International Tables for Crystallography (2006). Vol. C, Figure 8.7.4.1, p. 733.

8.7.4.10. *Magnetic X-ray scattering separation between spin and orbital magnetism*

8.7.4.10.1. *Introduction*

In addition to the usual Thomson scattering (charge scattering), there is a magnetic contribution to the X-ray amplitude (de Bergevin & Brunel, 1981; Blume, 1985; Brunel & de Bergvin, 1981; Blume & Gibbs, 1988). In units of the chemical radius r_e of the electron, the total scattering amplitude is

$$A_x = F_C + F_M, \qquad (8.7.4.95)$$

where F_C is the charge contribution, and F_M the magnetic part.

Let $\hat{\varepsilon}$ and $\hat{\varepsilon}'$ be the unit vectors along the electric field in the incident and diffracted direction, respectively. $\mathbf{k}$ and $\mathbf{k}'$ denote the wavevectors for the incident and diffracted beams. With these notations,

$$F_C = F(\mathbf{h})\,\hat{\varepsilon}\cdot\hat{\varepsilon}', \qquad (8.7.4.96)$$

where $F(\mathbf{h})$ is the usual structure factor, which was discussed in Section 8.7.3 [see also Coppens (1992)].

$$F_M = -i\,\frac{h\omega}{mc^2}\,\{\mathbf{M}_L(\mathbf{h})\cdot\mathbf{A} + \mathbf{M}_S(\mathbf{h})\cdot\mathbf{B}\}. \qquad (8.7.4.97)$$

$\mathbf{M}_L$ and $\mathbf{M}_S$ are the orbital and spin-magnetization vectors in reciprocal space, and $\mathbf{A}$ and $\mathbf{B}$ are vectors that depend in a rather complicated way on the polarization and the scattering geometry:

$$\begin{aligned}\mathbf{A} &= 4\sin^2\theta\,\hat{\varepsilon}\times\hat{\varepsilon}' - (\hat{\mathbf{k}}+\hat{\varepsilon})(\hat{\mathbf{k}}\cdot\hat{\varepsilon}') + (\hat{\mathbf{k}}'\times\hat{\varepsilon}')(\hat{\mathbf{k}}'\cdot\hat{\varepsilon})\\ \mathbf{B} &= \hat{\varepsilon}'\times\hat{\varepsilon} + (\mathbf{k}'+\varepsilon')(\mathbf{k}\cdot\varepsilon) - (\hat{\mathbf{k}}\times\hat{\varepsilon})(\hat{\mathbf{k}}\cdot\hat{\varepsilon}')\\ &\quad - (\hat{\mathbf{k}}'\times\hat{\varepsilon}')\times(\hat{\mathbf{k}}\times\hat{\varepsilon}).\end{aligned} \qquad (8.7.4.98)$$

For comparison, the magnetic neutron scattering amplitude can be written in the form

$$F_M^{\rm neutron} = [\mathbf{M}_L(\mathbf{h}) + M_S(\mathbf{h})]\cdot\mathbf{C}, \qquad (8.7.4.99)$$

with $\mathbf{C} = \hat{\mathbf{h}}\times\boldsymbol{\sigma}\times\hat{\mathbf{h}}$.

From (8.7.4.99), it is clear that spin and orbital contributions cannot be separated by neutron scattering. In contrast, the polarization dependencies of $\mathbf{M}_L$ and $\mathbf{M}_S$ are different in the X-ray case. Therefore, owing to the well defined polarization of synchrotron radiation, it is in principle possible to separate experimentally spin and orbital magnetization.

However, the prefactor $(h\omega/mc^2)\sim 10^{-2}$ makes the magnetic contributions weak relative to charge scattering. Moreover, F_C is roughly proportional to the total number of electrons, and F_M to the number of unpaired electrons. As a result, one expects $|F_M/F_C|$ to be about 10^{-3}.

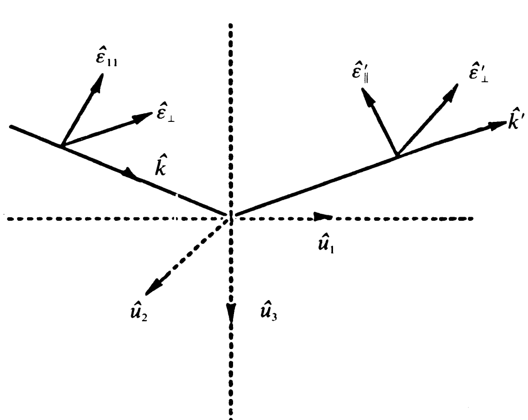

Fig. 8.7.4.1. Some geometrical definitions.

It should also be pointed out that F_M is in quadrature with F_C. In many situations, the total X-ray intensity is therefore

$$I_x = |F_C|^2 + |F_M|^2.$$

Thus, under these conditions, the magnetic effect is typically 10^{-6} times the X-ray intensity.

Magnetic contributions can be detected if magnetic and charge scattering occur at different positions (antiferromagnetic type of ordering). Furthermore, Blume (1985) has pointed out that the photon counting rate for $|F_M|^2$ at synchrotron sources is of the same order as the neutron rate at high-flux reactors.

Finally, situations where the 'interference' F_CF_M term is present in the intensity are very interesting, since the magnetic contribution becomes 10^{-3} times the charge scattering.

The polarization dependence will now be discussed in more detail.

8.7.4.10.2. *Magnetic X-ray structure factor as a function of photon polarization*

Some geometrical definitions are summarized in Fig. 8.7.4.1, where parallel ($\parallel$) and perpendicular ($\perp$) polarizations will be chosen in order to describe the electric field of the incident and diffracted beams. In this two-dimensional basis, vectors $\mathbf{A}$ and $\mathbf{B}$ of (8.7.4.98) can be written as (2×2) matrices:

$$\mathbf{A} = \sin^2\theta\begin{pmatrix} 0 & -(\hat{\mathbf{k}}+\hat{\mathbf{k}}') \\ (\hat{\mathbf{k}}+\hat{\mathbf{k}}') & 2(\hat{\mathbf{k}}\times\hat{\mathbf{k}}')\end{pmatrix}\begin{matrix}\perp\\ \parallel\end{matrix}$$
$$i\rightarrow\quad \perp \qquad\qquad \parallel \qquad\qquad \uparrow f$$

(i and f refer to the incident and diffracted beams, respectively);

$$\mathbf{B} = \begin{pmatrix} \hat{\mathbf{k}}\times\hat{\mathbf{k}}' & -2\hat{\mathbf{k}}'\sin^2\theta \\ 2\hat{\mathbf{k}}\sin^2\theta & \hat{\mathbf{k}}\times\hat{\mathbf{k}}'\end{pmatrix}. \qquad (8.7.4.100)$$

By comparison, for the Thomson scattering,

$$\hat{\varepsilon}\cdot\hat{\varepsilon}' = \begin{pmatrix} 1 & 0 \\ 0 & \cos 2\theta\end{pmatrix}. \qquad (8.7.4.101)$$

The major difference with Thomson scattering is the occurrence of off-diagonal terms, which correspond to scattering processes with a change of polarization. We obtain for the structure factors A_{if}:

$$\begin{aligned}A_{\perp\perp} &= F - i\,\frac{\hbar\omega}{mc^2}(\hat{\mathbf{k}}\times\hat{\mathbf{k}}')\cdot\mathbf{M}_S\\ A_{\perp\parallel} &= -2i\,\frac{\hbar\omega}{mc^2}\sin^2\theta\{(\hat{\mathbf{k}}+\hat{\mathbf{k}}')\cdot\mathbf{M}_L + \hat{\mathbf{k}}'\cdot\mathbf{M}_S\}\\ A_{\parallel\perp} &= 2i\,\frac{\hbar\omega}{mc^2}\sin 2\theta\{(\hat{\mathbf{k}}+\hat{\mathbf{k}}')\cdot\mathbf{M}_L + \hat{\mathbf{k}}'\cdot\mathbf{M}_S\}\\ A_{\parallel\parallel} &= F\cos^2\theta - i\frac{\hbar\omega}{mc^2}(\hat{\mathbf{k}}\times\hat{\mathbf{k}}')\cdot\{4\sin^2\theta\,\mathbf{M}_L\mathbf{M}_S\}.\end{aligned} \qquad (8.7.4.102)$$

For a linear polarization, the measured intensity in the absence of diffracted-beam polarization analysis is

$$I_\alpha = |A_{\perp\perp}\cos\alpha + A_{\parallel\perp}\sin\alpha|^2 + |A_{\perp\parallel}\cos\alpha + A_{\parallel\parallel}\sin\alpha|^2, \qquad (8.7.4.103)$$

where α is the angle between $\mathbf{E}$ and $\hat{\varepsilon}$. In the centrosymmetric system, without anomalous scattering, no interference term occurs in (8.7.4.103). However, if anomalous scattering is present, $F = F' + iF''$, and terms involving $F''M_S$ or $F''M_L$ appear in the intensity expression.

The radiation emitted in the plane of the electron or positron orbit is linearly polarized. The experimental geometry is

references