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Diffraction of X-rays by Magnetic Materials. I. General Formulae and Measurements on Ferro- and Ferrimagnetic Compounds

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Abstract

The calculation of the amplitude of X-rays scattered by a magnetically ordered substance, carried out in the relativistic quantum theory (*i.e.* taking the spin into account), is detailed. The effect of the orbital momentum is described in an appendix. The practical formulae dealing with the polarization of the beams are given both in a simple form for the usual experiments and in a complete form, using the Stokes vectors, for the most general case. The experiments show a change in the intensity of the X-rays diffracted by a ferromagnetic (pure iron) or a ferrimagnetic (zinc-substituted magnetite) powder when the magnetization, perpendicular to the diffraction plane, is reversed. The relative values of these intensity changes range from 10^{-4} to 5×10^{-3} and agree in sign and magnitude with the predictions. They are proportional to the spin-density structure factor multiplied by the imaginary part of the charge-density structure factor; the large anomalous scattering of the Cu $K\alpha$ radiation in the iron-containing samples is used in the present experiments.

Introduction

X-ray diffraction is usually interpreted through the Thomson scattering mechanism, *i.e.* the interaction between the electromagnetic radiation and the charge of the electrons. X-rays therefore seem to give information about the charge density only and not about the spin density. If one examines the phenomenon more thoroughly, it appears that the electronic spin also plays some role; the magnetic moment associated with the spin does interact with the magnetic field of the radiation (Fig. 1). This effect can

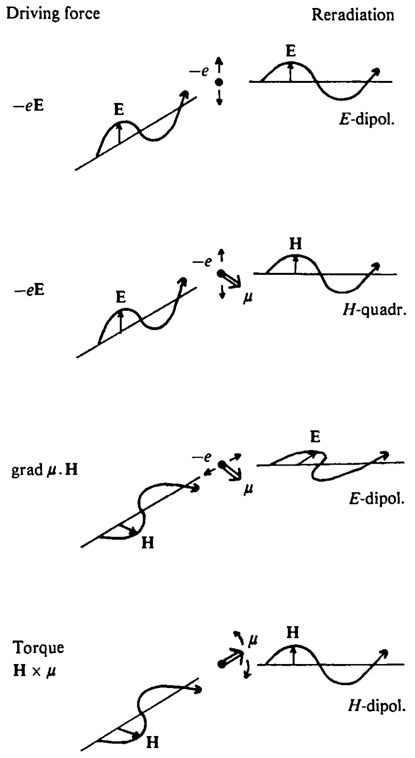

Fig. 1. The four mechanisms of scattering, in the classical description. The first one is the well known Thomson scattering. In each case, the electron (charge $-e$) or its magnetic moment μ is moved by the incident electromagnetic field. The force or torque is indicated in the left column. The type of reradiation (electric or magnetic, dipolar or quadrupolar) is given at the right.

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be treated with relativistic quantum theory. The Klein & Nishina (1929) formula for the Compton effect takes this effect into account, but only implicitly since it concerns mean values taken over all spin states.

In relativistic theory space and spin wave functions cannot be separated as they can be in the non-relativistic limit. A perturbation on the movement of an electron has an effect which depends upon the spin. During the collision with a photon of momentum $\mathbf{k}_{(i)}$ ($\mathbf{k}_{(f)}$ after collision) the electron is accelerated. One may admit that the effect of this acceleration depends upon the direction of the spin by some term of the order of $|\mathbf{k}_{(f)} - \mathbf{k}_{(i)}|/mc$, which expresses the relativistic character of the acceleration undergone by the electron (Fig. 2*a*). This is analogous to the Mott asymmetry (Tolhoek, 1956) observed in the scattering of an electron by the electric field of a nucleus, or to the Schwinger (1948) scattering (see a recent review by Felcher & Peterson, 1975), which is similar to the Mott assymetry but concerns neutrons instead of electrons (Fig. 2*b*). These effects can also be compared to the spin–orbit coupling (Fig. 2*c*), the magnitude of which is still determined by the ratio $|\mathbf{p}|/mc$ ($\mathbf{p}$ is the electron momentum). One should not forget that these comparisons do not account for the influence of the photon spin and for this reason cannot describe the phenomenon completely.

Spin-dependent scattering has been taken into account since 1950, but only in Compton or inelastic scattering; this scattering has been used in nuclear and particle physics in order to study the polarization of γ-rays. The early experiments were reviewed by Tolhoek (1956), and some of the more recent ones by Stephen & Fraunfelder (1965). The most fundamental application of the spin-dependent scattering is the determination of the sign of the neutrino helicity by Goldhaber, Grodzins & Sunyar (1958). The measurements of the momentum distribution of magnetic electrons in iron by Compton scattering of circularly polarized γ-rays (Sakai & Ono, 1976) is closer to the subject of the present paper. For many years, no attempt was made to observe similar effects in diffraction, since they become very weak when the scattering is elastic. The spin-dependent part of the scattering amplitude is roughly proportional to the momentum transferred from the photon to the electron. In Compton scattering this momentum can reach values as high as mc and the effects can be easily observed; the intensity scattered by a piece of iron may change by several per cent when one reverses its magnetization. In elastic scattering and in diffraction the transferred momentum (the scattering vector) does not greatly exceed $\hbar/r_B$, where r_B is the Bohr radius, which is about one hundredth of the preceding order of magnitude.

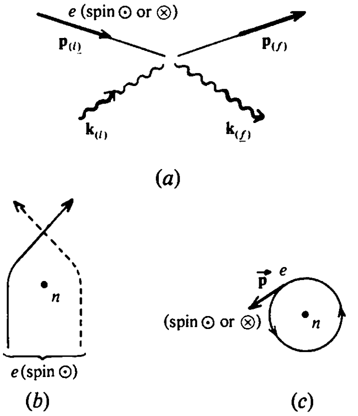

Fig. 2. (*a*) Collision between a photon and an electron whose spin is normal to the plane of scattering; the amplitude depends on the orientation of the spin and on $\mathbf{p}_{(i)} - \mathbf{p}_{(f)} = \mathbf{k}_{(f)} - \mathbf{k}_{(i)}$. (*b*) Scattering of an electron by the field of a nucleus *n* (Mott scattering): one line, continuous or dashed, represents a 'trajectory'; the amplitude depends on the direction of scattering relative to the orientation of the spin, normal to the plane. In Schwinger scattering, the electron is replaced by a neutron. (*c*) Spin–orbit coupling: the energy depends on the orientation of the spin relative to the rotation on the orbit.

The precise calculation of the effects to be expected in X-ray diffraction by magnetic substances is due to Platzman & Tsoar (1970), who suggested that these effects could be observed. An experimental study (de Bergevin & Brunel, 1972; Brunel & de Bergevin, 1974) confirmed their predictions; thus it is well established that measurements can be made similar to those performed in neutron diffraction.

The present paper recalls the fundamental formulae and describes the experiments made on ferro- (or ferri-) magnetic materials; those made on an antiferromagnetic material will be described in a subsequent article (Brunel & de Bergevin, 1981). We show here how the amplitude of a photon scattered by a free electron, initially at rest, is calculated. This amplitude can be used directly in diffraction problems, with reasonable approximations, when no orbital momentum contributes to magnetic order. For configurations of X-ray polarizations encountered in these experiments, the intensity can be calculated by a simplified procedure. Experiments are made on a ferrimagnetic spinel (chosen because it gives a relatively high effect) and on iron samples.

In Appendix *A* the approximations are discussed, along with the effect of the orbital momentum, and in Appendix *B* the treatment of X-ray polarization in the most general case is described with the formalism of Stokes vectors.

Amplitude of scattering

Lipps & Tolhoek (1954) published the complete formula giving the cross section for the scattering of photons by electrons as a function of the polarizations of all particles. We cannot make use of their results, derived for incoherent scattering, because what we need is the amplitude. This has been calculated by Platzman & Tsoar (1970). In the following we repeat their calculation and make explicit some of the steps because their paper is very concise. We also give an alternative formulation of the result.

The scattering amplitude M_i^f used in the present discussion is normalized so that the cross section for scattering in the solid angle dΩ, with initial and final states i and f, is (Berestetski, Lifchitz & Pitayevski, 1972)

$$\frac{d\sigma}{d\Omega}=\frac{|M_i^f|^2}{64\pi^2 m^2} \tag{1}$$

with m the electron mass. Note that we follow several of the conventions of these authors. It is supposed here that the recoil energy transferred to the scattering system is negligible. The units are such that $\hbar = c = 1$.

For one electron initially at rest, the value of M_i^f, approximated by the two second-order Feynman diagrams (Fig. 3), is (Schweber, 1961)

$$\begin{aligned}M_i^f &= -\frac{2\pi e^2}{m}\left\langle \bar{u}_{(f)}\left|\left(\not{\epsilon}^*_{(f)}\frac{\not{k}_{(i)}}{k_{(i)0}}\not{\epsilon}_{(i)}\right.\right.\right.\\ &\quad\left.\left.\left.+\not{\epsilon}_{(i)}\frac{\not{k}_{(f)}}{k_{(f)0}}\not{\epsilon}^*_{(f)}\right)\right|u_{(i)}\right\rangle\\ &= -(2\pi e^2/m)\,\langle \bar{u}_{(f)}|\,\Sigma|u_{(i)}\rangle. \end{aligned}\tag{2}$$

The 4-vector $k_{(i)}$ $(k_{(i)0}, k_{(i)1}, k_{(i)2}, k_{(i)3})$ is the energy momentum of the photon before scattering, and $k_{(f)}$ is the same after. The polarization of the photon, $\varepsilon_{(i)}$ or $\varepsilon_{(f)}$, is also a 4-vector but the gauges are chosen in such a way that $\varepsilon^0 = \boldsymbol{\varepsilon}.\mathbf{k} = 0$; the slashed quantities $\not{k}, \not{\epsilon}$ are the dot products of the 4-vectors by the four Dirac matrices

$$\begin{aligned}\not{k} &= k_\mu\,\gamma^\mu = k_0\,\gamma^0 - \mathbf{k}.\boldsymbol{\gamma}\\ \mathbf{k} &= (k^1, k^2, k^3) = -(k_1, k_2, k_3).\end{aligned}\tag{3}$$

These matrices obey the anticommutation rule

$$\gamma^\mu\,\gamma^\nu + \gamma^\nu\,\gamma^\mu = 2g^{\mu\nu} = \pm 2\delta^{\mu\nu}. \tag{4}$$

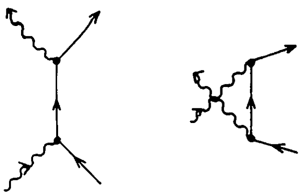

Fig. 3. One uses a perturbation calculation, each term of which is represented by a Feynman diagram: the wavy lines represent the photon, and the straight ones the electron. The order of the perturbation is the number of nodes. There are no first-order, and two second-order terms (proportional to e^2).

g is the metric tensor, and we adopt the convention $g^{00} = +1$. In the standard basis of spinors, here used,

$$\gamma^0=\begin{pmatrix}1 & & & 0\\ & 1 & & \\ & & -1 & \\ 0 & & & -1\end{pmatrix}\quad \boldsymbol{\gamma}=\begin{pmatrix}0 & \boldsymbol{\sigma}\\ -\boldsymbol{\sigma} & 0\end{pmatrix}, \tag{5}$$

where $\boldsymbol{\sigma}$ is the three Pauli matrices, $|u\rangle$ is the spinor part of the electronic wave function, and $\langle\bar{u}| = \langle u|\gamma^0$ its Dirac conjugate; they are normalized by $\langle\bar{u}|u\rangle = 2m$.

For some applications it is important to define unambiguously the sign of the imaginaries. As discussed by Ramaseshan, Ramesh & Ranganath (1975) and by Felcher & Peterson (1975) two conventions are commonly used: physicists and neutron diffractionists put the minus sign in front of the frequency × time product in the expression of the waves, and they take $\mathbf{k}_{(i)} - \mathbf{k}_{(f)}$ as the scattering vector, while X-ray crystallographers usually put the opposite sign in front of the frequency × time product and use an opposite scattering vector. For consistency with Berestetski *et al.* (1972) and other text books we use the first convention. We shall define the Fourier transform of a density $\rho(\mathbf{x})$ as

$$F(\boldsymbol{\kappa}) = \int d\mathbf{x}^3\,\rho(\mathbf{x})\exp i\boldsymbol{\kappa}.\mathbf{x}, \tag{6}$$

which is the formula used for the structure factor in X-ray crystallography, except for the fact that the imaginary atomic scattering factor will be taken here as negative and written $-f''$.

One may develop the operator Σ (2) by making an extensive use of (4); an intermediate step is the identity (valid only when $p_0 = q_0 = r_0 = 0$)

$$(\not{p}\not{q} - \not{q}\not{p})\,\not{r}/2 = -\mathbf{q}.\mathbf{r}\not{p} + \mathbf{p}.\mathbf{r}\not{q} - (\mathbf{p}\times\not{q}).\mathbf{r}\,\gamma^1\,\gamma^2\,\gamma^3. \tag{7}$$

Then the operator Σ becomes

$$\begin{aligned}\Sigma &= 2\boldsymbol{\varepsilon}_{(i)}.\boldsymbol{\varepsilon}^*_{(f)}\,\gamma^0 - \mathbf{q}.\boldsymbol{\gamma}\\ &\quad - (\boldsymbol{\varepsilon}_{(i)}\times\boldsymbol{\varepsilon}^*_{(f)}).(\hat{\mathbf{k}}_{(i)} - \hat{\mathbf{k}}_{(f)})\,\gamma^1\,\gamma^2\,\gamma^3\end{aligned}\tag{8}$$

with $\hat{\mathbf{k}}$ the unit vector $\mathbf{k}/k_0$ and $\mathbf{q}$ given as

$$\begin{aligned}\mathbf{q} &= \boldsymbol{\varepsilon}_{(i)}.\boldsymbol{\varepsilon}^*_{(f)}\,(\hat{\mathbf{k}}_{(i)} + \hat{\mathbf{k}}_{(f)}) - (\hat{\mathbf{k}}_{(i)} - \hat{\mathbf{k}}_{(f)})\times(\boldsymbol{\varepsilon}_{(i)}\times\boldsymbol{\varepsilon}^*_{(f)})\\ &= \boldsymbol{\varepsilon}^*_{(f)}\times(\hat{\mathbf{k}}_{(i)}\times\boldsymbol{\varepsilon}_{(i)}) + \boldsymbol{\varepsilon}_{(i)}\times(\hat{\mathbf{k}}_{(f)}\times\boldsymbol{\varepsilon}^*_{(f)}).\end{aligned}\tag{9}$$

In order to calculate the matrix element $\langle\bar{u}_{(f)}|\Sigma|u_{(i)}\rangle$, it is better to change the representation of the spinors; although they have four components, they belong, for a fixed energy momentum p, to a two-dimension subspace; the opposite energy states belong to a complementary subspace. The Foldy–Wouthuyssen (FW) representation (Schweber, 1961; Berestetski *et al.*, 1972) uses a basis set which separate out these two subspaces. The formulae are simplified as one makes use of two components only, but this is compensated by the fact that the representation now depends on the electron momentum $\mathbf{p}$. The two non-zero components of the FW representation are proportional to those which describe the non-relativistic spin in the rest frame of the electron. Let us write the components of a state in the FW representation as $|u(\mathbf{p})\rangle_F$, in the standard one as $|u\rangle_S$, and write the two components of the non-relativistic spin, normalized to 1, as $|S\rangle$; for the two first components, one has

$$\sqrt{2p_0}|S\rangle = |u(\mathbf{p})\rangle_F = T(\mathbf{p})|u\rangle_S \qquad (10)$$

with T the unitary matrix

$$T(\mathbf{p}) = (p_0 + m + \mathbf{p}.\boldsymbol{\gamma})/\sqrt{2p_0(p_0 + m)}. \qquad (11)$$

These relations allow the calculation of the matrix element A_i^f of any matrix A:

$$\begin{aligned} A_i^f &= \langle \bar{u}_{(f)}|_S A|u_{(i)}\rangle_S \\ &= \langle u_{(f)}(\mathbf{p}_{(f)})|_F\, T(\mathbf{p}_{(f)})\, \gamma^0 A\, |u_{(i)}(0)\rangle_F \end{aligned} \qquad (12)$$

when $\mathbf{p}_{(i)} = 0$. If we set

$$\begin{aligned} 2\mathbf{S}_i^f &= \langle S_{(f)}|\sigma|S_{(i)}\rangle \\ \delta_i^f &= \langle S_{(f)}|S_{(i)}\rangle \end{aligned} \qquad (13)$$

and use $m^2 = p_0^2 - \mathbf{p}^2$, we get (again when $\mathbf{p}_{(i)} = 0$)

$$\begin{aligned} (\gamma^0)_i^f &= \sqrt{2m(p_{(f)0} + m)}\, \delta_i^f \\ \gamma_i^f &= \sqrt{2m/(p_{(f)0} + m)}(\delta_i^f\, \mathbf{p}_{(f)} + 2i\, \mathbf{S}_i^f \times \mathbf{p}_{(f)}) \\ (\gamma^1 \gamma^2 \gamma^3)_i^f &= \sqrt{2m/(p_{(f)0} + m)}(-2i\, \mathbf{S}_i^f . \mathbf{p}_{(f)}) \end{aligned} \qquad (14)$$

and

$$\begin{aligned} M_i^f = -4\pi e^2 \sqrt{1 + \frac{k_{(i)0} - k_{(f)0}}{2m}} \Bigg[\Bigg(& 2\boldsymbol{\varepsilon}_{(i)}.\boldsymbol{\varepsilon}^*_{(f)} \\ & - \frac{\boldsymbol{\kappa}}{2m}.\mathbf{q}\Bigg)\delta_i^f \\ & - 2i\Bigg(\frac{\boldsymbol{\kappa}}{2m} \times \mathbf{q} + (\boldsymbol{\varepsilon}_{(i)} \times \boldsymbol{\varepsilon}^*_{(f)}).(\hat{\mathbf{k}}_{(f)} \\ & - \hat{\mathbf{k}}_{(i)})\frac{\boldsymbol{\kappa}}{2m}\Bigg).\mathbf{S}_i^f\Bigg], \end{aligned} \qquad (15)$$

where $\mathbf{q}$ is given by (9) and

$$\boldsymbol{\kappa} = 2m(\mathbf{k}_{(i)} - \mathbf{k}_{(f)})/(2m - k_{(f)0} + k_{(i)0}). \qquad (16)$$

In elastic scattering, $|\mathbf{k}_{(i)} - \mathbf{k}_{(f)}| \sim 1/r_B$; hence $|\mathbf{k}_{(i)} - \mathbf{k}_{(f)}|/m \sim \lambda\!\!\!^{-}_c/r_B = 1/137$ ($2\pi\lambda\!\!\!^{-}_c = \lambda_c$ is the Compton length of the electron). One may neglect terms of higher order in the parameter $|\mathbf{k}_{(i)} - \mathbf{k}_{(f)}|/m$ and simplify the formula (15) by using (O_2 represents any term of order 2, replaced by 0)

$$(k_{(i)0} - k_{(f)0})/m = O_2, \quad \boldsymbol{\kappa} = (\mathbf{k}_{(i)} - \mathbf{k}_{(f)})(1 + O_2), \quad \boldsymbol{\kappa}.\mathbf{q}/m = O_2. \qquad (17)$$

A further simplification comes from the fact that we may neglect spin-flip scattering. Since the spin-dependent part of the amplitude is small, it can be observed only along with the Bragg peaks of crystallographically and magnetically ordered substances, while spin-flip scattering is weakly inelastic (energy–momentum is transferred to some excitation) and occurs off the Bragg peaks. We shall then make $i = f$ in δ_i^f and $\mathbf{S}_i^f$.

We have considered so far the case of one free electron, initially at rest. In practice with the problem of many electrons bounded in a material one has to replace δ_i^f and $\mathbf{S}_i^f$ by the Fourier transforms of charge and spin densities, $F(\boldsymbol{\kappa})$ and $\mathbf{S}(\boldsymbol{\kappa})$; $\boldsymbol{\kappa}$ is the scattering vector, from (17). The approximations involved in this procedure are discussed in Appendix *A*. The most questionable of them consists in neglecting the initial momentum of the electron, which contributes to the scattering amplitude in the same order of magnitude as the spin; by integrating over all the momentum distribution one finds a term depending on the orbital angular momentum. However, for the interpretation of the present experiments, which concern compounds with very small orbital momentum, we can neglect it.

The expression finally used as the amplitude will be

$$\begin{aligned} M_i^f/(-8\pi e^2) = {} & \boldsymbol{\varepsilon}_{(i)}.\boldsymbol{\varepsilon}^*_{(f)}\, F(\kappa) \\ & + (i\lambda_c/2\lambda)\{[\boldsymbol{\varepsilon}^*_{(f)} \times (\hat{\mathbf{k}}_{(i)} \times \boldsymbol{\varepsilon}_{(i)}) \\ & + \boldsymbol{\varepsilon}_{(i)} \times (\hat{\mathbf{k}}_{(f)} \times \boldsymbol{\varepsilon}^*_{(f)})] \times (\hat{\mathbf{k}}_{(i)} - \hat{\mathbf{k}}_{(f)}) \\ & + (\boldsymbol{\varepsilon}_{(i)} \times \boldsymbol{\varepsilon}^*_{(f)}).(\hat{\mathbf{k}}_{(i)} - \hat{\mathbf{k}}_{(f)})(\hat{\mathbf{k}}_{(i)} - \hat{\mathbf{k}}_{(f)})\}.\mathbf{S}(\boldsymbol{\kappa}) \end{aligned} \qquad (18)$$

or the equivalent form given by Platzman & Tsoar (1970). We recall that the notation $\boldsymbol{\varepsilon}_{(i)}$ ($\boldsymbol{\varepsilon}_{(f)}$) represents the initial (final) photon polarization, which may be circular if these vectors are complex, $\hat{\mathbf{k}}_{(i)}$ ($\hat{\mathbf{k}}_{(f)}$) the unit vector along the initial (final) photon momentum, $F(\boldsymbol{\kappa})$ and $\mathbf{S}(\boldsymbol{\kappa})$ the Fourier transforms of charge and spin densities, this last being unchanged during scattering (photons scattered with spin-flip are supposed to be unobserved); $\mathbf{S}$ is a spin, so that each electron contributes to it by $\frac{1}{2}$; $\lambda_c = 0{\cdot}02426$ Å. $\lambda_c\boldsymbol{\kappa}$ may be factorized out of the magnetic term; this common factor has an order of magnitude of 1/100 whereas the remaining geometric part has an order of magnitude of 1. Since typical $|\mathbf{S}|/F$ ratio is about 1/10, the magnetic amplitude is about 1/1000 of Thomson's one.

Since the amplitude (18) is expressed as a bilinear function of photon polarizations, it is possible to write it in a simpler form as a matrix. We choose as the basis the linear polarization states normal and parallel ($\perp$

and $\|$) to the diffraction plane $\hat{\mathbf{k}}_{(i)}$, $\hat{\mathbf{k}}_{(f)}$; the signs are such that $\boldsymbol{\varepsilon}_{\|} = \hat{\mathbf{k}} \times \boldsymbol{\varepsilon}_{\perp}$. We set

$$\begin{aligned} M_i^f/(-8\pi e^2) &= (\boldsymbol{\varepsilon}_{(f)}|\mathscr{M}|\boldsymbol{\varepsilon}_{(i)}) \\ &= (\boldsymbol{\varepsilon}_{(f)}|A|\boldsymbol{\varepsilon}_{(i)})F(\boldsymbol{\kappa}) \\ &\quad + i(\lambda_c/\lambda)(\boldsymbol{\varepsilon}_{(f)}|\mathbf{B}|\varepsilon_{(i)}).\mathbf{S}(\boldsymbol{\kappa}) \end{aligned} \tag{19}$$

with the matrices A and $\mathbf{B}$ given as (θ being the Bragg angle; $\hat{\mathbf{k}}_{(i)}.\hat{\mathbf{k}}_{(f)} = \cos 2\theta$)

$$A = \begin{array}{c|cc} {}_{(f)}\diagdown^{(i)} & \perp & \| \\ \hline \perp & 1 & 0 \\ \| & 0 & \cos 2\theta \end{array} \qquad \mathbf{B} = \begin{array}{c|cc} {}_{(f)}\diagdown^{(i)} & \perp & \| \\ \hline \perp & -\hat{\mathbf{k}}_{(i)} \times \hat{\mathbf{k}}_{(f)} & 2\hat{\mathbf{k}}_{(f)} \sin^2\theta \\ \| & -2\hat{\mathbf{k}}_{(i)} \sin^2\theta & -\hat{\mathbf{k}}_{(i)} \times \hat{\mathbf{k}}_{(f)}. \end{array} \tag{20}$$

One may also choose as basis states the two circular polarizations; we do not write the corresponding matrices explicitly, but one obtains the following simple expression for the spin dependent amplitude when both initial and final photons are circularly polarized:

$$(-\lambda_c/\lambda)[i(\hat{\mathbf{k}}_{(i)} \times \hat{\mathbf{k}}_{(f)}).\mathbf{S} + \chi(\mathbf{P}_{(i)} + \mathbf{P}_{(f)}).\mathbf{S}\sin^2\theta] \tag{21}$$

($\mathbf{P}$ is the photon spin, a vector of unit length along $\pm\mathbf{k}$, χ is defined as $+1$ when photon helicity is unchanged, -1 when it is reversed during scattering). The second term of (21) contains all the dependency on polarizations. The first term is independent of them and corresponds to the effects shown in Fig. 2; the Schwinger scattering amplitude (Felcher & Peterson, 1975) is similar, if considered in the limiting case where the scatterer is a neutral atom much smaller than the wavelength [the electronic radius λ_c which appears in (21) is then replaced by the atomic radius].

The treatment of the polarizations

The X-ray beam may be polarized before and/or after diffraction; this is more complicated than in the case of the Thomson scattering, because the matrix $\mathbf{B}$ of formulae (19), (20) contains, unlike A, non-diagonal and non-symmetrical elements. In the experiments presented herein, we have used a conventional X-ray tube, with a monochromator which polarizes the beam perpendicularly to the plane of diffraction. In such a situation, a simple procedure, given in details below, may be used. In the general case, where several types of polarizations may be mixed up, one should represent the beam state by the density matrix, or equivalently by the Stokes vector. We give in Appendix *B* the corresponding formulae; they should be used when synchrotron radiation with elliptical and partial polarization is used, or in any other complicated case.

We suppose that three conditions are realized: the source is unpolarized, all the successive scatterings undergone by the beam occur in the same plane and only one of them contains some magnetic contributions. Under these conditions each of the beams may be represented as the sum of two, having polarizations parallel and perpendicular to the plane of scattering. We shall use, instead of M, the matrix $\mathscr{M}$ (19) and condense the notation, for example, by rewriting $(\perp\mathscr{M}\|)$ instead of $(\varepsilon_{\perp}|\mathscr{M}|\varepsilon_{\|})$. The intensity received in the detector is obtained by summing over the final polarization and averaging over the initial ones. If a monochromator, supposed to be ideally imperfect, with Bragg angle α, is put before the sample, we have the cross section (r_e is the Lorentz radius of the electron, e^2/mc^2)

$$\begin{aligned} \mathrm{d}\sigma/\mathrm{d}\Omega = (r_e^2/2)[&|(\perp\mathscr{M}\perp)|^2 + |(\|\mathscr{M}\perp)|^2 \\ &+ (|(\perp\mathscr{M}\|)|^2 \\ &+ |(\|\mathscr{M}\perp)|^2)\cos^2 2\alpha]/(1 + \cos^2 2\alpha) \end{aligned} \tag{22a}$$

and, if the monochromator is put after,

$$\begin{aligned} \mathrm{d}\sigma/\mathrm{d}\Omega = (r_e^2/2)[&|(\perp\mathscr{M}\perp)|^2 + |(\perp\mathscr{M}\|)|^2 \\ &+ (|(\|\mathscr{M}\perp)|^2 \\ &+ |(\|\mathscr{M}\|)|^2)\cos^2 2\alpha]. \end{aligned} \tag{22b}$$

The ferro- and ferrimagnetic cases

The magnetic diffraction is always superposed on the Thomson diffraction since magnetic and crystallographic periodicities are the same. In the formula which gives the diffracted intensity, the square $|\mathbf{B}.\mathbf{S}|^2$ (19), (22), of the magnetic amplitude is negligible since it is roughly 10^{-6} of the Thomson term $|AF|^2$, so that the main magnetic term is due to the cross term. Because of the factor i in the magnetic amplitude this term is the imaginary part of

$$2(\lambda_c/\lambda)AF(\mathbf{B}.\mathbf{S})^*. \tag{23}$$

If we restrict ourselves to centrosymmetric magnetic arrangements ($\mathbf{S}$ real), if the source is unpolarized, and if a monochromator is used (as it is in most of our experiments) in the diffracted beam, the formulae (19), (20), (22) give the intensity up to the first order in λ_c/λ:

$$\begin{aligned} I(hkl) = C\{&[F'^2(hkl) + F''^2(hkl)] \\ &\times (1 + \cos^2 2\alpha \cos^2 2\theta) \\ &- 2(\lambda_c/\lambda)F''(hkl)[(\hat{\mathbf{k}}_{(i)} \times \hat{\mathbf{k}}_{(f)}).\mathbf{S}(hkl)] \\ &\times (1 + \cos^2 2\alpha \cos 2\theta)\}. \end{aligned} \tag{24}$$

C is a constant including Lorentz factor, absorption, *etc.*$\cdots$, F' and F'' are the real and imaginary parts of the Thomson structure factor $F(hkl)$,

$$F(hkl) = \sum_j (f'_j - if''_j)\exp 2i\pi(hx_j + ky_j + lz_j)$$

with $f' - if''$ the atomic scattering factor, $\mathbf{S}$ the real spin density structure factor.

$$\mathbf{S}(hkl) = \sum_j (\mu_j/2)\, f_{M,j}\, \hat{\mathbf{S}}_j \exp 2i\pi(hx_j + ky_j + lz_j).$$

The magnetic atom j has the moment μ_j in Bohr magnetons opposite to the spin direction defined by the unit vector $\hat{\mathbf{S}}_j$; $f_{M,j}$ is its unitary magnetic form factor. In the case of a ferromagnetic, or collinear ferrimagnetic compound, $\hat{\mathbf{S}}_j$ is unique and may be factorized.

The last term in (24) is very weak compared to $F'^2 + F''^2$ and cannot be determined by absolute measurements, but the $\hat{\mathbf{S}}$ direction can be changed by an applied magnetic field and oriented successively parallel and antiparallel to the vector $(\hat{\mathbf{k}}_{(i)} \times \hat{\mathbf{k}}_{(f)})$, which is perpendicular to the diffraction plane. According to (24) the relative intensity change, when the field is reversed along this direction, is

$$\frac{\Delta I(hkl)}{I(hkl)} = \frac{1 + \cos^2 2\,\alpha \cos 2\theta}{1 + \cos^2 2\alpha\, \cos^2 2\theta}\, 4\, \frac{\lambda_c}{\lambda}\, \frac{F''\,|\mathbf{S}|}{F'^2 + F''^2} \sin 2\theta. \tag{25}$$

By a differential measurement this ratio can be obtained; one can see that its sign is reversed when θ is changed to $-\theta$ (Fig. 4).

Measurements

In a diffraction experiment with a conventional X-ray beam the variation $\Delta I/I$ is proportional to f'', the imaginary part of the atomic scattering factor. We have chosen to study an iron-containing compound with the Cu $K\alpha$ radiation, because in this case f'' is high (*International Tables for X-ray Crystallography*, 1962) and the magnetic moment μ is large.

Two such compounds have been studied, namely,

– *a ferromagnetic one: pure iron.*

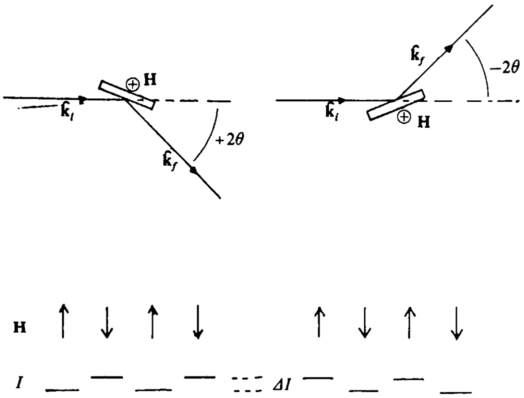

Fig. 4. Principle of the experiments: The intensity measured at the top of a reflection is changed by ΔI when the magnetic field **H** is inverted perpendicular to the diffraction plane $(\hat{\mathbf{k}}_i, \hat{\mathbf{k}}_f)$. When θ is changed to $-\theta$, ΔI is changed in $-\Delta I$.

Table 1. *Thomson* (*Durif, Bertaut & Pauthenet*, 1956) *and magnetic structure factors for spinel compounds*

$h^2 + k^2 + l^2$	F_{Thomson}	$2S$
$32n$	$4f_O \pm f_A + 2f_B$	$2f_{M,B}\mu_B - f_{M,A}\mu_A$
$16n + 11$	$(\sqrt{2}/2)f_A + f_B$	$f_{M,B}\mu_B - (\sqrt{2}/2)f_{M,A}\mu_A$
$16(2n+1)$	$4f_O - f_A + 2f_B$	$2f_{M,B}\mu_B + f_{M,A}\mu_A$
$32n + 12$	$-4f_O + 2f_B$	$2f_{M,B}\mu_B$
$16n + 8$	f_A	$-f_{M,A}\mu_A$
$16n + 3$	$(-\sqrt{2}/2)f_A + f_B$	$f_{M,B}\mu_B + (\sqrt{2}/2)f_{M,A}\mu_A$

The $\Delta I/I$ values calculated from the magnetic form factor determined by the neutron experiments of Shull & Yamada (1962) are around 4×10^{-4} ($\mu = 2.2\,\mu_B$).

– *a ferrimagnetic one: zinc-substituted magnetite*

Let AB_2O_4 be the formula of a compound with the spinel structure: A ions are in tetrahedral sites while B are in octahedral sites. If A and B are magnetic ions, the magnetic moments of the ions in the two sublattices are antiparallel and a ferrimagnetic magnetization appears. Thomson and magnetic structure factors are given in Table 1; they are calculated for an ideal oxygen position parameter, f_O, f_A and f_B are the Thomson form factors of oxygen, ion A and ion B, respectively, whereas $f_{M,A}$ and $f_{M,B}$ are the magnetic form factors of the magnetic ions in tetrahedral and octahedral sites, respectively. $\Delta I/I$ is maximum for reflection in which the Thomson contributions of the two sites have opposite signs, whereas the magnetic contributions have the same sign. The most favourable compound seems to be the zinc ferrite $Zn^{2+}_{0.5}Fe^{3+}_{0.5}(Fe^{3+}Fe^{2+})O_4$ (Gorter, 1954); our sample actually has the formula $Zn^{2+}_{0.53}Fe^{3+}_{0.47}(Fe^{3+}_{1.53}Fe^{2+}_{0.47})O_4$. By using the Fe^{3+} magnetic form factor given by Brockhouse, Corliss & Hastings (1955) and the Fe^{2+} one given by Scatturin, Corliss, Elliott & Hastings (1961), determined by neutron diffraction, one finds that $\Delta I/I$ ratio varies from 4×10^{-3} for the very favourable 531 reflection to $0{\cdot}10 \times 10^{-3}$ for the 440 reflection.

Since we are interested in relative changes of the intensity of strong Bragg reflections, the measurements can be made on a powder sample. We used a classical powder goniometer equipped with a 1500 W X-ray tube. In most experiments an oriented-graphite monochromator was placed between the sample and the detector in order to eliminate the X-ray fluorescence of iron. A water-cooled magnetic coil, hanging over the goniometer plate, created a vertical $\pm\mathbf{H}$ (2 kOe $\simeq$ 160 kA/m) magnetic field on the sample. A sketch of the apparatus is given in Fig. 5. By magnetic measurements we made sure that this field was sufficiently high to saturate our sample, which was a thin powder plate parallel to **H**.

Every reflection was measured at θ and $-\theta$. The $\Delta I/I$ variations are very weak and, in order to eliminate the errors due to fluctuations of the generator power, of the mechanical positions, of the temperature, *etc.*, measurements at $+\mathbf{H}$ and $-\mathbf{H}$ were made with the following sequences: 1·5 to 3 min with $+\mathbf{H}$, $|+\mathbf{H}$ to $-\mathbf{H}$ inversion$|$, 1·5 to 3 min with $-\mathbf{H}$, $|-\mathbf{H}$ to $+\mathbf{H}$ inversion$|$. Results were collected on punched tape and processed with a computer.

In order to eliminate mechanical-play problems, the intensity was measured at the peak of the reflection with stationary sample and stationary detector. Since the measurements were made between two symmetrical values of the magnetic field, the sample magnetostriction effects, which could change the θ position of the reflection, were eliminated. The systematic errors due to the field inversions were eliminated by measuring, before the experiments, the $\Delta I/I$ variations corresponding to the inversion from $+\mathbf{H}$ to $-\mathbf{H}$ for a non-magnetic sample. In order to have nearly the same experimental conditions as in the data collection, the aluminium back face of the sample holder was used. The magnetic sample was left on the other face, so that the magnetic mechanical effects were the same. The parasitic variations, which initially were larger than the ones we expected from the magnetic sample, were reduced, so that the experiment became significant, by replacing all the magnetic parts of the goniometer by non-magnetic ones and by shielding the X-ray tube with mumetal and the coil with iron sheets. The beam intensity of an X-ray tube is very sensitive to an external magnetic field. For instance, a field change of a few oersteds around the tube gives a $\Delta I/I$ variation too high for our measurements. This is probably due to an effect on the electron beam.

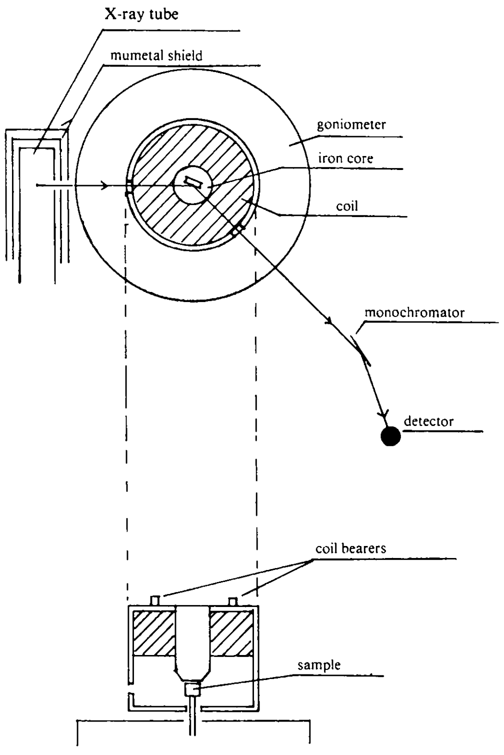

Fig. 5. Sketch of the apparatus.

Counting was performed over two or three days for each reflection; N photons were counted during this time; N was of the order of 10^8 to 10^9. We had to be sure that the uncertainty related to the technical fluctuations was smaller than the statistical uncertainty. We have therefore calculated the frequency spectrum $P(f)$ of the intensity $I(t)$ expressed as a function of time. The extrapolated value $P(f)$ for a frequency equal to the one of the cycle just described ($\frac{1}{3}$ or $\frac{1}{6}$ min^{-1}) was never greater than $N^{1/2}$.

Results

1. *Spinel compound*

The sample was prepared at high temperature by mixing the oxides, compressed in the sample holder and bound by glue. The experimental values $\Delta I/I$ for three Bragg reflections are reported in Table 2. The theoretical values $\Delta I/I$ reported in the same table are calculated by supposing that the magnetizations of the two sublattices vary like the total macroscopic magnetization; this has been determined by the extraction method and found to be 4·86 μ_B/mol. In Table 1 the spinel structure factors correspond to an ideal oxygen positional parameter of $u = 0{\cdot}250$. In Table 2 we have given the $\Delta I/I$ values corresponding to two extreme values of u for the reflections 222 and 531, which are sensitive to this parameter. σ is the standard deviation.

Table 2. *Values of $\Delta I/I$ for the ferrimagnetic compound*

$h\,k\,l$	θ (°)	$(\Delta I/I) \times 10^3$ experimental	$(\overline{\Delta I}/I) \times 10^3$ experimental	$\sigma \times 10^3$	$(\Delta I/I) \times 10^3$ theoretical
2 2 2	+18·5 −18·5	2·25 −2·33	2·29	0·12	2·50 $u = 0{\cdot}255$ 2·37 $u = 0{\cdot}260$
5 3 1	+32·84 −32·84	4·10 −4·70	4·40	0·30	5·94 $u = 0{\cdot}255$ 4·61 $u = 0{\cdot}260$
4 4 0	+31·23 −31·23	0·06 −0·12	0·10	0·10 0·06	0·15

Table 3. *Values of $\Delta I/I$ for the ferromagnetic compound*

$h\,k\,l$	θ (°)	$(\Delta I/I) \times 10^3$ experimental	$(\overline{\Delta I}/I) \times 10^3$ experimental	$\sigma \times 10^3$	$(\Delta I/I) \times 10^3$ theoretical
1 1 0	+22·50 −22·50	0·42 −0·40	0·41	0·04	0·36
2 1 1	+41·34 −41·34	0·44 −0·40	0·42	0·05	0·38

2. *Iron*

The sample was a very thin plate of soft iron, so as to diminish the demagnetizing field, fixed on the sample holder. In this case the $\Delta I/I$ values are smaller, while the reflections are strong with counting rates at the peak of the order of 20 000 counts s^{-1}. The results are reported in Table 3.

For every measured reflection, in zinc ferrite or in iron the observed sign of $\Delta I/I$ is the same as theoretically predicted (Fig. 6) and the difference between theoretical and experimental $\Delta I/I$ is of the order of σ. In order to be sure that the observed variations are really related to the imaginary part of Thomson structure factor, we made the same measurement on the 222 Bragg reflection of the spinel sample with the Co $K\alpha$ wavelength. In this case the value of f'' is 0·6 instead of 3·3 as with Cu $K\alpha$ and F'' is smaller. The experimental value of $\Delta I/I = 0{\cdot}73 \times 10^{-3}$ ($\sigma = 0{\cdot}21 \times 10^{-3}$) is in agreement with the theoretical one ($0{\cdot}72 \times 10^{-3}$ for $u = 0{\cdot}260$ and $0{\cdot}79 \times 10^{-3}$ for $u = 0{\cdot}255$).

Conclusion

We have presented the fundamental formulae for elastic scattering of X-rays by magnetic substances. The magnetic amplitude depends in a somewhat complicated way on spin direction and on incident and scattered photon wave vectors and polarizations. It becomes simpler if written in a matrix form, or when the polarizations are circular. It is roughly proportional to $\boldsymbol{\kappa}\lambda_c$ ($\boldsymbol{\kappa}$ the scattering vector and λ_c the Compton length of the electron). For a magnetic atom its order of magnitude is 10^{-3} of the Thomson amplitude. The orbital-momentum treatment and the calculation of the diffracted intensity in the most general case of polarization are reported in the Appendices.

According to these formulae, the experiments made on ferro- and ferrimagnetic substances (pure iron and zinc ferrite spinel) show some change in the ordinary Bragg intensities when the magnetization of the sample, perpendicular to the diffraction plane, is reversed. The observed relative-intensity change ranges from $\sim 10^{-3}$ to $\sim 10^{-4}$ and agrees in sign and magnitude with the calculated one. It must be emphasized that, since we use a conventional X-ray source, this change is proportional to the imaginary part of the structure factor F; in centrosymmetrical structures this part arises from anomalous scattering only. With other types of sources, the beam may be circularly polarized and this gives rise to an effect depending on the real part of F. Such an experiment will be described elsewhere.

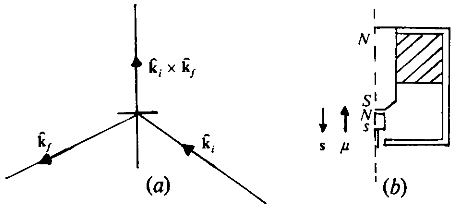

Fig. 6. For an experiment in which the vector $\hat{\mathbf{k}}_i \times \hat{\mathbf{k}}_f$ has the orientation (*a*) and a field which gives the orientation (*b*) to the spin **S**, the intensity $I(222)$ is minimum.

We would like to thank Dr P. M. Platzman for an enlightening discussion. We also thank Dr G. P. Felcher who drew our attention to the similarity between Schwinger scattering and the scattering here studied.

APPENDIX *A*

The approximations and the orbital momentum

One obtains the scattering amplitude (15) by making two types of approximation.

The first approximation concerns the scattering by a free electron and consists in limiting the perturbation expansion to the second-order Feynman diagram. Its validity has to be discussed, because when the transferred momentum is of the order $1/r_B$, the magnetic amplitude has the same order of magnitude as a radiative correction. The present result is nevertheless correct because a non-perturbative calculation has been carried out by Gell-Mann & Goldberger (1954) and by Low (1954). They obtained an exact expression of the amplitude up to the first order in the photon energy (and valid for any scattering particle with spin ½). Apart from some supplementary term arising from the anomalous magnetic moment of the electron, which is small enough to be neglected, the result of the above authors is equivalent to (18). Furthermore the first two authors have obtained the same result by using classical electromagnetic theory. Therefore it can be concluded that the contribution of higher-order diagrams to the magnetic amplitude is less than 1/100.

The second approximation comes from the fact that in an atom or a solid the electrons are bounded instead of free. This problem has been discussed in the case of Compton scattering by Eisenberger & Platzman (1970) and by Platzman & Tsoar (1977). Although they have not explicitly examined the polarization terms in which we are interested, it seems reasonable to consider the electrons as free because their binding energy is small as compared to the photon energy (the ratio is <1/100). We must nevertheless take into account the electron initial momentum. This has a non-zero distribution which can be described by the wave function, instead of being zero as supposed until now. Let us call $M_i^f(\mathbf{p}_{(i)})$ the scattering amplitude when the electron has the initial momentum $\mathbf{p}_{(i)}$. It can be obtained easily in the first order of $\mathbf{p}_{(i)}$ by applying a Lorentz transformation to (18) so as to give the momentum $\mathbf{p}_{(i)}$ to the electron; only the Thomson term gives rise to a first-order correction. Since the Lorentz transformation changes the gauge, one should not forget to return to the usual gauge (where the photon polarization has no time component). Another way to obtain $M_i^f(\mathbf{p}_{(i)})$ is given by Jauch & Rohrlich (1976), formula (11–13). The result is

$$M_i^f(\mathbf{p}_{(i)}) = M_i^f(0) - 8\pi e^2[(\hat{\mathbf{k}}_{(i)} - \hat{\mathbf{k}}_{(f)}) \times (\boldsymbol{\varepsilon}_{(i)} \times \boldsymbol{\varepsilon}^*_{(f)})] . (\mathbf{p}_{(i)}/m) \qquad (A\text{-}1)$$

with $M_i^f(0)$ given by (18). If we neglect the spin–orbit coupling, the spinor part of the electronic wave function may be factorized out and the spatial one $\psi(\mathbf{x})$ developed in plane waves,

$$\psi(\mathbf{x}) = (2\pi)^{-3} \int \mathrm{d}^3 p \phi(\mathbf{p}) \exp i\mathbf{p}.\mathbf{x}, \qquad (A\text{-}2)$$

which allow one to write the scattering amplitude as

$$\begin{aligned} M'^f_i &= (2\pi)^{-3} \int\int \mathrm{d}^3 p_{(f)}\, \mathrm{d}^3 p_{(i)}\, \phi^*_{(f)}(\mathbf{p}_{(f)}) M_i^f(\mathbf{p}_{(i)}) \\ &\quad \times \phi_{(i)}(\mathbf{p}_{(i)})\, \delta^{(3)}(\mathbf{k}_{(f)} + \mathbf{p}_{(f)} - \mathbf{k}_{(i)} - \mathbf{p}_{(i)}) \\ &= (2\pi)^{-3} \int \mathrm{d}^3 p_{(i)}\, \phi^*_{(f)}(\mathbf{p}_{(i)} + \boldsymbol{\kappa}) M_i^f(\mathbf{p}_{(i)})\, \phi_{(i)}(\mathbf{p}_{(i)}) \end{aligned} \qquad (A\text{-}3)$$

with $\boldsymbol{\kappa} = \mathbf{k}_{(i)} - \mathbf{k}_{(f)}$. The definition of M'^f_i differs from that of the M_i^f by the $\delta^{(3)}$ function; this function is implied in M'^f_i, whereas it has to be put explicitly as a factor of M_i^f when calculating the cross section.

In order to integrate (*A*-3) one splits $M_i^f(\mathbf{p}_{(i)})$ into two terms, as in (*A*-1). The first one $M_i^f(0)$ is independent of $\mathbf{p}_{(i)}$; it corresponds to the Thomson and spin scattering and its integration gives rise to the form factors $F(\boldsymbol{\kappa})$ and $\mathbf{S}(\boldsymbol{\kappa})$. The second is linear in $\mathbf{p}_{(i)}$; it gives rise to an integral which is the matrix element of an operator between the initial and final electron states, namely

$$\begin{aligned} &(2\pi)^{-3} \int \mathrm{d}^3 p \phi^*_{(f)}(\mathbf{p} + \boldsymbol{\kappa})\, \mathbf{p} \times (\hat{\mathbf{k}}_{(i)} - \hat{\mathbf{k}}_{(f)})\, \phi_{(i)}(\mathbf{p}) \\ &= \langle \psi_{(f)} | (\exp i\boldsymbol{\kappa}.\mathbf{x})\, \mathbf{p} \times (\hat{\mathbf{k}}_{(i)} - \hat{\mathbf{k}}_{(f)}) | \psi_{(i)} \rangle. \end{aligned} \qquad (A\text{-}4)$$

The operator between brackets appears in the calculation of the neutron scattering by orbital momentum. It has been shown (Trammel, 1953; Steinsvoll *et al.*, 1967; Marshall & Lovesey, 1971) that it is equal to

$$(i/2)\{\boldsymbol{\kappa} \times [\mathbf{M}_L(\boldsymbol{\kappa})/\mu_B]\} \times (\hat{\mathbf{k}}_{(i)} - \hat{\mathbf{k}}_{(f)}), \qquad (A\text{-}5)$$

where $\mathbf{M}_L(\boldsymbol{\kappa})/\mu_B$ is the Fourier transform of the orbital magnetic-moment density expressed with the Bohr magneton as a unit.

The contribution of the orbital momentum to the amplitude is therefore

$$\begin{aligned} &-8\pi e^2(i\lambda_c/2\lambda)\{[(\hat{\mathbf{k}}_{(i)} - \hat{\mathbf{k}}_{(f)}) \times (\mathbf{M}_L(\boldsymbol{\kappa})/\mu_B)] \\ &\quad \times (\hat{\mathbf{k}}_{(i)} - \hat{\mathbf{k}}_{(f)})\} . (\boldsymbol{\varepsilon}_{(i)} \times \boldsymbol{\varepsilon}^*_{(f)}). \end{aligned} \qquad (A\text{-}6)$$

In elastic scattering $\mathbf{M}_L$ is the average value of the operator on the state of the atom.

APPENDIX *B*

The general case of polarization

The polarization may be represented either by the density matrix, or by the Stokes vector. This formalism is exposed for example by Lipps & Tolhoek (1954), Robson (1974), and in the treatise of Jauch & Rohrlich (1976), p. 40. A one-photon state can be represented by $\sum c^j | j \rangle$ where j is summed over a basis made up of two polarization states. The density matrix is comprised of the elements

$$\rho^{jj'} = c^j (c^{j'})^*. \qquad (B\text{-}1)$$

When a beam contains N^0 photons its density matrix is the sum of the N^0 individual matrices. It is easy to see that it is Hermitian and its trace equal to N^0. We may write it as

$$\rho = \tfrac{1}{2}\begin{pmatrix} N^0 + N^1 & N^2 - iN^3 \\ N^2 + iN^3 & N^0 - N^1 \end{pmatrix} \qquad (B\text{-}2)$$

or

$$\rho^{jj'} = \tau_m^{jj'} N^m.$$

The four real N^m are considered as the components of a vector N (Stokes vector) and are such that

$$(N^0)^2 \geq (N^1)^2 + (N^2)^2 + (N^3)^2. \qquad (B\text{-}3)$$

The equality occurs when all the photons have the same polarization. The ratios N^m/N^0 represent different degrees of polarization: if the basis states $| j \rangle$ are linearly polarized parallel and perpendicular to a basal plane [*cf.* formula (19)], N^1/N^0 is the degree of polarization parallel to this plane (+1 when the polarization is totally parallel to the plane, and −1 when it is totally perpendicular), N^2/N^0 is the polarization at 45° from the preceding, and N^3/N^0 is the circular one.

After scattering the coefficients $c^l_{(f)}$ are obtained, on an arbitrary scale, by applying the matrix operator $\mathscr{M}$ (19) to the initial coefficients $c^j_{(i)}$

$$c^l_{(f)} \sim (l | \mathscr{M} | j)\, c^j_{(i)} = \mathscr{M}^l{}_j\, c^j_{(i)}. \qquad (B\text{-}4)$$

From (1), (18), (*B*-1), (*B*-2) and (*B*-4) we obtain the final Stokes vector $\mathrm{d}N_{(f)}$ in a solid angle $\mathrm{d}\Omega$

$$\mathrm{d}N^m_{(f)} = \mathrm{d}\Omega\, r_e^2 (\tau^{-1})^m_{ll'}\, \mathscr{M}^l_j (\mathscr{M}^{l'}{}_{j'})^*\, \tau_n^{jj'}\, N^n_{(i)}. \qquad (B\text{-}5)$$

Table 4. *Matrix E, formula* (*B*-6)

The elements of this matrix are represented, divided by r_e^2. The indices here called (*i*) and (*f*) are respectively *n* and *m* in (*B*-6).

In order to condense this table, we here make use of notations which are not self-evident, as follows (Re and Im are the real and imaginary part).

$$S'_v = (\lambda_c/\lambda)\,\mathrm{Re}\,\mathbf{S}(\kappa)\cdot(\hat{\mathbf{k}}_{(i)} \times \mathbf{k}_{(f)})$$
$$S''_v = (\lambda_c/\lambda)\,\mathrm{Im}\,\mathbf{S}(\kappa)\cdot(\hat{\mathbf{k}}_{(i)} \times \mathbf{k}_{(f)})$$
$$S'_i = (\lambda_c/\lambda)\,\mathrm{Re}\,\mathbf{S}(\kappa)\cdot(\hat{\mathbf{k}}_{(i)}\,(1 - \cos 2\theta)$$
$$S''_i = (\lambda_c/\lambda)\,\mathrm{Im}\,\mathbf{S}(\kappa)\cdot(\hat{\mathbf{k}}_{(i)}\,(1 - \cos 2\theta)$$

S'_f and S''_f = the same with $\mathbf{S}(\kappa)\cdot(\hat{\mathbf{k}}_{(f)}$ instead of $\mathbf{S}(\kappa)\cdot(\hat{\mathbf{k}}_{(i)}$

$$F' = \mathrm{Re}\,F(\kappa) \quad F'' = \mathrm{Im}\,F(\kappa)$$

The quantities without primes are the moduli of complex quantities, namely

F^2 is written for $|F(\kappa)|^2 = F'^2 + F''^2$
$S_v^2 = S_v'^2 + S_v''^2$
$S_i^2 = S_i'^2 + S_i''^2$ *etc.*

(*i*)	(*f*)	
0	0	$F^2(1+\cos^2 2\theta)/2 + (F'S''_v - F''S'_v)(2\cos^2\theta) + S_v^2 + (S_i^2 + S_f^2)/2$
0	1	$F^2(\sin^2 2\theta)/2 + (F'S''_v - F''S'_v)(2\sin^2\theta) - (S_i^2 - S_f^2)/2$
1	0	$F^2(\sin^2 2\theta)/2 + (F'S''_v - F''S'_v)(2\sin^2\theta) + (S_i^2 - S_f^2)/2$
0	2	$-F''(S'_i - S'_f\cos 2\theta) + F'(S''_i - S''_f\cos 2\theta) + S'_v(S'_i - S'_f) + S''_v(S''_i - S''_f)$
2	0	$-F''(S'_i\cos 2\theta - S'_f) + F'(S''_i\cos 2\theta - S''_f) + S'_v(S'_i - S'_f) + S''_v(S''_i - S''_f)$
0	3	$-F'(S'_i + S'_f\cos 2\theta) - F''(S''_i + S''_f\cos 2\theta) - S''_v(S'_i + S'_f) + S'_v(S''_i + S''_f)$
3	0	$-F'(S'_i\cos 2\theta + S'_f) - F''(S''_i\cos 2\theta + S''_f) - S''_v(S'_i + S'_f) + S'_v(S''_i + S''_f)$
1	1	$F^2(1+\cos^2 2\theta)/2 + (F'S''_v - F''S'_v)(2\cos^2\theta) + S_v^2 - (S_i^2 + S_f^2)/2$
1	2	$F'(S''_i + S''_f\cos 2\theta) - F''(S'_i + S'_f\cos 2\theta) + S'_v(S'_i + S'_f) + S''_v(S''_i + S''_f)$
2	1	$-F'(S''_i\cos 2\theta + S''_f) + F''(S'_i\cos 2\theta + S'_f) - S'_v(S'_i + S'_f) - S''_v(S''_i + S''_f)$
1	3	$-F'(S'_i - S'_f\cos 2\theta) - F''(S''_i - S''_f\cos 2\theta) + S'_v(S''_i - S''_f) - S''_v(S'_i - S'_f)$
3	1	$F'(S'_i\cos 2\theta - S'_f) + F''(S''_i\cos 2\theta - S''_f) - S'_v(S''_i - S''_f) + S''_v(S'_i - S'_f)$
2	2	$F^2\cos 2\theta + (F'S''_v - F''S'_v)(2\cos^2\theta) + S_v^2 - (S'_iS'_f + S''_iS''_f)$
2	3	$-(F'S'_v + F''S''_v)(2\sin^2\theta) + (S'_iS''_f - S'_fS''_i)$
3	2	$(F'S'_v + F''S''_v)(2\sin^2\theta) + (S'_iS''_f - S'_fS''_i)$
3	3	$F^2\cos 2\theta + (F'S''_v - F''S'_v)(2\cos^2\theta) + S_v^2 + S'_iS'_f + S''_iS''_f$

We see that $\mathrm{d}N_{(f)}$ can be deduced from $N_{(i)}$ by applying a linear operator *E* which depends only on the diffracting sample (Mueller operator)

$$\mathrm{d}N^m_{(f)} = E^m_n\,N^n_{(i)}\,\mathrm{d}\Omega. \qquad (B\text{-}6)$$

For an automatic computation of *E*, we have made use of the computer program *SCHOONSCHIP* from CERN, on the Centre de Calcul de Physique Nucléaire CDC-6600; the result is given in Table 4. It differs from the corresponding result given by Lipps & Tolhoek (1954) for Compton scattering, because we have to take into account the Fourier transforms *F* and **S**, which are different from one another and complex; other differences come from the final electron state, from the order of approximation, and from slightly different definitions of the final polarization.

Experimental set up often includes a monochromator, which plays the role of a polarizer or analyzer. Suppose it is placed after the sample; let *A* be its Mueller operator (including experimental factors such as beam apertures, absorption, *etc.*⋯) and $N_{(d)}$ the Stokes vector of the beam going into the detector (Fig. 7); only $N^0_{(d)}$ is measured:

$$N^0_{(d)} = A^0_m\,E^m_n\,N^n_{(i)}. \qquad (B\text{-}7)$$

Vaillant (1977) has computed the matrix *A* for any orientation of the monochromator. Formula (24), or explicit development of (22*a*,*b*), may be obtained by this way.

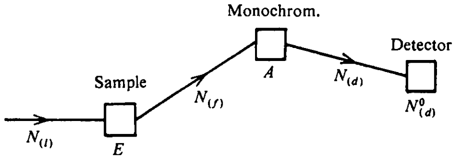

Fig. 7. Schematic drawing of an experimental set-up, with a monochromator after the sample. The *N* are the Stokes vectors of the beams, *E* and *A* the matrices which transform them into one another; the measured quantity is $N^0_{(d)}$.

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Diffraction of X-rays by Magnetic Materials.
II. Measurements on Antiferromagnetic Fe_2O_3

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Abstract

Two of the magnetic superlattice Bragg reflections of a single crystal of hematite (Fe_2O_3) have been measured by diffraction of X-rays produced from a conventional source, and compared to the intensities expected from the photon–spin scattering. Several orientations of the spins relative to the beams have been realized by rotating the crystal and by changing its temperature through the Morin (spin-flip) transition; in some of the measurements, the polarization produced by the monochromator was enhanced and this produced a visible asymmetry in the dependence of the intensities on the spin direction. The variations of the intensities during these changes of configuration are characteristic of magnetic scattering; the observed variations, as well as the absolute intensities, agree with the theory apart from some discrepancies. These may be due to intense multiple-scattering effects, and to some possible anomalies in the spin direction near the sample surface. As an application of this technique, changes of the direction of magnetization when a magnetic field is applied to the weakly ferromagnetic room-temperature phase have been investigated.

I. Introduction

In paper I (de Bergevin & Brunel, 1981), we have developed the general formulae for the diffraction of X-rays by a magnetic compound by taking into account the interaction between photons and spins. We have also described the experiments in which this effect is detected with ferro- and ferrimagnetic compounds.

The occurence of antiferromagnetic ordering lowers the symmetry of a crystal, and eventually enlarges the unit cell. This generally produces in the X-ray diffraction diagram some superstructure reflections due to the photon–spin interaction (except in the cases, for example Cr_2O_3, where the symmetry centre disappears). In a previous paper (de Bergevin & Brunel, 1972), we have shown the existence of the magnetic reflections $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and $\frac{3}{2}\frac{3}{2}\frac{3}{2}$ in nickel oxide NiO; these reflections disappeared at the Néel point. In order to make a complete and convincing check of the theoretical predictions we have undertaken the same type of experiments on Fe_2O_3.

In the first part of this article, we derive the principle of our measurements from the expression for the intensity of the magnetic reflections (§ II) and describe the application of this to Fe_2O_3 (§ III). In the second part, after a description of our apparatus (§ IV) and of the experimental procedure (§ V), the results are given and compared to the expected ones.

II. Principle of the experiment

In a study made with an unpolarized source, and with a monochromator diffracting in the same plane as the sample, the diffracted intensity is given by the formulae (19), (20) and (22) of paper I. The intensity of a pure superstructure reflection (without any contribution from the non-magnetic atoms) is proportional to $|\mathbf{B}.\mathbf{S}|^2$. We assume all the spins to be collinear and define the spin-density structure factor $\mathbf{S}(hkl)$ as in the ferromagnetic case:

$$\mathbf{S}(hkl) = \hat{\mathbf{S}}F_T(hkl)f_M(\theta)\mu/2, \qquad (1)$$

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