$. It is derived in the appendix.
8. D. Gibbs, D.R. Harshman, E.D. Isaacs, D.B. McWhan, D. Mills and C. Vettier, Phys. Rev. Lett. 61 (1988) 1241.
9. V.E. Dmitrienko, Acta Cryst. A39 (1983) 29; A40 (1984) 89; V.A. Belyakov and V.E. Dmitrienko, Usp. Fiz. Nauk 158 (1989) 679 [Sov. Phys. Usp. 32 (1989) 697]. Dmitrienko considers the *symmetric* part of the tensor, but, since he was not looking at magnetic effects, omits the antisymmetric part.
10. D.H. Templeton and L.K. Templeton, Acta Cryst. A36 (1980) 237.
11. J.P. Hannon, G.T. Trammell, M. Blume, and D. Gibbs, Phys. Rev. Lett. 61 (1988) 1245; 62 (1989) 264 (E).
12. D.B. McWhan, C. Vettier, E.D. Isaacs, G.E. Ice, D.P. Siddons, J.B. Hastings, C. Peters, and O. Vogt, Phys. Rev. B42 (1990) 6007.
13. K.D. Finkelstein, Q. Shen, and S. Shastri, Phys. Rev. Lett. 69 (1992) 1612.
14. M. Blume and O.C. Kistner, Phys. Rev. 171 (1968) 417.