1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

Table 1.11.2.2. *The indices of the forbidden reflections and corresponding tensors of structure factors $F_{jk}(hk\ell)$ for the cubic space groups ($n = 0, \pm1, \pm2, \ldots$)*

Space group	Indices of reflections	Expressions for $F_{jk}(hk\ell)$ and additional restrictions
$P2_13$	$00\ell: \ell = 2n + 1$	(1.11.2.23)
$Pn\bar{3}$	$0k\ell: \ell = 2n + 1$	(1.11.2.6); $F_2 = 0$ for 00ℓ
$Fd\bar{3}$	$0k\ell: k, \ell = 2n, k + \ell = 4n + 2$	(1.11.2.6); $F_2 = 0$ for 00ℓ
$Pa\bar{3}$	$0k\ell: k = 2n + 1$	(1.11.2.6); $F_2 = 0$ for $0k0$
$Ia\bar{3}$	$0k\ell: k, \ell = 2n + 1$	(1.11.2.6)
$P4_232$	$00\ell: \ell = 2n + 1$	(1.11.2.24)
$F4_132$	$00\ell: \ell = 4n + 2$	(1.11.2.24)
$P4_332$	$00\ell: \ell = 4n \pm 1$	(1.11.2.23); $F_2 = \mp iF_1$
	$00\ell: \ell = 4n + 2$	(1.11.2.24)
$P1_332$	$00\ell: \ell = 4n \pm 1$	(1.11.2.23); $F_2 = \pm iF_1$
	$00\ell: \ell = 4n + 2$	(1.11.2.24)
$I4_132$	$00\ell: \ell = 4n + 2$	(1.11.2.24)
$P\bar{4}3n$	$hh\ell: \ell = 2n + 1$	(1.11.2.22); $F_2 = 0$ for 00ℓ, $F_1 = F_2 = 0$ for hhh
$F\bar{4}3c$	$hh\ell: h, \ell = 2n + 1$	(1.11.2.22); $F_1 = F_2 = 0$ for hhh
$I\bar{4}3d$	$hh\ell: 2h + \ell = 4n + 2$	(1.11.2.22); $F_2 = 0$ for 00ℓ, $F_1 = F_2 = 0$ for hhh
$Pn\bar{3}n$	$hh\ell: \ell = 2n + 1$	(1.11.2.22); $F_1 = F_2 = 0$ for hhh
	$0k\ell: k + \ell = 2n + 1$	(1.11.2.6); $F_1 = F_2 = 0$ for 00ℓ
$Pm\bar{3}n$	$hh\ell: \ell = 2n + 1$	(1.11.2.22); $F_1 = F_2 = 0$ for hhh
$Pn\bar{3}m$	$0k\ell: k + \ell = 2n + 1$	(1.11.2.6); $F_2 = 0$ for 00ℓ
$Fm\bar{3}c$	$hh\ell: h, \ell = 2n + 1$	(1.11.2.22); $F_1 = F_2 = 0$ for hhh
$Fd\bar{3}m$	$0k\ell: k, \ell = 2n, k + \ell = 4n + 2$	(1.11.2.6); $F_2 = 0$ for 00ℓ
$Fd\bar{3}c$	$0k\ell: k, \ell = 2n, k + \ell = 4n + 2$	(1.11.2.6); $F_2 = 0$ for 00ℓ
	$hh\ell: h, \ell = 2n + 1$	(1.11.2.22); $F_1 = F_2 = 0$ for hhh
$Ia\bar{3}d$	$0k\ell: k, \ell = 2n + 1$	(1.11.2.6); $F_2 = -F_1$ for $0kk$
	$hh\ell: 4h + \ell = 4n + 2$	(1.11.2.22); $hhh: F_1 = F_2 = 0$, $F_2 = 0$ for 00ℓ

$Fd\bar{3}m$: (1.11.2.10), (1.11.2.14) and (1.11.2.19).
$Fd\bar{3}c$: (1.11.2.10), (1.11.2.13) and (1.11.2.20).
$Ia\bar{3}d$: (1.11.2.11), (1.11.2.12) and (1.11.2.21).

For all $a_i(x, y, z)$, the sets of coordinates are chosen here as in *International Tables for Crystallography* Volume A (Hahn, 2005); the first one being adopted if Volume A offers two alternative origins. The expressions (1.11.2.10) or (1.11.2.11) appear for all space groups because all of them are supergroups of $P23$ or $P2_13$.

The tensor structure factors of forbidden reflections can be further restricted by the cubic symmetry, see Table 1.11.2.2. For the glide plane c, the tensor structure factor of $0k\ell: \ell = 2n + 1$ reflections is given by (1.11.2.6), whereas for the diagonal glide plane n, it is given by

$$F_{jk}(hh\ell; \ell = 2n + 1) = \begin{pmatrix} F_1 & 0 & F_2 \\ 0 & -F_1 & -F_2 \\ F_2 & -F_2 & 0 \end{pmatrix}, \qquad (1.11.2.22)$$

and additional restrictions on F_1 and F_2 can become effective for $k = \ell$ or $h = \ell$. For forbidden reflections of the 00ℓ type, the tensor structure factor is either

$$F_{jk}(00\ell) = \begin{pmatrix} 0 & 0 & F_1 \\ 0 & 0 & F_2 \\ F_1 & F_2 & 0 \end{pmatrix} \qquad (1.11.2.23)$$

or

$$F_{jk}(00\ell) = \begin{pmatrix} F_1 & F_2 & 0 \\ F_2 & -F_1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \qquad (1.11.2.24)$$

see Table 1.11.2.2.

$Pn\bar{3}$: (1.11.2.10) and

$$a_i(x, y, z) = a_i(\tfrac{1}{2} - x, \tfrac{1}{2} - y, \tfrac{1}{2} - z). \qquad (1.11.2.13)$$

$Fd\bar{3}$: (1.11.2.10) and

$$a_i(x, y, z) = a_i(\tfrac{1}{4} - x, \tfrac{1}{4} - y, \tfrac{1}{4} - z). \qquad (1.11.2.14)$$

$Pa\bar{3}, Ia\bar{3}$: (1.11.2.11) and (1.11.2.12).
$P432, F432, I432$: (1.11.2.10) and

$$a_i(x, y, z) = a_i(\bar{x}, \bar{z}, \bar{y}). \qquad (1.11.2.15)$$

$P4_232$: (1.11.2.10) and

$$a_i(x, y, z) = a_i(\tfrac{1}{2} - x, \tfrac{1}{2} - z, \tfrac{1}{2} - y). \qquad (1.11.2.16)$$

$F4_132, P4_332, I4_132$: (1.11.2.11) and

$$a_i(x, y, z) = a_i(\tfrac{1}{4} - x, \tfrac{1}{4} - z, \tfrac{1}{4} - y). \qquad (1.11.2.17)$$

$P4_132$: (1.11.2.11) and

$$a_i(x, y, z) = a_i(\tfrac{3}{4} - x, \tfrac{3}{4} - z, \tfrac{3}{4} - y). \qquad (1.11.2.18)$$

$P\bar{4}3m, F\bar{4}3m, I\bar{4}3m$: (1.11.2.10) and

$$a_i(x, y, z) = a_i(x, z, y). \qquad (1.11.2.19)$$

$P\bar{4}3n, F\bar{4}3c$: (1.11.2.10) and

$$a_i(x, y, z) = a_i(\tfrac{1}{2} + x, \tfrac{1}{2} + z, \tfrac{1}{2} + y). \qquad (1.11.2.20)$$

$I\bar{4}3d$: (1.11.2.11) and

$$a_i(x, y, z) = a_i(\tfrac{1}{4} + x, \tfrac{1}{4} + z, \tfrac{1}{4} + y). \qquad (1.11.2.21)$$

$Pm\bar{3}m, Fm\bar{3}m, Im\bar{3}m$: (1.11.2.10), (1.11.2.12) and (1.11.2.19).
$Pn\bar{3}n$: (1.11.2.10), (1.11.2.13) and (1.11.2.15).
$Pm\bar{3}n, Fm\bar{3}c$: (1.11.2.10), (1.11.2.12) and (1.11.2.20).
$Pn\bar{3}m$: (1.11.2.10), (1.11.2.13) and (1.11.2.19).

1.11.3. Polarization properties and azimuthal dependence

There are two important properties that distinguish forbidden reflections from conventional ('allowed') ones: non-trivial polarization effects and strong azimuthal dependence of intensity (and sometimes also of polarization) corresponding to the symmetry of the direction of the scattering vector. The azimuthal dependence means that the intensity and polarization properties of the reflection can change when the crystal is rotated around the direction of the reciprocal-lattice vector, *i.e.* they change with the azimuthal angle of the incident wavevector **k** defined relative to the scattering vector. The polarization and azimuthal proper-ties, both mainly determined by symmetry, are two of the most informative characteristics of forbidden reflections. A third one, energy dependence, is determined by physical interactions, electronic and/or magnetic, where the role of symmetry is indirect but nevertheless also important (*e.g.* in splitting of atomic levels *etc.*, see Section 1.11.4).

In the kinematical theory, usually used for weak reflections, one obtains for unpolarized incident radiation the intensity of a conventional reflection as given by

$$I_{\mathbf{H}} = A_{\mathbf{H}}|F(\mathbf{H})|^2 (1 + \cos^2 2\theta)/2, \qquad (1.11.3.1)$$

where θ is the Bragg angle, $F(\mathbf{H})$ is the scalar structure factor of reflection **H**, and $A_{\mathbf{H}}$ is a scale factor, which depends on the incident beam intensity, the sample volume, the geometry of diffraction *etc.* (see *International Tables for Crystallography* Volume B), and can be set to $A_{\mathbf{H}} = 1$ hereafter.

If the structure factor is a tensor of rank 2, then the reflection intensity obtained with incident and reflected radiation with polarization vectors, respectively, $\mathbf{e}$ and $\mathbf{e}'$ (prepared and analysed by a corresponding polarizer and analyser) is given by

$$I_{\mathbf{H}}(\mathbf{e}', \mathbf{e}) = |F_{jk}(\mathbf{H})e_j'^* e_k|^2, \qquad (1.11.3.2)$$

where the star denotes the complex conjugate. The maximum of this expression is reached when $\mathbf{e}'$ is equal to the polarization of the diffracted beam. In general, the polarization of the diffracted secondary radiation, $\mathbf{e}'_{\mathbf{H}}$, depends on the incident beam polarization $\mathbf{e}$:

$$\mathbf{e}'_{\mathbf{H}} = \mathbf{C}_{\mathbf{H}} / \sqrt{|\mathbf{C}_{\mathbf{H}}|^2}, \qquad (1.11.3.3)$$

where

$$(\mathbf{C}_{\mathbf{H}})_j = \left[\mathbf{k}^2 F_{jk}(\mathbf{H}) - k_j' k_n' F_{nk}(\mathbf{H}) \right] e_k \qquad (1.11.3.4)$$

(the second term in this expression provides orthogonality between the polarization vector and the corresponding wavevector). If the polarization of the diffracted beam is not analysed, the total intensity of the diffracted beam $I_{\mathbf{H}}^{tot}(\mathbf{e})$ is equal to $I_{\mathbf{H}}(\mathbf{e}'_{\mathbf{H}}, \mathbf{e})$. If the tensor structure factor is a direct product of two vectors, then the polarization of the diffracted beam does not depend on the incident polarization.

The polarization analysis of forbidden reflections frequently uses the linear polarization vectors $\boldsymbol{\sigma}$ and $\boldsymbol{\pi}$. Vector $\boldsymbol{\sigma}$ is perpendicular to the scattering plane, whereas the vectors $\boldsymbol{\pi}$ and $\boldsymbol{\pi}'$ are in the scattering plane so that $\boldsymbol{\sigma}, \boldsymbol{\pi}, \mathbf{k}$ and $\boldsymbol{\sigma}, \boldsymbol{\pi}', \mathbf{k}'$ form right-hand triads. Note that the components of the polarization vectors, $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ etc., change with the azimuthal angle if the crystal is rotated about the scattering vector.

In special cases, circular polarizations are very useful and sometimes even indispensable, because they enable us to distinguish right- and left-hand crystals or to unravel interferences between magnetic and electric scattering (see below).

If the incident radiation is $\boldsymbol{\sigma}$- or $\boldsymbol{\pi}$-polarized or non-polarized, then the total reflection intensities for these three cases are given by the following expressions:

$$I_\sigma = I_{\mathbf{H}}(\boldsymbol{\sigma}, \boldsymbol{\sigma}) + I_{\mathbf{H}}(\boldsymbol{\pi}', \boldsymbol{\sigma}), \qquad (1.11.3.5)$$

$$I_\pi = I_{\mathbf{H}}(\boldsymbol{\sigma}, \boldsymbol{\pi}) + I_{\mathbf{H}}(\boldsymbol{\pi}', \boldsymbol{\pi}), \qquad (1.11.3.6)$$

$$I_{\mathbf{H}} = (I_\sigma + I_\pi)/2. \qquad (1.11.3.7)$$

A more general approach uses the Stokes parameters for the description of partially polarized X-rays and the Müller matrices for the scattering process (see a survey by Detlefs *et al.*, 2012). This issue will, however, not be discussed further since there is no principal difference to conventional optics.

Let us consider the polarization and azimuthal characteristics of screw-axis forbidden reflections listed in Table 1.11.2.1. These characteristics are rather different for two types of reflections: type I reflections are those for which $F_{xx} = F_{yy} = F_{xy} = 0$, while all other reflections constitute the rest, type II.

The type-I forbidden reflections have the simplest polarization properties. From equations (1.11.3.5)–(1.11.3.7) and Table 1.11.2.1, one obtains $I_{\mathbf{H}}(\boldsymbol{\sigma}, \boldsymbol{\sigma}) = I_{\mathbf{H}}(\boldsymbol{\pi}', \boldsymbol{\pi}) = 0$ and $I_{\mathbf{H}} = I_\sigma = I_\pi = I_{\mathbf{H}}(\boldsymbol{\sigma}, \boldsymbol{\pi}) = I_{\mathbf{H}}(\boldsymbol{\pi}', \boldsymbol{\sigma})$, where $I_{\mathbf{H}}(\boldsymbol{\pi}', \boldsymbol{\sigma})$ is given by

$$I_{\mathbf{H}}(\boldsymbol{\pi}', \boldsymbol{\sigma}) = [|F_1|^2 \sin^2 \varphi + |F_2|^2 \cos^2 \varphi, \qquad (1.11.3.8)$$
$$- Re(F_1 F_2^*) \sin 2\varphi] \cos^2 \theta \qquad (1.11.3.9)$$

for a 2_1 screw axis and

$$I_{\mathbf{H}}(\boldsymbol{\pi}', \boldsymbol{\sigma}) = |F_1|^2 \cos^2 \theta \qquad (1.11.3.10)$$

for 4_1, 4_3, 6_1 and 6_5 screw axes, where φ is the azimuthal angle of crystal rotation about the scattering vector $\mathbf{H}$. Thus, $\boldsymbol{\sigma}$-polarized incident radiation results in reflected radiation with $\boldsymbol{\pi}$ polarization and *vice versa*; and unpolarized incident radiation gives unpolarized reflected radiation.

Note that there is no azimuthal dependence of intensity in (1.11.3.10). Nevertheless, the phase of the diffracted beams changes with azimuthal rotation, as might be observed *via* interference with another scattering process, for example, with multiple (Renninger) diffraction. Such measurements could also be useful for determining the phases of the complex F_1 and F_2 above.

The polarization properties of type-II reflections are quite distinct from those of type-I reflections. The intensities belonging to various polarization channels, *i.e.* combinations of primary and secondary beam polarizations ($\sigma \rightarrow \sigma$, $\sigma \rightarrow \pi'$ *etc.*), exhibit different azimuthal symmetries for different screw axes.

For 3_1 and 3_2 screw axes, the azimuthal symmetry is threefold:

$$I_\sigma = |F_1|^2(1 + \sin^2 \theta) + |F_2|^2 \cos^2 \theta + D(\varphi),$$
$$I_\pi = |F_1|^2 \sin^2 \theta(1 + \sin^2 \theta) + |F_2|^2 \cos^2 \theta + D(\varphi),$$
$$I_{\mathbf{H}} = |F_1|^2(1 + \sin^2 \theta)^2/2 + |F_2|^2 \cos^2 \theta + D(\varphi),$$

$$(1.11.3.11)$$

where $D(\varphi) = \sin 2\theta \left[Re(F_1 F_2^*) \cos 3\varphi \mp Im(F_1 F_2^*) \sin 3\varphi \right]$. The $\mp$ sign corresponds to $F_{xy} = \pm i F_{xx}$ in Table 1.11.2.1.

For 4_1, 4_3, and 4_2 screw axes, the symmetry is fourfold:

$$I_\sigma = |F_1|^2 B(\varphi) + |F_2|^2 C(\varphi)$$
$$+ Re(F_1 F_2^*) \cos^2 \theta \sin 4\varphi,$$
$$I_\pi = \sin^2 \theta \left[|F_1|^2 C(\varphi) + |F_2|^2 B(\varphi) \right.$$
$$\left. + Re(F_1 F_2^*) \cos^2 \theta \sin 4\varphi \right],$$
$$I_{\mathbf{H}} = (I_\sigma + I_\pi)/2, \qquad (1.11.3.12)$$

where $B(\varphi) = 1 - \cos^2 \theta \sin^2 2\varphi$ and $C(\varphi) = 1 - \cos^2 \theta \cos^2 2\varphi$.

No azimuthal dependence exists for the screw axes 6_1, 6_2, 6_4 and 6_5:

$$I_\sigma = |F_1|^2(1 + \sin^2 \theta),$$
$$I_\pi = |F_1|^2(1 + \sin^2 \theta) \sin^2 \theta,$$
$$I_{\mathbf{H}} = |F_1|^2(1 + \sin^2 \theta)^2/2. \qquad (1.11.3.13)$$

Unlike the type-I reflections, the intensities of the type-II reflections are different for $\boldsymbol{\sigma}$- and $\boldsymbol{\pi}$-polarized incident beams. What is more interesting is that type-II reflections are 'chiral', *i.e.* their intensities differ for right-hand and left-hand circularly polarized incident radiation. As an example, we take the type-II back-reflections ($\theta = \pi/2$) for three- and sixfold screw axes. We find from Table 1.11.2.1 and equations (1.11.3.1) and (1.11.3.3) that only the beams with definite circular polarization (right-hand if $F_{xy} = i F_{xy}$ and left-hand if $F_{xy} = -i F_{xy}$) are reflected and that the back-reflected radiation has the same circular polarization in both cases. For opposite polarization, the reflection is absent. Thus, under these circumstances, the crystal may be regarded as a circular polarizer or analyser. If $\theta < \pi/2$, the *eigen*-polarizations are elliptic and the axial ratio of the polarization ellipse is equal to $\sin \theta$ for the sixfold screw axes (whereas for the three- and fourfold screw axes, this ratio depends on the parameters F_1 and F_2).

The chirality of type-II reflections can be used to distinguish enantiomorphous crystals. Although this was suggested many years ago, its potential was only recently proved by experiments, first on α-quartz, SiO_2, and berlinite, $AlPO_4$ (Tanaka *et al.*, 2008; Tanaka, Kojima *et al.*, 2010), later for tellurium (Tanaka, Collins *et al.*, 2010). All three candidates crystallize in the space groups $P3_121$ or $P3_221$. The case of tellurium is particularly interesting because standard X-ray diffraction methods for absolute structure determination fail in elemental crystals.

The non-trivial polarization and azimuthal properties discussed above are, in most cases, determined by symmetry, and they are used as evidence confirming the origin of the forbidden reflections. They are also used for obtaining detailed information about anisotropy of local susceptibility and, hence, about structural and electronic properties. For instance, careful analysis of polarization and azimuthal dependences allows one to distinguish between different scenarios of the Verwey phase transition in magnetite, Fe_3O_4 – a longstanding and confusing problem (see Hagiwara *et al.*, 1999; García *et al.*, 2000; Renevier *et al.*, 2001; García & Subías, 2004; Nazarenko *et al.*, 2006; Subías *et al.*, 2012).

1.11.4. Physical mechanisms for the anisotropy of atomic X-ray susceptibility

Conventional non-resonant Thomson scattering in condensed matter is the result of the interaction of the electric field of the electromagnetic wave with the charged electron subsystem. However, there are also other mechanisms of interaction, *e.g.* interaction of electromagnetic waves with spin and orbital moments, which was first considered by Platzman & Tzoar (1970) for molecules and solids. They predicted the sensitivity of X-ray diffraction to a magnetic structure of a crystal, as later observed in the pioneering works of de Bergevin & Brunel (de Bergevin & Brunel, 1972, 1981; Brunel & de Bergevin, 1981). It is reasonable to describe all X-ray–electron interactions by the Pauli equation (Berestetskii *et al.*, 1982), which is a low-energy approximation to the Dirac equation (typical X-ray energies are $\hbar\omega \ll mc^2 \approx 0.5$ MeV where m is the electron mass). The equation accounts for charge and spin interaction with the electromagnetic field of the wave, and spin–orbit interaction (Blume, 1985, 1994) using the following Hamiltonian:

$$H' = \frac{e^2}{2mc^2}\sum_p \mathbf{A}^2(\mathbf{r}_p) - \frac{e}{mc}\sum_p \mathbf{P}_p \cdot \mathbf{A}(\mathbf{r}_p)$$
$$- \frac{e\hbar}{mc}\sum_p \mathbf{s}_p \cdot [\nabla \times \mathbf{A}(\mathbf{r}_p)]$$
$$- \frac{e^2\hbar}{2(mc^2)^2}\sum_p \mathbf{s}_p \cdot [\dot{\mathbf{A}}(\mathbf{r}_p) \times \mathbf{A}(\mathbf{r}_p)], \qquad (1.11.4.1)$$

where $\mathbf{P}_p$ is the momentum of the pth electron, and $\mathbf{A}(\mathbf{r}_p)$ is the vector potential of the electromagnetic wave with wavevector $\mathbf{k}$ and polarization $\mathbf{e}$.

Here and below $\mathbf{A} = \sum_{\mathbf{k},\alpha}(2\pi\hbar c^2/V\omega_k)^{1/2}[\mathbf{e}(\mathbf{k}\alpha)c(\mathbf{k}\alpha)\exp(i\mathbf{k}\cdot\mathbf{r}) + \mathbf{e}^*(\mathbf{k}\alpha)c^+(\mathbf{k}\alpha)\exp(-i\mathbf{k}\cdot\mathbf{r})]$, where V is a quantization volume, index α labels two polarizations of each wave, $\mathbf{e}(\mathbf{k}\alpha)$ are the polarizations vectors, and $c(\mathbf{k}\alpha)$ and $c^+(\mathbf{k}\alpha)$ are the photon annihilation and creation operators.

Considering X-ray scattering by different atoms in solids as independent processes [in Section 1.2.4 of *International Tables for Crystallography* Volume B, this is called 'the isolated-atom

approximation in X-ray diffraction'; the validity of this approximation has been discussed by Kolpakov *et al.* (1978)], the atomic scattering amplitude f, which describes the scattering of a wave with wavevector $\mathbf{k}$ and polarization $\mathbf{e}$ into a wave with wavevector $\mathbf{k}'$ and polarization $\mathbf{e}'$, can be written as

$$f(\mathbf{k}, \mathbf{e}, \mathbf{k}', \mathbf{e}') = -\frac{e^2}{mc^2}f_{jk}(\mathbf{k}', \mathbf{k})e_j'^* e_k, \qquad (1.11.4.2)$$

where the tensor atomic factor $f_{jk}(\mathbf{k}', \mathbf{k})$ depends not only on the wavevectors but also on the atomic environment, magnetic and orbital moments *etc*. From equation (1.11.4.1) and with the help of perturbation theory (Berestetskii *et al.*, 1982), the atomic factor $f_{jk}(\mathbf{k}', \mathbf{k})$ can be expressed as

$$f_{jk}(\mathbf{k}', \mathbf{k})$$
$$= \sum_a p_a \Bigg\{ \langle a| \sum_p \exp(i\mathbf{G}\cdot\mathbf{r}_p)|a\rangle\delta_{jk}$$
$$- i\frac{\hbar\omega}{mc^2}\langle a| \sum_p \exp(i\mathbf{G}\cdot\mathbf{r}_p)\left(-i\frac{[\mathbf{G}\times\mathbf{P}_p]_l}{\hbar H^2}A_{jkl} + s_l^p B_{jkl}\right)|a\rangle$$
$$- \frac{1}{m}\sum_c \left(\frac{E_a - E_c}{\hbar\omega}\right)\frac{\langle a|O_j^+(\mathbf{k}')|c\rangle\langle c|O_k(\mathbf{k})|a\rangle}{E_a - E_c + \hbar\omega - i\frac{\Gamma}{2}}$$
$$+ \frac{1}{m}\sum_c \left(\frac{E_a - E_c}{\hbar\omega}\right)\frac{\langle a|O_k(\mathbf{k})|c\rangle\langle c|O_j^+(\mathbf{k}')|a\rangle}{E_a - E_c - \hbar\omega} \Bigg\},$$
$$(1.11.4.3)$$

where the first line describes the non-resonant Thomson scattering and Γ is the energy width of the excited state $|c\rangle$. The second line gives non-resonant magnetic scattering with the spin and orbital terms given by the rank-3 tensors B_{jkl} (1.11.5.2) and A_{jkl} (1.11.5.1), respectively. Compared to the second-to-last line, where the energy denominator can be close to zero, the last line is usually neglected, but sometimes it has to be added to the non-resonant terms, in particular at photon energies far from resonance. The third term gives the dispersion corrections also addressed as resonant scattering, magnetic and non-magnetic. In equation (1.11.4.3), E_a and E_c are the ground and excited states energies, respectively; p_a is the probability that the incident state of the scatterer $|a\rangle$ is occupied; and $\mathbf{G} = \mathbf{k} - \mathbf{k}'$ is the scattering vector (in the case of diffraction $|\mathbf{G}| = 4\pi\sin\theta/\lambda$, where θ is the Bragg angle). The vector operator $\mathbf{O}(\mathbf{k})$ has the form

$$\mathbf{O}(\mathbf{k}) = \sum_p \exp(i\mathbf{k}\cdot\mathbf{r}_p)(\mathbf{P}_p - i\hbar[\mathbf{k}\times\mathbf{s}_p]). \qquad (1.11.4.4)$$

The second term in this equation is small and is frequently omitted.

In general, the total atomic scattering factor looks like

$$f_{jk}(\mathbf{k}', \mathbf{k}, E) = [f_0(|\mathbf{k}' - \mathbf{k}|) + f_0'(E) + if_0''(E)]\delta_{ij}$$
$$+ f_{jk}'(\mathbf{k}', \mathbf{k}, E) + if_{jk}''(\mathbf{k}', \mathbf{k}, E) + f_{jk}^{\mathrm{mag}},$$
$$(1.11.4.5)$$

where f_0 is the ordinary Thomson (non-resonant) factor, $f_0'(E)$ and $f_0''(E)$ are the isotropic corrections to the dispersion and absorption, which become stronger near absorption edges ($\sim 10^{-1}f_0$), and $f_{ij}'(\mathbf{k}', \mathbf{k}, E)$ and $f_{ij}''(\mathbf{k}', \mathbf{k}, E)$ are the real and imaginary contributions accounting for resonant anisotropic scattering and are sensitive to the local symmetry of the resonant atom and its magnetism. In the latter case, one should add the tensor f_{ij}^{mag} ($\sim 10^{-2}$–$10^{-3}f_0$) describing magnetic non-resonant scattering, which is also anisotropic (see the next section).

references