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1.11. Tensorial properties of local crystal susceptibilities

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1.11.1. Introduction

The tensorial characteristics of macroscopic physical properties (as described in Chapters 1.3, 1.4 and 1.6–1.8 of this volume) are determined by the crystal point group, whereas the symmetry of local crystal properties, such as atomic displacement parameters (Chapter 1.9) or electric field gradient tensors (Section 2.2.15) are regulated by the crystal space group. In the present chapter, we consider further examples of the impact of symmetry on local physical properties, particularly both symmetry and physical phenomena that allow and restrict forbidden reflections excited at radiation energies close to X-ray absorption edges of atoms, and reflections caused by magnetic scattering.

We begin with the X-ray dielectric susceptibility, which expresses the response of crystalline matter to an incident X-ray wave characterized by its energy (frequency), polarization and wavevector. The response is a polarization of the medium, finally resulting in a scattered wave with properties generally different from the initial ones. Thus, the dielectric susceptibility plays the role of a scattering amplitude, which relates the scattered wave to the incident wave. This is the basis of the different approaches to X-ray diffraction theories presented in Chapters 1.2 and 5.1 of *International Tables for Crystallography* Volume B (2008). Here, we consider only elastic scattering, *i.e.* the energies of the incident and scattered waves are identical, and the X-ray susceptibility is assumed to comply with the periodicity of the crystalline matter.

It is important that the dielectric susceptibility is (i) a local crystal property and (ii) a tensor physical property, because it relates the polarization vectors of the incident and scattered radiation. Consequently, the symmetry of the tensor is determined by the symmetry of the crystal space group, rather than by that of the point group as in conventional optics. In the vast majority of X-ray applications, this tensor can reasonably be assumed to be given by the product of the unit tensor and a scalar susceptibility, which is proportional to the electron density plus exclusively energy-dependent dispersion corrections as considered in Section 4.2.6 of *International Tables for Crystallography* Volume C (2004). As a result of atomic wavefunction distortions caused by neighbouring atoms, these scalar dispersion corrections can also become anisotropic tensors, namely in the close vicinity (usually less than about 50 eV) of absorption edges of elements. For heavy elements, the anisotropy of the tensor atomic factor can exceed 20 e atom^{-1}. Appropriate references to detailed descriptions of the phenomenon can be found in Brouder (1990), Materlik *et al.* (1994) and in Section 4.2.6 of Volume C (2004).

However, even if the anisotropy of the atomic factor is small, it can be crucial for some effects, for instance the excitation of so-called 'forbidden' reflections, which vanish in absence of anisotropy. Indeed, the crystal symmetry imposes strong restrictions on the indices of possible ('allowed') reflections. The systematic reflection conditions for the different space groups and for special atomic sites in the unit cell are listed in *International Tables for Crystallography* Volume A (Hahn, 2005). The resulting extinctions are due to (i) the translation symmetry of the non-primitive Bravais lattices, (ii) the symmetry elements of the space group (glide planes and/or screw axes) and (iii) special sites. The first kind cannot be violated. The other extinctions are obtained if the atomic scattering factor (as the Fourier transform of an independent atom/ion with spherically symmetric electron-density distribution) is an element-specific scalar that depends only on the scattering-vector length and the dispersion corrections. Then the intensities of extinct reflections generally vanish. These reflections are 'forbidden', but for different physical reasons not all of their intensities are necessarily strictly zero. Such reflections can appear owing to an asphericity of (i) an atomic electron-density distribution caused by chemical bonding and/or (ii) atomic vibrations (Dawson, 1975) if the atom in question occupies a special site.

In contrast, an anisotropy of the atomic factor affects all reflections and can therefore violate general extinction rules related to glide planes and/or screw axes, *i.e.* symmetry elements with translation components, in nonsymmorphic space groups. Even a very small X-ray anisotropy can be quantitatively studied with this type of forbidden reflections, and yield information about electronic states of crystals or partial structures of resonant scatterers. This was first recognized by Templeton & Templeton (1980), and a detailed theory was developed only a few years later (Dmitrienko, 1983, 1984). The excitation of forbidden reflections caused by anisotropic anomalous scattering was first observed in an $NaBrO_3$ crystal (Templeton & Templeton, 1985, 1986) and then studied for Cu_2O (Eichhorn & Kirfel, 1988), TiO_2 and MnF_2 (Kirfel & Petcov, 1991), and for many other compounds with different crystal symmetries. Within the dipole approximation, a systematic compilation of 'forbidden' reflection properties for all relevant space groups up to tetragonal symmetry and an application to partial-structure analysis followed (Kirfel *et al.*, 1991; Kirfel & Petcov, 1992; Kirfel & Morgenroth, 1993; Morgenroth *et al.*, 1994). Today, there are numerous surveys devoted to this well developed subject, and further details, applications and references can be found therein (Belyakov & Dmitrienko, 1989; Carra & Thole, 1994; Hodeau *et al.*, 2001; Lovesey *et al.*, 2005; Dmitrienko *et al.*, 2005; Altarelli, 2006; Collins *et al.*, 2007; Collins & Bombardi, 2010; Finkelstein & Dmitrienko, 2012). Forbidden reflections of the last type have also been observed (well before corresponding X-ray studies) in diffraction of Mössbauer radiation (Belyakov & Aivazyan, 1969; Belyakov, 1975; Champeney, 1979) and, at optical wavelengths, in the blue phases of chiral liquid crystals (Belyakov & Dmitrienko, 1985; Wright & Mermin, 1989; Seideman, 1990; Crooker, 2001). Similar phenomena have also been reported to exist in chiral smectic liquid crystals (Gleeson & Hirst, 2006; Barois *et al.*, 2012) and, considering neutron diffraction, in crystals with local anisotropy of the magnetic susceptibility (Gukasov & Brown, 2010). All these latter findings are, however, beyond the scope of this chapter.

X-ray polarization phenomena similar to those in visible optics and spectroscopy (birefringence, linear and circular dichroism, the Faraday rotation) have been discussed since the beginning of the 20th century (Hart & Rodriques, 1981; Templeton & Templeton, 1980, 1982). Experimental studies and applications were mainly prompted by the development of synchrotrons and storage devices as sources of polarized X-rays (a historical overview can be found in Rogalev *et al.*, 2006). In particular, for non-magnetic media, X-ray natural circular dichroism (XNCD) is used as a method for studying electronic states with mixed parity (Natoli *et al.*, 1998; Goulon *et al.*, 2003). Various kinds of X-ray absorption spectroscopies using polarized X-rays have been developed for magnetic materials; examples are XMCD (X-ray magnetic circular dichroism) (Schütz *et al.*, 1987; Thole *et al.*, 1992; Carra *et al.*, 1993) and XMLD (X-ray magnetic linear dichroism) (Thole *et al.*, 1986; van der Laan *et al.*, 1986; Arenholz *et al.*, 2006; van der Laan *et al.*, 2008). X-ray magnetochiral dichroism (XMχD) was discovered by Goulon *et al.* (2002) and is used as a probe of toroidal moment in solids. Sum rules connecting X-ray spectral parameters with the physical properties of the medium have also been developed (Thole *et al.*, 1992; Carra *et al.*, 1993; Goulon *et al.*, 2003) for various kinds of X-ray spectroscopies and are widely used for applications. These types of X-ray absorption spectroscopies are not considered here, as this chapter is mainly devoted to X-ray tensorial properties observed in single-crystal diffraction.

1.11.2. Symmetry restrictions on local tensorial susceptibility and forbidden reflections

Several different approaches can be used to determine the local susceptibility with appropriate symmetry. For illustration, we start with the simple but very important case of a symmetric tensor of rank 2 defined in the Cartesian system, $\mathbf{r} = (x, y, z)$ (in this case, we do not distinguish covariant and contravariant components, see Chapter 1.1). From the physical point of view, such tensors appear in the dipole–dipole approximation (see Section 1.11.4).

1.11.2.1. *General symmetry restrictions*

The most general expression for the tensor of susceptibility is exclusively restricted by the crystal symmetry, *i.e.* $\chi_{ij}(\mathbf{r})$ must be invariant against all the symmetry operations g of the given space group G:

$$\chi_{jk}(\mathbf{r}) = R^g_{jm} R^{gT}_{nk} \chi_{mn}(\mathbf{r}^g), \qquad (1.11.2.1)$$

where R^g_{jk} is the matrix of the point operation (rotation or mirror reflection), $r^g_j = R^g_{kj}(r_k - a^g_k)$, and a^g_k is the associated vector of translation. The index T indicates a transposed matrix, and summation over repeated indices is implied hereafter. To meet the above demand, it is obviously sufficient for $\chi_{ij}(\mathbf{r})$ to be invariant against all generators of the group G.

There is a simple direct method for obtaining $\chi_{ij}(\mathbf{r})$ obeying equation (1.11.2.1): we can take an arbitrary second-rank tensor $\alpha_{ij}(\mathbf{r})$ and average it over all the symmetry operations g:

$$\chi_{jk}(\mathbf{r}) = N^{-1} \sum_{g \in G} R^g_{jm} R^{gT}_{nk} \alpha_{mn}(\mathbf{r}^g), \qquad (1.11.2.2)$$

where N is the number of elements g in the group G. A small problem is that N is infinite for any space group, but this can be easily overcome if we take $\alpha_{ij}(\mathbf{r})$ as periodic and obeying the translation symmetry of the given Bravais lattice. Then the number N of the remaining symmetry operations becomes finite (an example of this approach is given in Section 1.11.2.3).

1.11.2.2. *Tensorial structure factors and forbidden reflections*

In spite of its simplicity, equation (1.11.2.1) provides non-trivial restrictions on the tensorial structure factors of Bragg reflections. The sets of allowed reflections, listed in *International Tables for Crystallography* Volume A (Hahn, 2005) for all space groups and for all types of atom sites, are based on scalar X-ray susceptibility. In this case, reflections can be forbidden (*i.e.* they have zero intensity) owing to glide-plane and/or screw-axis symmetry operations. This is because the scalar atomic factors remain unchanged upon mirror reflection or rotation, so that the contributions from symmetry-related atoms to the structure factors can cancel each other. In contrast, atomic tensors are sensitive to both mirror reflections and rotations, and, in general, the tensor atomic factors of symmetry-related atoms have different orientations in space. As a result, forbidden reflections can in fact be excited just due to the anisotropy of susceptibility, so that the selection rules for possible reflections change.

It is easy to see how the most general tensor form of the structure factors can be deduced from equation (1.11.2.1). The structure factor of a reflection with reciprocal-lattice vector $\mathbf{H}$ is proportional to the Fourier harmonics of the susceptibility. The corresponding relations (Authier, 2005, 2008) simply have to be rewritten in tensorial form:

$$F_{jk}(\mathbf{H}) = -\frac{\pi V}{r_0 \lambda^2} \chi_{jk}(\mathbf{H}) \equiv -\frac{\pi V}{r_0 \lambda^2} \int \chi_{jk}(\mathbf{r}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}) \, \mathrm{d}\mathbf{r}, \qquad (1.11.2.3)$$

where $r_0 = e^2/mc^2$ is the classical electron radius, λ is the X-ray wavelength and V is the volume of the unit cell.

1.11.2.2.1. *Glide-plane forbidden reflections*

Considering first the glide-plane forbidden reflections, there may, for instance, exist a glide plane c perpendicular to the x axis, *i.e.* any point x, y, z is transformed by this plane into $\bar{x}, y, z + \frac{1}{2}$. The corresponding matrix of this symmetry operation changes the sign of x,

$$R^c_{jk} = R^{cT}_{jk} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \qquad (1.11.2.4)$$

and the translation vector into $\mathbf{a}^c = (0, 0, \frac{1}{2})$. Substituting (1.11.2.4) into (1.11.2.1) and exchanging the integration variables in (1.11.2.3), one obtains for the structure factors of reflections $0k\ell$

$$F_{jk}(0k\ell) = \exp(-i\pi\ell) R^c_{jm} R^{cT}_{nk} F_{mn}(0k\ell). \qquad (1.11.2.5)$$

If $F_{jk}(0k\ell)$ is scalar, *i.e.* $F_{jk}(0k\ell) = F(0k\ell)\delta_{jk}$, then $F(0k\ell) = -F(0k\ell)$ for odd ℓ, hence $F(0k\ell)$ vanishes. This is the well known conventional extinction rule for a c glide plane, see *International Tables for Crystallography* Volume A (Hahn, 2005). If, however, $F_{jk}(0k\ell)$ is a tensor, the mirror reflection $x \to -x$ changes the signs of the xy and xz tensor components [as is also obvious from equation (1.11.2.5)]. As a result, the xy and xz components should not vanish for $\ell = 2n + 1$ and the tensor structure factor becomes

$$F_{jk}(0k\ell; \ell = 2n + 1) = \begin{pmatrix} 0 & F_1 & F_2 \\ F_1 & 0 & 0 \\ F_2 & 0 & 0 \end{pmatrix}. \qquad (1.11.2.6)$$

Table 1.11.2.1. *The indices ℓ of the screw-axis/glide-plane forbidden reflections ($n = 0, \pm1, \pm2, \ldots$) and independent components of their tensorial structure factors $F_{jk}^{\mathbf{H}}$*

Other components: $F_{yy}^{\mathbf{H}} = -F_{xx}^{\mathbf{H}}$, $F_{zz}^{\mathbf{H}} = 0$, $F_{jk}^{\mathbf{H}} = F_{kj}^{\mathbf{H}}$. The direction of the z axis is selected along the corresponding screw axes. The last column lists different types of polarization properties defined in Section 1.11.3.

Screw axis or glide plane	ℓ	$F_{xx}^{\mathbf{H}}$	$F_{xy}^{\mathbf{H}}$	$F_{xz}^{\mathbf{H}}$	$F_{yz}^{\mathbf{H}}$	Type
2_1	$2n+1$	0	0	F_1	F_2	I
3_1	$3n\pm1$	F_1	$\mp iF_1$	F_2	$\pm iF_2$	II
3_2	$3n\pm1$	F_1	$\pm iF_1$	F_2	$\mp iF_2$	II
4_1	$4n\pm1$	0	0	F_1	$\pm iF_1$	I
4_1	$4n+2$	F_1	F_2	0	0	II
4_2	$2n+1$	F_1	F_2	0	0	II
4_3	$4n\pm1$	0	0	F_1	$\mp iF_1$	I
4_3	$4n+2$	F_1	F_2	0	0	II
6_1	$6n\pm1$	0	0	F_1	$\pm iF_1$	I
6_1	$6n\pm2$	F_1	$\pm iF_1$	0	0	II
6_1	$6n+3$	0	0	0	0	
6_2	$3n\pm1$	F_1	$\pm iF_1$	0	0	II
6_3	$2n+1$	0	0	0	0	
6_4	$3n\pm1$	F_1	$\mp iF_1$	0	0	II
6_5	$6n\pm1$	0	0	F_1	$\mp iF_1$	I
6_5	$6n\pm2$	F_1	$\mp iF_1$	0	0	II
6_5	$6n+3$	0	0	0	0	
c	$2n+1$	0	F_1	F_2	0	II

In general, the elements F_1 and F_2 are complex, and it should be emphasized from the symmetry point of view that they are different and arbitrary for different k and ℓ. However, from the physical point of view, they can be readily expressed in terms of tensor atomic factors, where only those chemical elements are relevant whose absorption-edge energies are close to the incident radiation energy (see below).

It is also easy to see that for the non-forbidden (= allowed) reflections $0k\ell$; $\ell = 2n$, the non-zero tensor elements are just those which vanish for the forbidden reflections:

$$F_{jk}(0k\ell;\ \ell = 2n) = \begin{pmatrix} F_1 & 0 & 0 \\ 0 & F_2 & F_4 \\ 0 & F_4 & F_3 \end{pmatrix}. \qquad (1.11.2.7)$$

Here the result is mainly provided by the diagonal elements $F_1 \approx F_2 \approx F_3$, but there is still an anisotropic part that contributes to the structure factor, as expressed by the off-diagonal element. In principle, the effect on the total intensity as well as the element itself can be assessed by careful measurements using polarized radiation.

1.11.2.2.2. *Screw-axis forbidden reflections*

For the screw-axis forbidden reflections, the most general form of the tensor structure factor can be found as before (Dmitrienko, 1983; see Table 1.11.2.1). Again, as in the case of the glide plane, for each forbidden reflection all components of the tensor structure factor are determined by at most two independent complex elements F_1 and F_2. There may, however, exist further restrictions on these tensor elements if other symmetry operations of the crystal space group are taken into account. For example, although there are 2_1 screw axes in space group $I2_13$, $F_1 = F_2 = 0$ and reflections 00ℓ; $\ell = 2n+1$ remain forbidden because the lattice is body centred, and this applies not only to the dipole–dipole approximation considered here, but also within any other multipole approximation.

In Table 1.11.2.1, resulting from the dipole–dipole approximation, some reflections still remain forbidden. For instance, in the case of a 6_3 screw axis, there is no anisotropy of susceptibility in the xy plane due to the inevitable presence of the threefold rotation axis. For 6_1 and 6_5 axes, the reflections with $\ell = 6n+3$ also remain forbidden because only dipole–dipole interaction (of X-rays) is taken into account, whereas it can be shown that, for example, quadrupole interaction permits the excitation of these reflections.

1.11.2.3. *Local tensorial susceptibility of cubic crystals*

Let us consider in more detail the local tensorial properties of cubic crystals. This case is particularly interesting because for cubic symmetry the second-rank tensor is isotropic, so that a global anisotropy is absent (but it exists for tensors of rank 4 and higher). Local anisotropy is of importance for some physical parameters, and it can be described by tensors depending periodically on the three space coordinates. This does not only concern X-ray susceptibility, but can also, for instance, result from describing orientation distributions in chiral liquid crystals (Belyakov & Dmitrienko, 1985) or atomic displacements (Chapter 1.9 of this volume) and electric field gradients (Chapter 2.2 of this volume) in conventional crystals.

The symmetry element common to all cubic space groups is the threefold axis along the cube diagonal. The matrix R_3 of the symmetry operation is

$$R_3 = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}. \qquad (1.11.2.8)$$

This transformation results in the circular permutation $x, y, z \rightarrow z, x, y$, and from equation (1.11.2.1) it is easy to see that invariance of $\chi_{jk}(x, y, z)$ demands the general form

$$\chi_{jk}(x, y, z) = \begin{pmatrix} a_1(x, y, z) & a_2(z, x, y) & a_2(y, z, x) \\ a_2(z, x, y) & a_1(y, z, x) & a_2(x, y, z) \\ a_2(y, z, x) & a_2(x, y, z) & a_1(z, x, y) \end{pmatrix}, \qquad (1.11.2.9)$$

where $a_1(x, y, z)$ and $a_2(x, y, z)$ are arbitrary functions with the periodicity of the corresponding Bravais lattice: $a_i(x + n_x, y + n_y, z + n_z) = a_i(x, y, z)$ for primitive lattices (n_x, n_y, n_z being arbitrary integers) plus in addition $a_i(x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}) = a_i(x, y, z)$ for body-centered lattices or $a_i(x + \frac{1}{2}, y + \frac{1}{2}, z) = a_i(x, y + \frac{1}{2}, z + \frac{1}{2}) = a_i(x + \frac{1}{2}, y, z + \frac{1}{2}) = a_i(x, y, z)$ for face-centered lattices.

Depending on the space group, other symmetry elements can enforce further restrictions on $a_1(x, y, z)$ and $a_2(x, y, z)$:

$P23, F23, I23$:

$$\begin{aligned} a_1(x, y, z) &= a_1(x, \bar{y}, \bar{z}) = a_1(\bar{x}, \bar{y}, z) = a_1(\bar{x}, y, \bar{z}), \\ a_2(x, y, z) &= a_2(x, \bar{y}, \bar{z}) = -a_2(\bar{x}, \bar{y}, z) = -a_2(\bar{x}, y, \bar{z}). \end{aligned} \qquad (1.11.2.10)$$

$P2_13, I2_13$:

$$\begin{aligned} a_1(x, y, z) &= a_1(\tfrac{1}{2} + x, \tfrac{1}{2} - y, \bar{z}) \\ &= a_1(\tfrac{1}{2} - x, \bar{y}, \tfrac{1}{2} + z) = a_1(\bar{x}, \tfrac{1}{2} + y, \tfrac{1}{2} - z), \\ a_2(x, y, z) &= a_2(\tfrac{1}{2} + x, \tfrac{1}{2} - y, \bar{z}) \\ &= -a_2(\tfrac{1}{2} - x, \bar{y}, \tfrac{1}{2} + z) = -a_2(\bar{x}, \tfrac{1}{2} + y, \tfrac{1}{2} - z). \end{aligned} \qquad (1.11.2.11)$$

$Pm\bar{3}, Fm\bar{3}, Im\bar{3}$: (1.11.2.10) and

$$a_i(x, y, z) = a_i(\bar{x}, \bar{y}, \bar{z}). \qquad (1.11.2.12)$$

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
$P2_13$	00ℓ: $\ell = 2n+1$	(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)
$P4_232$	00ℓ: $\ell = 2n+1$	(1.11.2.24)
$F4_132$	00ℓ: $\ell = 4n+2$	(1.11.2.24)
$P4_332$	00ℓ: $\ell = 4n\pm1$	(1.11.2.23); $F_2 = \mp iF_1$
	00ℓ: $\ell = 4n+2$	(1.11.2.24)
$P1_332$	00ℓ: $\ell = 4n\pm1$	(1.11.2.23); $F_2 = \pm iF_1$
	00ℓ: $\ell = 4n+2$	(1.11.2.24)
$I4_132$	00ℓ: $\ell = 4n+2$	(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

$Pn\bar{3}$: (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).
$Fd\bar{3}m$: (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.

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 properties, 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

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

where θ is the Bragg angle, $F(\mathbf{H})$ is the scalar structure factor of reflection $\mathbf{H}$, 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, **e** and **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 **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 **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 $I^{\rm tot}_{\mathbf{H}}(\mathbf{e})$ 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 **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 ($\boldsymbol{\sigma} \to \boldsymbol{\sigma}$, $\boldsymbol{\sigma} \to \boldsymbol{\pi}'$ *etc.*), exhibit different azimuthal symmetries for different screw axes.

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

$$\begin{aligned} I_\sigma &= |F_1|^2(1 + \sin^2\theta) + |F_2|^2 \cos^2\theta + D(\varphi), \\ I_\pi &= |F_1|^2 \sin^2\theta (1 + \sin^2\theta) + |F_2|^2 \cos^2\theta + D(\varphi), \\ I_{\mathbf{H}} &= |F_1|^2 (1 + \sin^2\theta)^2/2 + |F_2|^2 \cos^2\theta + D(\varphi), \end{aligned} \qquad (1.11.3.11)$$

where $D(\varphi) = \sin 2\theta\, [Re(F_1 F_2^*) \cos 3\varphi \mp Im(F_1 F_2^*) \sin 3\varphi]$. 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:

$$\begin{aligned} I_\sigma &= |F_1|^2 B(\varphi) + |F_2|^2 C(\varphi) \\ &\quad + Re(F_1 F_2^*) \cos^2\theta \sin 4\varphi, \\ I_\pi &= \sin^2\theta \big[|F_1|^2 C(\varphi) + |F_2|^2 B(\varphi) \\ &\quad + Re(F_1 F_2^*) \cos^2\theta \sin 4\varphi\big], \\ I_{\mathbf{H}} &= (I_\sigma + I_\pi)/2, \end{aligned} \qquad (1.11.3.12)$$

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:

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

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 $F_{xy} = iF_{xy}$ and left-hand if $F_{xy} = -iF_{xy}$) 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:

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

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

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

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

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

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

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

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

In general, the total atomic scattering factor looks like

$$\begin{aligned} f_{jk}(\mathbf{k}',\mathbf{k},E) &= [f_0(|\mathbf{k}'-\mathbf{k}|) + f_0'(E) + if_0''(E)]\delta_{ij} \\ &\quad + f_{jk}'(\mathbf{k}',\mathbf{k},E) + if_{jk}''(\mathbf{k}',\mathbf{k},E) + f_{jk}^{\rm mag}, \end{aligned} \tag{1.11.4.5}$$

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 $f_{ij}^{\rm mag}$ ($\sim 10^{-2}$–$10^{-3}f_0$) describing magnetic non-resonant scattering, which is also anisotropic (see the next section).

1.11.5. Non-resonant magnetic scattering

Far from resonance ($\hbar\omega \gg E_c - E_a$), the non-resonant parts of the scattering factor, f_0 and $f_{ij}^{\rm mag}$, described by the first two terms in (1.11.4.3) are the most important. In the classical approximation (Brunel & de Bergevin, 1981), there are four physical mechanisms (electric or magnetic, dipolar or quadrupolar) describing the interaction of an electron and its magnetic moment with an electromagnetic wave, causing the re-emission of radiation. The non-resonant magnetic term $f^{\rm magn}$ is small compared to the charge (Thomson) scattering owing (*a*) to small numbers of unpaired (magnetic) electrons and (*b*) to the factor $\hbar\omega/mc^2$ of about 0.02 for a typical X-ray energy $\hbar\omega = 10$ keV. This is the reason why it is so difficult to observe non-resonant magnetic scattering with conventional X-ray sources (de Bergevin & Brunel, 1972, 1981; Brunel & de Bergevin, 1981), in contrast to the nowadays normal use of synchrotron radiation.

Non-resonant magnetic scattering yields polarization properties quite different from those obtained from charge scattering. Moreover, it can be divided into two parts, which are associated with the spin and orbital moments. In contrast to the case of neutron magnetic scattering, the polarization properties of these two parts are different, as described by the tensors (Blume, 1994)

$$A_{ijk} = -2(1 - \mathbf{k}\cdot\mathbf{k}'/k^2)\epsilon_{ijk}, \qquad (1.11.5.1)$$

$$\begin{aligned}B_{ijk} = \epsilon_{ijk} - \big[&\epsilon_{ilk}k'_l k'_j - \epsilon_{jlk}k_l k_i + \tfrac{1}{2}\epsilon_{ijl}(k'_l k_k + k_l k'_k)\\ &- \tfrac{1}{2}[\mathbf{k}\times\mathbf{k}']_i\delta_{jk} - \tfrac{1}{2}[\mathbf{k}\times\mathbf{k}']_j\delta_{ik}\big]/k^2, \qquad (1.11.5.2)\end{aligned}$$

where ϵ_{ijk} is a completely antisymmetric unit tensor (the Levi-Civita symbol).

Being convoluted with polarization vectors (Blume, 1985; Lovesey & Collins, 1996; Paolasini, 2012), the non-resonant magnetic term can be rewritten as

$$\begin{aligned}&f_{\rm nonres}^{\rm magn}(\mathbf{G})\\ &= -i\frac{\hbar\omega}{mc^2}\langle a|\sum_p(\mathbf{A}\cdot[\mathbf{G}\times\mathbf{P}_p]/\hbar k^2 + \mathbf{B}\cdot\mathbf{s}_p)\exp(i\mathbf{G}\cdot\mathbf{r}_p)|a\rangle,\\ &\qquad (1.11.5.3)\end{aligned}$$

with vectors **A** and **B** given by

$$\mathbf{A} = [\mathbf{e}'^{*}\times\mathbf{e}], \qquad (1.11.5.4)$$

$$\begin{aligned}\mathbf{B} = [\mathbf{e}'^{*}\times\mathbf{e}] - \{&[\mathbf{k}\times\mathbf{e}](\mathbf{k}\cdot\mathbf{e}'^{*}) - [\mathbf{k}'\times\mathbf{e}'^{*}](\mathbf{k}'\cdot\mathbf{e})\\ &+ [\mathbf{k}'\times\mathbf{e}'^{*}]\times[\mathbf{k}\times\mathbf{e}]\}/k^2. \qquad (1.11.5.5)\end{aligned}$$

According to (1.11.5.4) and (1.11.5.5), the polarization dependences of the spin and orbit contributions to the atomic scattering factor are significantly different. Consequently, the two contributions can be separated by analysing the polarization of the scattered radiation with the help of an analyser crystal (Gibbs *et al.*, 1988). Usually the incident (synchrotron) radiation is σ-polarized, *i.e.* the polarization vector is perpendicular to the scattering plane. If due to the orientation of the analysing crystal only the σ-polarized part of the scattered radiation is recorded, we can see from (1.11.5.4) that the orbital contribution to the scattering atomic factor vanishes, whereas it differs from zero considering the $\sigma \to \pi$ scattering channel.

Table 1.11.6.1. *Coefficients γ corresponding to various kinds of tensor symmetry with respect to space inversion $\bar{1}$, rotations R, and time reversal $1'$*

		Transformation type			
Tensor type	Example	R	$\bar{1}R$	$1'R$	$\bar{1}'R$
Even	Strain	1	1	1	1
Electric	Electric field	1	−1	1	−1
Magnetic	Magnetic field	1	1	−1	−1
Magnetoelectric	Toroidal moment	1	−1	−1	1

1.11.6. Resonant atomic factors: multipole expansion

Strong enhancement of resonant scattering occurs when the energy of the incident radiation gets close to the energy of an electron transition from an inner shell to an empty state (be it localized or not) above the Fermi level. There are two widely used approaches for calculating resonant atomic amplitudes. One uses Cartesian, the other spherical (polar) coordinates, and both have their own advantages and disadvantages. Supposing in (1.11.4.3)

$$\exp(i\mathbf{k}\cdot\mathbf{r}_p) \approx 1 + i\mathbf{k}\cdot\mathbf{r}_p + \tfrac{1}{2}(i\mathbf{k}\cdot\mathbf{r}_p)^2 + \ldots \qquad (1.11.6.1)$$

and using the expression for the velocity matrix element v_{ac} (Berestetskii *et al.*, 1982) $v_{ac} = i\omega_{ac}r_{ac}$, it is possible to present the resonant part of the atomic factor (1.11.4.3) as

$$\begin{aligned}f_{jk}^{\rm res} = \sum_c p_a\frac{m\omega_{ca}^3}{\omega}\Bigg\{&\frac{\langle a|R_j|c\rangle\langle c|R_k|a\rangle}{E_a - E_c + \hbar\omega - i\Gamma/2}\\ &+\frac{i}{2}\left[\frac{\langle a|R_j|c\rangle\langle c|R_kR_lk_l|a\rangle}{E_a - E_c + \hbar\omega - i\Gamma/2} - \frac{\langle a|R_jR_lk'_l|c\rangle\langle c|R_k|a\rangle}{E_a - E_c + \hbar\omega - i\Gamma/2}\right]\\ &+\frac{1}{4}\frac{\langle a|R_jR_lk'_l|c\rangle\langle c|R_kR_mk_m|a\rangle}{E_a - E_c + \hbar\omega - i\Gamma/2}\Bigg\} \qquad (1.11.6.2)\\ = D_{jk} + \frac{i}{2}I_{jkl}k_l - \frac{i}{2}&I_{kjl}k'_l + \frac{1}{4}Q_{jlkm}k_mk'_l, \qquad (1.11.6.3)\end{aligned}$$

where $\hbar\omega_{ca} = E_c - E_a$, D_{jk} is a dimensionless tensor corresponding to the dipole–dipole ($E1E1$) contribution, I_{jkl} is the dipole–quadrupole ($E1E2$) contribution and Q_{jklm} is the quadrupole–quadrupole ($E2E2$) term. All the tensors are complex and depend on the energy and the local properties of the medium. The expansion (1.11.6.1) over the wavevectors is possible near X-ray absorption edges because the products $\mathbf{k}\cdot\mathbf{r}_p$ are small for the typical sizes of the inner shells involved. In resonant X-ray absorption and scattering, the contribution of the magnetic multipole ML transitions is usually much less than that of the electric multipole EL transitions. Nevertheless, the scattering amplitude corresponding to $E1M1$ events has also been considered (Collins *et al.*, 2007). The tensors I_{jkl} and Q_{jklm} describe the spatial dispersion effects similar to those in visible optics.

1.11.6.1. *Tensor atomic factors: internal symmetry*

Different types of tensors transform under the action of the extended orthogonal group (Sirotin & Shaskolskaya, 1982) as

$$A_{i'_1\ldots i'_n} = \gamma r_{i'_1k_1}\ldots r_{i'_nk_n}A_{k_1\ldots k_n}, \qquad (1.11.6.4)$$

where the coefficients $\gamma = \pm1$ depend on the kind of tensor (see Table 1.11.6.1) and $r_{i'_1k_1}$ are coefficients describing proper rotations.

Various parts of the resonant scattering factor (1.11.6.3) possess different kinds of symmetry with respect to: (1) space inversion $\bar{1}$ or parity, (2) rotations R and (3) time reversal $1'$. Both dipole–dipole and quadrupole–quadrupole terms are parity-even, whereas the dipole–quadrupole term is parity-odd. Thus, dipole–quadrupole events can exist only for atoms at positions without inversion symmetry.

It is convenient to separate the time-reversible and time-non-reversible terms in the contributions to the atomic tensor factor (1.11.6.3). The dipole–dipole contribution to the resonant atomic factor can be represented as a sum of an isotropic, a symmetric and an antisymmetric part, written as (Blume, 1994)

$$D_{jk} = D_0^{\rm res}\delta_{jk} + D_{jk}^{+} + D_{jk}^{-}, \qquad (1.11.6.5)$$

where $D_0^{\rm res} = (1/3)({\rm Tr}D)$,

$$\begin{aligned} D_{jk}^{+} &= \frac{1}{2}(D_{jk} + D_{kj}) - \frac{1}{3}({\rm Tr}D)\delta_{jk} \\ &= \frac{1}{4}\sum_{a,c}\frac{m\omega_{ca}^3}{\hbar\omega}(p'_a + p'_{\bar{a}})(\langle a|R_j|c\rangle\langle c|R_k|a\rangle + \langle a|R_k|c\rangle\langle c|R_j|a\rangle \end{aligned} \qquad (1.11.6.6)$$

and

$$\begin{aligned} D_{jk}^{-} &= \frac{1}{2}(D_{jk}^{-} - D_{kj}^{-}) \\ &= \frac{1}{4}\sum_{a,c}\frac{m\omega_{ca}^3}{\hbar\omega}(p'_a - p'_{\bar{a}})(\langle a|R_j|c\rangle\langle c|R_k|a\rangle - \langle a|R_k|c\rangle\langle c|R_j|a\rangle, \end{aligned} \qquad (1.11.6.7)$$

$p'_a = p_a/[\omega - \omega_{ca} - i\Gamma/(2\hbar)]$ and $p'_{\bar{a}} = p_{\bar{a}}/[\omega - \omega_{c\bar{a}} - i\Gamma/(2\hbar)]$; $p_{\bar{a}}$ means the probability of the time-reversed state $|\bar{a}\rangle$. If, for example, $|a\rangle$ has a magnetic quantum number m, then $|\bar{a}\rangle$ has a magnetic quantum number $-m$.

In non-magnetic crystals, the probability of states with $\pm m$ is the same, so that $p_{\bar{a}} = p_a$ and $\langle\bar{a}|R_j^s|\bar{c}\rangle = \langle c|R_k^s|a\rangle$; in this case D_{jk} is symmetric under permutation of the the indices.

Similarly, the dipole–quadrupole atomic factor can be represented as (Blume, 1994)

$$\begin{aligned} f_{jk}^{dq} &= \frac{i}{2}\sum_{ac} p_a\frac{m\omega_{ca}^3}{\hbar\omega} \times \{\langle a|R_j|c\rangle\langle c|R_kR_l|a\rangle k_l \\ &\quad - \langle a|R_jR_l|c\rangle\langle c|R_k|a\rangle k'_l\} \qquad (1.11.6.8) \\ &= \frac{i}{8}\sum_{ac}\frac{m\omega_{ca}^3}{\hbar\omega}\{I_{jkl}^{++}(k_l - k'_l) + I_{jkl}^{--}(k_l - k'_l) \\ &\quad + I_{jkl}^{-+}(k_l + k'_l) + I_{jkl}^{+-}(k_l + k'_l)\}, \qquad (1.11.6.9) \end{aligned}$$

where

$$\begin{aligned} I_{jkl}^{\mu\nu} = \sum_{ac}(p'_a + \mu p'_{\bar{a}})\{&\langle a|R_j|c\rangle\langle c|R_kR_l|a\rangle k_l \\ &+ \nu\langle a|R_jR_l|c\rangle\langle c|R_k|a\rangle k'_l\} \end{aligned} \qquad (1.11.6.10)$$

with $\mu, \nu = \pm 1$. In (1.11.6.10) the first plus ($\mu = 1$) corresponds to the non-magnetic case (time reversal) and the minus ($\mu = -1$) corresponds to the time-non-reversal magnetic term, while the second ± corresponds to the symmetric and antisymmetric parts of the atomic factor. We see that $I_{jkl}^{--}(k_l - k'_l)$ can contribute only to scattering, while $I_{jkl}^{-+}(k_l + k'_l)$ can contribute to both resonant scattering and resonant X-ray propagation. The latter term is a source of the so-called magnetochiral dichroism, first observed in Cr_2O_3 (Goulon *et al.*, 2002, 2003), and it can be associated with a toroidal moment in a medium possessing magnetoelectric properties. The symmetry properties of magnetoelectic tensors are described well by Sirotin & Shaskolskaya (1982), Nye (1985) and Cracknell (1975). Which magnetoelectric properties can be studied using X-ray scattering are widely discussed by Marri & Carra (2004), Matsubara *et al.* (2005), Arima *et al.* (2005) and Lovesey *et al.* (2007).

It follows from (1.11.6.8) and (1.11.6.10) that $I_{jkl} = I_{jlk}$ and the dipole–quadrupole term can be represented as a sum of the symmetric $I_{jkl}^{+} = I_{kjl}^{+}$ and antisymmetric $I_{jkl}^{-} = -I_{kjl}^{-}$ parts. From the physical point of view, it is useful to separate the dipole–quadrupole term into I_{jkl}^{+} and I_{jkl}^{-}, because only I_{jkl}^{-} works in conventional optics where $\mathbf{k}' = \mathbf{k}$. The dipole–quadrupole terms are due to the hybridization of excited electronic states with different spacial parities, *i.e.* only for atomic sites without an inversion centre.

The pure quadrupole–quadrupole term in the tensor atomic factor is equal to

$$f_{jk}^{qq} = \tfrac{1}{4}Q_{jlkm}k'_lk_m \qquad (1.11.6.11)$$

with the fourth-rank tensor Q_{jklm} given by

$$Q_{jlkm} = \sum_{ac} p_a\frac{m\omega_{ca}^3}{\hbar\omega}\frac{\langle a|R_jR_l|c\rangle\langle c|R_kR_m|a\rangle}{\omega - \omega_{ca} - i(\Gamma/2\hbar)}. \qquad (1.11.6.12)$$

This fourth-rank tensor Q_{ijkm} has the following symmetries:

$$Q_{jlkm} = Q_{ljkm} = Q_{jlmk}. \qquad (1.11.6.13)$$

We can define

$$Q_{jlkm} = Q_{jlkm}^{+} + Q_{jlkm}^{-} \qquad (1.11.6.14)$$

with $Q_{jlkm}^{\pm} = \pm Q_{kmjl}$, where

$$\begin{aligned} Q_{jlkm}^{\pm} = \tfrac{1}{4}\sum_{a}(p'_a \pm p'_{\bar{a}})(&\langle a|R_jR_l|c\rangle\langle c|R_kR_m|a\rangle \\ &\pm \langle a|R_kR_m|c\rangle\langle c|R_jR_l|a\rangle). \end{aligned} \qquad (1.11.6.15)$$

We see that Q_{jlkm}^{-} vanishes in time-reversal invariant systems, which is true for non-magnetic structures.

1.11.6.2. *Tensor atomic factors (non-magnetic case)*

In time-reversal invariant systems, equation (1.11.6.3) can be rewritten as

$$f_{jk}^{\rm res} = D_{jk}^{+} + iI_{jkl}^{+}(k'_l - k_l) + iI_{jkl}^{-}(k'_l + k_l) + Q_{jlkm}^{+}k'_lk_m + \ldots, \qquad (1.11.6.16)$$

where D_{jk}^{+} corresponds to the symmetric part of the dipole–dipole contribution, I_{jkl}^{+} and I_{jkl}^{-} mean the symmetric and antisymmetric parts of the third-rank tensor describing the dipole–quadrupole term, and Q_{jlkm}^{+} denotes a symmetric quadrupole–quadrupole contribution. From the physical point of view, it is useful to separate the dipole–quadrupole term into I_{jkl}^{+} and I_{jkl}^{-}, because in conventional optics, where $\mathbf{k}' = \mathbf{k}$, only I_{jkl}^{-} is relevant.

The tensors contributing to the atomic factor in (1.11.6.16), D_{jk}, I_{jkl}^{+}, I_{jkl}^{-}, Q_{jlkm}, are of different ranks and must obey the site symmetry of the atomic position. Generally, the tensors can be different, even for crystallographically equivalent positions, but all tensors of the same rank can be related to one of them, because all are connected through the symmetry operations of the crystal space group. In contrast, the scattering amplitude tensor $f_{jm}^{\rm res}$ does not necessarily comply with the point symmetry of the atomic position, because this symmetry is usually violated considering the arbitrary directions of the radiation wavevectors $\mathbf{k}$ and $\mathbf{k}'$.

Equation (1.11.6.16) is also frequently considered as a phenomenological expression of the tensor atomic factor where each tensor possesses internal symmetry (with respect to index permutations) and external symmetry (with respect to the atomic environment of the resonant atom). For instance, the tensor D_{jk} is symmetric, the rank-3 tensor has a symmetric and a antisymmetric part, and the rank-4 tensor is symmetric with respect to the permutation of each pair of indices. The external symmetry of D_{jk} coincides with the symmetry of the dielectric susceptibility tensor (Chapter 1.6). Correspondingly, the third-rank tensors I^-_{jkl} and I^+_{jkl} are similar to the gyration susceptibility and electro-optic tensors (Chapter 1.6), and Q_{jlkm} has the same tensor form as that for elastic constants (Chapter 1.3). The symmetry restrictions on these tensors (determining the number of independent elements and relationships between tensor elements) are very important and widely used in practical work on resonant X-ray scattering. Since they can be found in Chapters 1.3 and 1.6 or in textbooks (Sirotin & Shaskolskaya, 1982; Nye, 1985), we do not discuss all possible symmetry cases in the following, but consider in the next section one specific example for X-ray scattering when the symmetries of the tensors given by expression (1.11.6.3) do not coincide with the most general external symmetry that is dictated by the atomic environment.

1.11.6.3. *Hidden internal symmetry of the dipole–quadrupole tensors in resonant atomic factors*

It is fairly obvious from expressions (1.11.6.3) and (1.11.6.16) that in the non-magnetic case the symmetric and antisymmetric third-rank tensors, I^+_{jkl} and I^-_{jlk}, which describe the dipole–quadrupole contribution to the X-ray scattering factor, are not independent: the antisymmetric part, which is also responsible for optical-activity effects, can be expressed *via* the symmetric part (but not *vice versa*). Indeed, both of them can be described by a symmetric third-rank tensor $t_{ijk} = t_{ikj}$ resulting from the second-order Born approximation (1.11.6.3),

$$I^+_{ijk} = (t_{ijk} + t_{jik})/2, \qquad (1.11.6.17)$$

$$I^-_{ijk} = (t_{ijk} - t_{jik})/2, \qquad (1.11.6.18)$$

where

$$t_{ijk} = -\tfrac{1}{2} I_{ijk}. \qquad (1.11.6.19)$$

From equation (1.11.6.17), one can infer that the symmetry restrictions for I^+_{ijk} and t_{ijk} are the same. Then it can be seen that I^-_{ijk} can be expressed *via* I^+_{ijk}.

For any symmetry, I^+_{ijk} and t_{ijk} have the same number of independent elements (with a maximum 18 for site symmetry 1). Thus, one can reverse equation (1.11.6.17) and express t_{ijk} directly in terms of I^+_{ijk}:

$$\begin{gathered}
t_{111} = I^+_{111}, \quad t_{211} = 2I^+_{121} - I^+_{112}, \quad t_{311} = 2I^+_{311} - I^+_{113},\\
t_{122} = 2I^+_{122} - I^+_{221}, \quad t_{222} = I^+_{222}, \quad t_{322} = 2I^+_{232} - I^+_{223},\\
t_{133} = 2I^+_{313} - I^+_{331}, \quad t_{233} = 2I^+_{233} - I^+_{332}, \quad t_{333} = I^+_{333},\\
t_{123} = I^+_{123} + I^+_{312} - I^+_{231}, \quad t_{223} = I^+_{223}, \quad t_{332} = I^+_{332},\\
t_{113} = I^+_{113}, \quad t_{231} = I^+_{231} + I^+_{123} - I^+_{312}, \quad t_{331} = I^+_{331},\\
t_{112} = I^+_{112}, \quad t_{221} = I^+_{221}, \quad t_{312} = I^+_{312} + I^+_{231} - I^+_{123}.
\end{gathered} \qquad (1.11.6.20)$$

Using equations (1.11.6.18) and (1.11.6.20), one can express all nine elements of I^-_{ijk} through I^+_{ijk}:

$$\begin{gathered}
I^-_{231} = I^+_{123} - I^+_{312}, \quad I^-_{232} = I^+_{223} - I^+_{232}, \quad I^-_{233} = I^+_{233} - I^+_{332},\\
I^-_{311} = I^+_{311} - I^+_{113}, \quad I^-_{312} = I^+_{231} - I^+_{123}, \quad I^-_{313} = I^+_{331} - I^+_{313},\\
I^-_{121} = I^+_{112} - I^+_{121}, \quad I^-_{122} = I^+_{122} - I^+_{221}, \quad I^-_{123} = I^+_{312} - I^+_{231},
\end{gathered} \qquad (1.11.6.21)$$

according to which the antisymmetric part of the dipole–quadrupole term is a linear function of the symmetric one [however, not *vice versa*: equations (1.11.6.21) cannot be reversed].

Note that the equations (1.11.6.21) impose an additional restriction on I^-_{ijk}, which applies to all atomic site symmetries:

$$I^-_{123} + I^-_{231} + I^-_{312} = 0. \qquad (1.11.6.22)$$

This is, in fact, a well known result: the pseudo-scalar part of I^-_{ijk} vanishes in the dipole–quadrupole approximation used in equation (1.11.6.3). Thus, for point symmetry 1, I^-_{ijk} has only eight independent elements rather than nine. This additional restriction works in all cases of higher symmetries provided the pseudo-scalar part is allowed by the symmetry (*i.e.* point groups 2, 3, 4, 6, 222, 32, 422, 622, 23 and 432). All other symmetry restrictions on I^-_{ijk} arise automatically from equation (1.11.6.21) taking into account the symmetry of I^+_{ijk} [symmetry limitations on I^+_{ijk} and I^-_{ijk} for all crystallographic point groups can be found in Sirotin & Shaskolskaya (1982) and Nye (1985)].

Let us consider two examples, ZnO and anatase, TiO_2, where the dipole–dipole contributions to forbidden reflections vanish, whereas both the symmetric and antisymmetric dipole-quadrupole terms are in principal allowed. In these crystals, the dipole–quadrupole terms have been measured by Goulon *et al.* (2007) and Kokubun *et al.* (2010).

In ZnO, crystallizing in the wurtzite structure, the $3m$ symmetry of the atomic positions imposes the following restrictions on t_{ijk}:

$$t_{131} = t_{223} = e_{15}, \qquad (1.11.6.23)$$

$$t_{222} = -t_{112} = -t_{211} = e_{22}, \qquad (1.11.6.24)$$

$$t_{311} = t_{322} = e_{31}, \qquad (1.11.6.25)$$

$$t_{333} = e_{33}, \qquad (1.11.6.26)$$

where e_{15}, e_{31}, e_{22}, e_{33} are energy-dependent complex tensor elements [keeping the notations by Sirotin & Shaskolskaya (1982), the x axis is normal to the mirror plane, the y axis is normal to the glide plane and the z axis corresponds to the c axis of ZnO]. If we suppose these restrictions for Zn at $\frac{1}{3}, \frac{2}{3}, z$, then for the other Zn at $\frac{2}{3}, \frac{1}{3}, z + \frac{1}{2}$, which is related to the first site by the glide plane, there is the following set of elements: $e_{15}, e_{31}, -e_{22}, e_{33}$. Therefore, the structure factors of the glide-plane forbidden reflections are proportional to e_{22}.

For the symmetric and antisymmetric parts one obtains from equations (1.11.6.17) and (1.11.6.18) the non-zero components

$$I^+_{131} = I^+_{232} = (e_{15} + e_{31})/2, \qquad (1.11.6.27)$$

$$I^+_{222} = -I^+_{121} = -I^+_{112} = e_{22}, \qquad (1.11.6.28)$$

$$I^+_{113} = I^+_{223} = e_{15}, \qquad (1.11.6.29)$$

$$I^+_{333} = e_{33} \qquad (1.11.6.30)$$

and

$$I^-_{232} = -I^-_{311} = I^+_{113} - I^+_{131} = (e_{15} - e_{31})/2. \qquad (1.11.6.31)$$

Physically, we can expect that $|e_{15} + e_{31}| \gg |e_{15} - e_{31}|$ because $e_{15} + e_{31}$ survives even for tetrahedral symmetry $\bar{4}3m$, whereas $e_{15} - e_{31}$ is non-zero owing to a deviation from tetrahedral symmetry; in ZnO, the local coordinations of the Zn positions are only approximately tetrahedral.

In the anatase structure of TiO_2, the $\bar{4}m2$ symmetry of the atomic positions imposes restrictions on the tensors t_{ijk} [keeping the notations of Sirotin & Shaskolskaia (1982): the x and y axes are normal to the mirror planes, and the z axis is parallel to the c axis]:

$$t_{131} = -t_{223} = e_{15}, \qquad (1.11.6.32)$$

$$t_{311} = -t_{322} = e_{31}, \qquad (1.11.6.33)$$

where e_{15} and e_{31} are energy-dependent complex parameters. If we apply these restrictions to the Ti atoms at $0, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, then for the other two inversion-related Ti atoms at $0, \frac{1}{2}, \frac{1}{4}$ and $\frac{1}{2}, 0, \frac{3}{4}$ (centre $2/m$), the parameters are $-e_{15}$ and $-e_{31}$.

For the symmetric and antisymmetric parts one obtains as non-vanishing components

$$I^+_{131} = -I^+_{232} = (e_{15} + e_{31})/2, \qquad (1.11.6.34)$$

$$I^+_{113} = -I^+_{223} = e_{15} \qquad (1.11.6.35)$$

and

$$I^-_{232} = I^-_{311} = I^+_{131} - I^+_{113} = (e_{31} - e_{15})/2. \qquad (1.11.6.36)$$

It is important to note that the symmetric part I^+_{ijk} of the atomic factor can be affected by a contribution from thermal-motion-induced dipole–dipole terms. The latter terms are tensors of rank 3 proportional to the spatial derivatives $\partial f^{dd}_{ij}/\partial x_k$, which take the same tensor form as I^+_{ijk} but are not related to I^-_{ijk} by equations (1.11.6.21). In ZnO, which was studied in detail by Collins *et al.* (2003), the thermal-motion-induced contribution is rather significant, while for anatase the situation is less clear.

1.11.6.4. *Tensor structure factors*

Once the tensor atomic factors have been determined [either from phenomenological expressions like (1.11.6.16), according to the site-symmetry restrictions, or from given microscopic expressions, *e.g.* (1.11.4.3)], tensor structure factors are obtained by summation over the contributions of all atoms in the unit cell, as in conventional diffraction theory:

$$F_{jm}(\mathbf{H}) = \sum_{t,u} o_t D^{tu}_{jm} \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}^{tu}) \exp[-W^{tu}(\mathbf{H})], \qquad (1.11.6.37)$$

$$F^+_{jmn}(\mathbf{H}) = \sum_{t,u} o_t I^{tu+}_{jmn} \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}^{tu}) \exp[-W^{tu}(\mathbf{H})], \qquad (1.11.6.38)$$

$$F^-_{jmn}(\mathbf{H}) = \sum_{t,u} o_t I^{tu-}_{jmn} \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}^{tu}) \exp[-W^{tu}(\mathbf{H})], \qquad (1.11.6.39)$$

$$F_{jmnp}(\mathbf{H}) = \sum_{t,u} o_t Q^{tu}_{jmnp} \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}^{tu}) \exp[-W^{tu}(\mathbf{H})], \qquad (1.11.6.40)$$

where the index t enumerates the crystallographically different types of scatterers (atoms belonging to the same or different chemical elements), the index u denotes the crystallographically equivalent positions; $o_t \le 1$ is a site-occupancy factor, and $W^{tu}(\mathbf{H})$ is the Debye–Waller temperature factor. The tensors of the atomic factors, D^{tu}_{jm}, I^{tu+}_{jmn}, I^{tu-}_{jmn}, Q^{tu}_{jmnp}, are, in general, different for crystallographically equivalent positions, that is for different u, and it is exactly this difference that enables the excitation of the resonant forbidden reflections.

Extinction rules and polarization properties for forbidden reflections are different for tensor structure factors of different ranks, a circumstance that may be used for experimental separation of different tensor contributions (for tensors of rank 2, information is given in Tables 1.11.2.1 and 1.11.2.2). In the harmonic approximation, anisotropies of the atomic thermal displacements (Debye–Waller factor) are also described by tensors of rank 2 or higher, but, owing to these, excitations of glide-plane and screw-axis forbidden reflections are not possible.

1.11.6.5. *Tensor atomic factors (magnetic case)*

Magnetic crystals possess different densities of states with opposite spin directions. During a multipole transition from the ground state to an excited state (or the reverse), the projection of an electron spin does not change, but the projection of the orbital moment varies. The consideration of all possible transitions allows for the formulation of the sum rules (Carra *et al.*, 1993; Strange, 1994) that are widely used in X-ray magnetic circular dichroism (XMCD). When measuring the differences of the absorption coefficients at the $L_{2,3}$ absorption edges of transition elements or at the M edges of rare-earth elements (Erskine & Stern, 1975; Schütz *et al.*, 1987; Chen *et al.*, 1990), these rules allow separation of the spin and orbital contributions to the XMCD signal, and hence the study of the spin and orbital moments characterizing the ground state. In magnetic crystals, the tensors change their sign with time reversal because $p'_a \neq p'_{\bar{a}}$ if $p_a \neq p_{\bar{a}}$ and/or $\omega_{ca} \neq \omega_{c\bar{a}}$ (Zeeman splitting in a magnetic field). That the antisymmetric parts of the tensors differ from zero follows from equations (1.11.6.7), (1.11.6.10) and (1.11.6.15).

Time reversal also changes the incident and scattered vectors corresponding to permutation of the Cartesian tensor indices. For dipole–dipole resonant events, the symmetric part D^+_{jk} does not vary with exchange of indices, hence it is time- and parity-even. The antisymmetric part D^-_{jk} changes its sign upon permutation of the indices, so it is parity-even and time-odd, being associated with a magnetic moment (1.11.6.41). This part of the tensor is responsible for the existence of X-ray magnetic circular dichroism (XMCD) and the appearance of the magnetic satellites in various kinds of magnetic structures.

If the rotation symmetry of a second-rank tensor is completely described by rotation about the magnetic moment $\mathbf{m}$, then the antisymmetric second-rank tensor D^-_{jk} can be represented as $D^-_{jk} = \epsilon_{jkl} m_l$, where ϵ_{jmk} is an antisymmetric third-rank unit tensor and m_l are the coordinates of the magnetic moment of the resonant atom. So, the scattering amplitude for the dipole–dipole $E1E1$ transition can be given as

$$f^{dd} = -\frac{e^2}{mc^2} \Big\{ (\mathbf{e}'^* \cdot \mathbf{e}) C_{0s} + i[\mathbf{e}'^* \times \mathbf{e}] \cdot \mathbf{m}_s C_{1s} + [(\mathbf{e}'^* \cdot \mathbf{m}_s)(\mathbf{e} \cdot \mathbf{m}_s) - \tfrac{1}{3}(\mathbf{e}'^* \cdot \mathbf{e})] C_{2s} \Big\}. \qquad (1.11.6.41)$$

C_{0s}, C_{1s} and C_{2s} are energy-dependent coefficients referring to the sth atom in the unit cell and $\mathbf{m}_s$ is a unit vector along the magnetic moment. The third term in (1.11.6.41) is time non-reversal, and it is responsible for the magnetic linear dichroism (XMLD). This kind of X-ray dichroism is also influenced by the crystal field (Thole *et al.*, 1986; van der Laan *et al.*, 1986).

The coefficients C_{0s}, C_{1s} and C_{2s} involved in (1.11.6.41) may be represented in terms of spherical harmonics. Using the relations (Berestetskii *et al.*, 1982; Hannon *et al.*, 1988)

$$\begin{aligned}&[\mathbf{e}'^* \cdot \mathbf{Y}_{1\pm1}(\mathbf{k}')\mathbf{Y}^*_{1\pm1}(\mathbf{k}) \cdot \mathbf{e}] \\ &\quad = \frac{3}{16\pi}\left[(\mathbf{e}'^* \cdot \mathbf{e}) \mp i[\mathbf{e}'^* \times \mathbf{e}] \cdot \mathbf{m}_s - (\mathbf{e}'^* \cdot \mathbf{m}_s)(\mathbf{e} \cdot \mathbf{m}_s)\right]\end{aligned} \tag{1.11.6.42}$$

and

$$[\mathbf{e}'^* \cdot \mathbf{Y}_{10}(\mathbf{k}')\mathbf{Y}^*_{10}(\mathbf{k}) \cdot \mathbf{e}] = \frac{3}{8\pi}(\mathbf{e}'^* \cdot \mathbf{m}_s)(\mathbf{e} \cdot \mathbf{m}_s) \tag{1.11.6.43}$$

for $L = 1$, $M = \pm1$ and $L = 0$, $M = 0$, respectively, one obtains

$$\begin{aligned}f_s^{dd} = -\frac{3}{4k}\Big[&(\mathbf{e}'^* \cdot \mathbf{e})(F_{11} + F_{1-1}) - i[\mathbf{e}'^* \times \mathbf{e}] \cdot \mathbf{m}_s(F_{11} - F_{1-1}) \\ &+ (\mathbf{e}'^* \cdot \mathbf{m}_s)(\mathbf{e} \cdot \mathbf{m}_s)(2F_{10} - F_{11} - F_{1-1})\Big]\end{aligned} \tag{1.11.6.44}$$

with

$$F_{LM}(\omega) = \sum_{a,c} p_a p_{ac} \frac{\Gamma_x(aMc; EL)}{E_c - E_a - \hbar\omega - i\Gamma/2}, \tag{1.11.6.45}$$

where p_a is the probability of the initial state a, p_{ac} is that for the transition from state a to a final state c, and Γ_x/Γ is the ratio of the partial line width of the excited state due to a pure 2^L (EL) radiative decay and the width due to all processes, both radiative and non-radiative (for example, the Auger decay).

Magnetic ordering is frequently accompanied by a local anisotropy in the crystal. In this case, both kinds of local anisotropies exist simultaneously and must be taken into account in, for example, XMLD (van der Laan *et al.*, 1986) and XMχD (Goulon *et al.*, 2002). In resonant X-ray scattering experiments, simultaneous existence of forbidden reflections provided by spin and orbital ordering (Murakami *et al.*, 1998) as well as magnetic and crystal anisotropy (Ji *et al.*, 2003; Paolasini *et al.*, 2002, 1999) have been observed. The explicit Cartesian form of the tensor atomic factor in the presence of both a magnetic moment and crystal anisotropy has been proposed by Blume (1994). When the symmetry of the atomic site is high enough, *i.e.* the atom lies on an n-order axis ($n > 2$), then the tensors D^+ and D^- can be represented as

$$\begin{aligned}D^+_{jk} = {}&(z_j z_k - \tfrac{1}{3}\delta_{jk})[a_1 + b_1(\mathbf{z} \cdot \mathbf{m})^2] + c_1(m_j m_k - \tfrac{1}{3}m^2\delta_{jk}) \\ &+ d_1[z_j m_k + z_k m_j - \tfrac{2}{3}(\mathbf{z} \cdot \mathbf{m})\delta_{jk})](\mathbf{z} \cdot \mathbf{m})\end{aligned} \tag{1.11.6.46}$$

and

$$D^-_{jk} = i\epsilon_{jkl}[a_2 m_l + b_2 z_l(\mathbf{z} \cdot \mathbf{m})], \tag{1.11.6.47}$$

where a_i and b_i depend on the energy, and $\mathbf{z}$ is a unit vector along the symmetry axis under consideration. One can see that the atomic tensor factor is given by a sum of three terms: the first is due to the symmetry of the local crystal anisotropy, the second describes pure magnetic scattering, and the last ('combined') term is induced by interference between magnetic and non-magnetic resonant scattering. This issue was first discussed by Blume (1994) and later in more detail by Ovchinnikova & Dmitrienko (1997, 2000). All the terms can give rise to forbidden reflections, *i.e.* sets of pure resonant forbidden magnetic and non-magnetic reflections can be observed for the same crystal, see Ji *et al.* (2003) and Paolasini *et al.* (2002, 1999). Only reflections caused by the 'combined' term (Ovchinnikova & Dmitrienko, 1997) have not been observed yet.

Neglecting the crystal field, an explicit form of the fourth-rank tensors describing the quadrupole–quadrupole $E2E2$ events in magnetic structures was proposed by Hannon *et al.* (1988) and Blume (1994):

$$\begin{aligned}Q^-_{ijkm} = {}&a_1\{\epsilon_{ikl}m_l\delta_{jm} + \epsilon_{jml}m_l\delta_{ik} + \epsilon_{iml}m_l\delta_{jk} + \epsilon_{jkl}m_l\delta_{im}\} \\ &+ b_2\{\epsilon_{ikl}m_l m_j m_m + \epsilon_{jml}m_l m_i m_k + \epsilon_{iml}m_l m_j m_k \\ &+ \epsilon_{jkl}m_l m_i m_m\},\end{aligned} \tag{1.11.6.48}$$

$$\begin{aligned}Q^+_{ijkm} = {}&a_2\delta_{ij}\delta_{km} + b_2\{\delta_{ik}\delta_{jm} + \delta_{im}\delta_{jk}\} \\ &+ c_2\{\delta_{ik}m_j m_m + \delta_{im}m_j m_k + \delta_{jm}m_i m_k + \delta_{jk}m_i m_m\} \\ &+ d_2\{\delta_{ij}m_k m_m + \delta_{km}m_i m_j\} + e_2 m_i m_j m_k m_m \\ &+ f_2\{\epsilon_{ikl}\epsilon_{jmp}m_l m_p + \epsilon_{iml}\epsilon_{jkp}m_l m_p\}.\end{aligned} \tag{1.11.6.49}$$

Then, being convoluted with polarization vectors, the scattering amplitude of the quadrupole transition ($L = 2$) can be written as a sum of 13 terms belonging to five orders of magnetic moments (Hannon *et al.*, 1988; Blume, 1994). The final expression that gives the quadrupole contribution to the magnetic scattering amplitude in terms of individual spin components is rather complicated and can be found, for example, in Hill & McMorrow (1996). In the presence of both a magnetic moment and local crystal anisotropy, the fourth-rank tensor describing $E2E2$ events depends on both kinds of anisotropy and can include the 'combined' part in explicit form, as found by Ovchinnikova & Dmitrienko (2000).

1.11.6.6. *Tensor atomic factors (spherical tensor representation)*

Another representation of the scattering amplitude is widely used in the scientific literature (Hannon *et al.*, 1988; Luo *et al.*, 1993; Carra *et al.*, 1993; Lovesey & Collins, 1996) for the description of resonant multipole transitions. In order to obtain the scattering amplitude and intensity for a resonant process described by some set of spherical tensor components, the tensor that describes the atomic scattering must be contracted by a tensor of the same rank and inversion/time-reversal symmetry which describes the X-ray probe, so that the result would be a scalar. There are well known relations between the components of the atomic factor tensor, both in Cartesian and spherical representations. For the dipole–dipole transition, the resonant scattering amplitude can be written as (Hannon *et al.*, 1988; Collins *et al.*, 2007; Paolasini, 2012; Joly *et al.*, 2012)

$$f^{dd} \sim \sum_{jm} e'^*_j e_m D_{jm} = \sum_{p=0}^{2}\sum_{q=-p}^{p}(-1)^{p+q}X_q^{(p)}F_{-q}^{(p)}, \tag{1.11.6.50}$$

where D_{jm} are the Cartesian tensor components, $X_q^{(p)}$ depends only on the incident and scattered radiation and the polarization vectors, and $F_{-q}^{(p)}$ is associated with the tensor properties of the absorbing atom and can be represented in terms of a multipole expansion.

It is convenient to decompose each tensor into its irreducible parts. For example, an $E1E1$ tensor containing nine Cartesian components can be represented as a sum of three irreducible tensors with ranks $p = 0$ (one component), $p = 1$ (three components) and $p = 2$ (five components). This decomposition is unique.

For $p = 0$:

$$F_0^{(0)} = \tfrac{1}{3}(D_{xx} + D_{yy} + D_{zz}). \tag{1.11.6.51}$$

For $p = 1$:

$$\begin{aligned} F_0^{(1)} &= \tfrac{1}{2}(D_{xy} - D_{yx}),\\ F_{\pm1}^{(1)} &= \mp\tfrac{1}{2\sqrt{2}}[(D_{yz} - D_{zy} \mp i(D_{xz} - D_{zx})]. \end{aligned} \tag{1.11.6.52}$$

For $p = 2$:

$$\begin{aligned} F_0^{(2)} &= D_{zz} - F_0^{(0)},\\ F_{\pm1}^{(2)} &= \mp\tfrac{1}{2}\sqrt{\tfrac{2}{3}}[(D_{xz} + D_{zx} \mp i(D_{yz} + D_{zy})], \end{aligned} \tag{1.11.6.53}$$

$$F_{\pm2}^{(2)} = \tfrac{1}{6}[2D_{xx} - 2D_{yy} \pm i(D_{xy} + D_{yx})]. \tag{1.11.6.54}$$

It follows from (1.11.6.14) that the fourth-rank tensor describing the quadrupole–quadrupole X-ray scattering can also be divided into two parts: the time-reversal part, Q^{+}_{jklm}, and the non-time-reversal part, Q^{-}_{jklm}. Both can be explicitly represented by (1.11.6.3) and (1.11.6.2), in which all these tensors are parity-even. The explicit form of the fourth-rank tensors is suitable for the analysis of possible effects in resonant X-ray absorption and scattering. Nevertheless, sometimes the following representation of the scattering amplitude as a product of spherical tensors is preferable:

$$f^{qq} = \tfrac{1}{4}\sum_{ijmn} e_i'^{*} e_m k_j' k_n Q_{ijmn} = \sum_{p=0}^{4} \sum_{q=-p}^{p} (-1)^{p+q} X_q^{(p)} F_{-q}^{(p)}. \tag{1.11.6.55}$$

Here, the dipole–quadrupole tensor atomic factor given by (1.11.6.10) is represented by a sum over several tensors with different symmetries. All tensors are parity-odd, but the tensors I^{--}_{jml} and I^{-+}_{jml} are also non-time-reversal. The scattering amplitude corresponding to the dipole–quadrupole resonant X-ray scattering can be represented as

$$\begin{aligned} f^{dq} &= \tfrac{1}{2} i \sum_{ijm} e_i'^{*} e_j (k_m I_{ijm} - k_m' I_{jim})\\ &= \sum_{p=1}^{3} \sum_{q=-p}^{p} (-1)^{p+q} (X_q^{(p)} F_{-q}^{(p)} + \bar{X}_q^{(p)} \bar{F}_{-q}^{(p)}). \end{aligned} \tag{1.11.6.56}$$

The explicit form of $F_{-q}^{(p)}$ can be found in Marri & Carra (2004). Various parts of $F_{-q}^{(p)}$ possess different symmetry with respect to the reversal of space P and time T.

The spherical representation of the tensor atomic factor allows one to analyse its various components, as they possess different symmetries with respect to rotations or space and time inversion. For each p, $F_{-q}^{(p)}$ is related to a specific term of the multipole expansion of the system. Multipole expansions of electric and magnetic fields generated by charges and permanent currents are widely used in characterizing the electromagnetic state of a physical system (Berestetskii *et al.*, 1982). The transformation rules for electric and magnetic multipoles of both parities under space inversion and time reversal are of great importance for electromagnetic effects in crystals. The correspondence between the $F_{-q}^{(p)}$ and electromagnetic multipoles is shown in Table 1.11.6.2. In this table, the properties of the tensors $F_{-q}^{(p)}$ under time reversal and space inversion on one side are identified with multipole terms describing the physical system on the other. In fact, for any given tensor of rank $p = 1, 2, 3, 4$ there is one electromagnetic multipole of the same rank (1 → dipole, 2 → quadrupole, 3 → octupole, 4 → hexadecapole) and with the same T and P properties. Note that P-odd $E1E2$ tensors have both T-odd (−) and T-even (+) terms for any p, whereas P-even tensors (both $E1E1$ and $E2E2$) are T-odd for odd rank and T-even for even rank, respectively (Di Matteo *et al.*, 2005).

Table 1.11.6.2. *Identification of properties under time inversion T and space inversion P of tensors associated with multipole expansion*

After Di Matteo *et al.* (2005) and Paolasini (2012).

Rank of tensor	Resonant process	T	P	Type	Multipole
0	$E1E1$	+	+	charge	monopole
0	$E2E2$	+	+	charge	monopole
1	$E1E1$	−	+	magnetic	dipole
1	$E2E2$	−	+	magnetic	dipole
1	$E1E2$	+	−	electric	dipole
1	$E1E2$	−	−	polar toroidal	dipole
2	$E1E1$	+	+	electric	quadrupole
2	$E2E2$	+	+	electric	quadrupole
2	$E1E2$	+	−	axial toroidal	quadrupole
2	$E1E2$	−	−	magnetic	quadrupole
3	$E2E2$	−	+	magnetic	octupole
3	$E1E2$	+	−	electric	octupole
3	$E1E2$	−	−	polar toroidal	octupole
4	$E2E2$	+	+	electric	hexadecapole

An important contribution of Luo *et al.* (1993) and Carra *et al.* (1993) consisted of expressing the amplitude coefficients in terms of experimentally significant quantities, electron spin and orbital moments. This procedure is valid within the fast-collision approximation, when either the deviation from resonance, $\Delta E = E_c - E_a - \hbar\omega$, or the width, Γ, is large compared to the splitting of the excited-state configuration. The approximation is expected to hold for the L_2 and L_3 edges of the rare earths and actinides, as well as for the M_4 and M_5 edges of the actinides. In this energy regime, the resonant factors can be summed independently, leaving amplitude coefficients that may be written in terms of multipole moment operators, which are themselves single-particle operators summed over the valence electrons in the initial state.

Magnetic scattering has become a powerful method for understanding magnetic structures (Tonnere, 1996; Paolasini, 2012), particularly as it is suitable even for powder samples (Collins *et al.*, 1995). Since the first studies (Gibbs *et al.*, 1988), resonant magnetic X-ray scattering has been observed at various edges of transition metals and rare earths. The studies include magnetics and multiferroics with commensurate and incommensurate modulation (Walker *et al.*, 2009; Kim *et al.*, 2011; Ishii *et al.*, 2006; Partzsch *et al.*, 2012; Lander, 2012; Beale *et al.*, 2012; Lovesey *et al.*, 2012; Mazzoli *et al.*, 2007) as well as multi-*k* magnetic structures (Bernhoeft *et al.*, 2012), and structures with orbital ordering (Murakami *et al.*, 1998) and higher-order multipoles (Princep *et al.*, 2011). It has also been shown that effects can be measured not only at the edges of magnetic atoms [*K* edges of transition metals, *L* edges of rare-earth elements and *M* edges of actinides (Vettier, 2001, 2012)], but also at the edges of non-magnetic atoms (Mannix *et al.*, 2001; van Veenendaal, 2003).

Thus, magnetic and non-magnetic resonant X-ray diffraction clearly has the potential to be an important working tool in modern materials research. The advantage of polarized X-rays is their sensitivity to both the local atomic environments of resonant atoms and their partial structures. The knowledge of the local and global crystal symmetries and of the interplay of their effects is therefore of great value for a better understanding of structural, electronic and magnetic features of crystalline condensed matter.

1.11.7. Glossary

$\chi(\mathbf{r})$	local susceptibility tensor in direct space
$\chi(\mathbf{H})$	Fourier components of the local susceptibility tensor
$\mathbf{H}$	reciprocal-lattice vector
$\mathbf{e}$	polarization vector of an X-ray wave
$\mathbf{k}$	wavevector of an X-ray wave
R^g_{ij}	matrix corresponding to point-group operator *g*
$\boldsymbol{\sigma}$	polarization vector perpendicular to the scattering plane
$\boldsymbol{\pi}$	polarization vector in the scattering plane
θ	Bragg angle
φ	azimuthal angle of rotation about a reciprocal-lattice vector
$\mathbf{A}(\mathbf{r})$	vector potential of the electromagnetic wave
$\mathbf{P}(\mathbf{r})$	momentum of an electron
ω	frequency of an electromagnetic wave
λ	wavelength of the radiation
E_i	energy of a discrete atomic level
$\mathbf{s}$	spin of an electron
$f(\mathbf{k}, \mathbf{e}, \mathbf{k}', \mathbf{e}')$	scattering amplitude
$\mathbf{G}$	scattering vector
ϵ_{ijk}	Levi-Civita symbol
ω_{ca}	transition frequency for states *a* and *c*
Γ	energy width of the excited state
p_a	probability that the state $\lvert a\rangle$ of the scatterer is occupied
f_{jk}	tensor atomic factor
$F_{jk}(\mathbf{H})$	structure-factor tensor of rank 2
$I_{\mathbf{H}}(\mathbf{e}', \mathbf{e})$	intensity of the reflection
EL	notation of the electric multipole transition. $E1$: the dipole; $E2$: the quadrupole
ML	notation of the magnetic multipole transition
L	orbital moment of electron
D_{jk}	dipole–dipole tensor atomic factor
D^+_{jk}	symmetric part of the dipole–dipole tensor atomic factor
D^-_{jk}	antisymmetric part of the dipole–dipole tensor atomic factor
I_{jkl}	third-rank tensor describing the dipole–quadrupole resonant X-ray scattering
I^{++}_{jkl}	part of the third-rank tensor invariant under time inversion and symmetric under the permutation of *j* and *k*
I^{+-}_{jkl}	part of the third-rank tensor non-invariant under time inversion and symmetric under the permutation of *j* and *k*
I^{-+}_{jkl}	part of the third-rank tensor invariant under time inversion and antisymmetric under the permutation of *j* and *k*
I^{--}_{jkl}	part of the third-rank tensor non-invariant under time inversion and antisymmetric under the permutation of *j* and *k*
Q_{ijkl}	fourth-rank tensor describing the quadrupole–quadrupole resonant X-ray scattering
Tr	trace of matrix
$\mathbf{m}$	magnetic moment of an atom
$\mathbf{Y}_{LM}$	spherical tensor
$X^{(p)}_q$	component of the spherical tensor depending only on the incident and scattered radiation
$F^{(p)}_{-}q$	component of the spherical tensor associated with the tensor properties of the absorbing atom

References

Altarelli, M. (2006). *Resonant X-ray scattering: a theoretical introduction. Lecture Notes in Physics*, Vol. 697, pp. 201–242. Heidelberg: Springer.

Arenholz, E., van der Laan, G., Chopdekar, R. V. & Suzuki, Y. (2006). *Anisotropic X-ray magnetic linear dichroism at the Fe $L_{2,3}$ edges in Fe_3O_4. Phys. Rev. B*, **74**, 094407.

Arima, T., Jung, J.-H., Matsubara, M., Kubota, M., He, J.-P., Kaneko, Y. & Tokura, Y. (2005). *Resonant magnetochiral X-ray scattering in $LaFeO_3$: observation of ordering of toroidal moments. J. Phys. Soc. Jpn*, **74**, 1419–1422.

Authier, A. (2005). *Dynamical Theory of X-ray Diffraction*. Oxford University Press.

Authier, A. (2008). In *International Tables for Crystallography*, Volume B, *Reciprocal Space*, edited by U. Shmueli, 3rd ed., pp. 626–646. Heidelberg: Springer.

Barois, P., Gleeson, H., Huang, C. & Pindak, R. (2012). *Application of X-ray resonant diffraction to structural studies of liquid crystals. Eur. Phys. J. Spec. Top.* **208**, 333–350.

Beale, T. A. W., Beutier, G., Bland, S. R., Bombardi, A., Bouchenoire, L., Bunau, O., Di Matteo, S., Fernández-Rodríguez, J., Hamann-Borrero, J. E., Herrero-Martin, J., Jacques, V. L. R., Johnson, R. D., Juhin, A., Matsumura, T., Mazzoli, C., Mulders, A. M., Nakao, H., Okamoto, J., Partzsch, S., Princep, A. J., Scagnoli, V., Strempfer, J., Vecchini, C., Wakabayashi, Y., Walker, H. C., Wermeille, D. & Yamasaki, Y. (2012). *REXS contribution to electronic ordering investigation in solids. Eur. Phys. J. Spec. Top.* **208**, 89–98.

Belyakov, V. A. (1975). *Diffraction of Mössbauer gamma-radiation in crystals. Sov. Phys. Usp.* **18**, 267–299.

Belyakov, V. A. & Aivazyan, Y. M. (1969). *Quadrupole diffraction maxima in Mossbauer scattering. JETP Lett.* **9**, 393.

Belyakov, V. A. & Dmitrienko, V. E. (1985). *The blue phase of liquid crystals. Sov. Phys. Usp.* **28**, 535–562.

Belyakov, V. A. & Dmitrienko, V. E. (1989). *Polarisation phenomena in X-ray optics. Sov. Phys. Usp.* **32**, 697–719.

Berestetskii, V. B., Lifshitz, E. M. & Pitaevskii, L. P. (1982). *Quantum Electrodynamics*. Oxford: Pergamon Press.

Bergevin, F. de & Brunel, M. (1972). *Observation of magnetic superlattice peaks by X-ray diffraction on an antiferromagnetic NiO crystal. Phys. Lett. A*, **39**, 141–142.

Bergevin, F. de & Brunel, M. (1981). *Diffraction of X-rays by magnetic materials. I. General formulae and measurements on ferro- and ferrimagnetic compounds. Acta Cryst.* A**37**, 314–324.

Bernhoeft, N., Paixao, J. A., Detlefs, C., Wilkins, S. B., Javorsky, P., Blackburn, E. & Lander, G. H. (2012). *Resonant X-ray scattering from $UAs_{0.8}Se_{0.2}$: multi-k configurations. Phys. Rev. B*, **69**, 174415.

Blume, M. (1985). *Magnetic scattering of X-rays. J. Appl. Phys.* **57**, 3615–3618.

Blume, M. (1994). *Resonant X-ray diffraction and polarization analysis at the iron K-edge.* In *Resonant Anomalous X-ray Scattering. Theory and Applications*, edited by G. Materlik, C. J. Sparks & K. Fischer, pp. 91–97. Amsterdam: North-Holland.

Brouder, C. (1990). *Angular dependence of X-ray absorption spectra. J. Phys. Condens. Matter*, **2**, 701–738.

Brunel, M. & de Bergevin, F. (1981). *Diffraction of X-rays by magnetic materials. II. Measurements on antiferromagnetic Fe_2O_3. Acta Cryst.* A**37**, 324–331.

Carra, P. & Thole, B. T. (1994). *Anisotropic X-ray anomalous diffraction and forbidden reflections. Rev. Mod. Phys.* **66**, 1509–1515.

Carra, P., Thole, B. T., Altarelli, M. & Wang, X. (1993). *X-ray circular dichroism and local magnetic fields. Phys. Rev. Lett.* **70**, 694–697.

Champeney, D. C. (1979). *The scattering of Mössbauer radiation by condensed matter. Rep. Prog. Phys.* **42**, 1017–1054.

Chen, C. T., Sette, F., Ma, Y. & Modesti, S. (1990). *Soft X-ray magnetic circular dichroism at the $L_{2,3}$ edges of nickel. Phys. Rev. B*, **42**, 7363–7265.

Collins, S. & Bombardi, A. (2010). *Resonant X-ray scattering and absorption*. In *Magnetism and Synchrotron Radiation*, edited by E. Beaurepaire, H. Bulou, F. Scheurer & K. Jean-Paul. *Springer Proceedings in Physics*, Vol. 133, pp. 223–262. Berlin, Heidelberg: Springer.

Collins, S., Lovesey, S. & Balcar, E. (2007). *Dichroism and resonant diffraction in X-ray scattering by complex materials. J. Phys. Condens. Matter*, **19**, 213201.

Collins, S. P., Laundy, D., Dmitrienko, V., Mannix, D. & Thompson, P. (2003). *Temperature-dependent forbidden resonant X-ray scattering in zinc oxide. Phys. Rev. B*, **68**, 064110.

Collins, S. P., Laundy, D., Tang, C. C. & Cernik, R. J. (1995). *Magnetic X-ray powder diffraction from antiferromagnetic uranium oxide. J. Phys. Condens. Matter*, **7**, L223–L229.

Cracknell, A. P. (1975). *Group Theory in Solid-State Physics*. London: Taylor and Francis Ltd.

Crooker, P. P. (2001). *Blue phases*. In *Chirality in Liquid Crystals*, edited by H.-S. Kitzerow & C. Bahr, pp. 186–222. New York: Springer.

Dawson, B. (1975). *Studies of atomic charge density by X-ray and neutron diffraction – a perspective*. In *Advances in Structure Research by Diffraction Methods*, Vol. 6, edited by W. Hoppe & R. Mason. Oxford: Pergamon Press.

Detlefs, C., Sanchez del Rio, M. & Mazzoli, C. (2012). *X-ray polarization: general formalism and polarization analysis. Eur. Phys. J. Spec. Top.* **208**, 359–371.

Di Matteo, S., Joly, Y. & Natoli, C. R. (2005). *Detection of electromagnetic multipoles by X-ray spectroscopies. Phys. Rev. B*, **72**, 144406.

Dmitrienko, V. E. (1983). *Forbidden reflections due to anisotropic X-ray susceptibility of crystals. Acta Cryst.* A**39**, 29–35.

Dmitrienko, V. E. (1984). *Anisotropy of X-ray susceptibility and Bragg reflections in cubic crystals. Acta Cryst.* A**40**, 89–95.

Dmitrienko, V. E., Ishida, K., Kirfel, A. & Ovchinnikova, E. N. (2005). *Polarization anisotropy of X-ray atomic factors and 'forbidden' resonant reflections. Acta Cryst.* A**61**, 481–493.

Eichhorn, K. & Kirfel, A. (1988). *Genaue Strukturuntersuchung mit Synchrotron Strahlung. II. Anisotropie der anomalen Dispersion in Cuprit, Cu$_2$O. Z. Kristallogr.* **185**, 56–58.

Erskine, J. L. & Stern, E. A. (1975). *Calculation of the M_{23} magneto-optical absorption spectrum of ferromagnetic nickel. Phys. Rev. B*, **12**, 5016–5024.

Finkelstein, K. D. & Dmitrienko, V. E. (2012). *Resonant scattering techniques*. In *Characterization of Materials*, edited by E. N. Kaufmann, pp. 1–15. New Jersey: John Wiley & Sons, Inc.

García, J. & Subías, G. (2004). *The Verwey transition – a new perspective. J. Phys. Condens. Matter*, **16**, R145–R178.

García, J., Subías, G., Proietti, M. G., Renevier, H., Joly, Y., Hodeau, J. L., Blasco, J., Sánchez, M. C. & Bérar, J. F. (2000). *Resonant forbidden reflections in magnetite. Phys. Rev. Lett.* **85**, 578–581.

Gibbs, D., Harshmann, D. R., Isaacs, E. D., McWhan, D. B., Mills, D. & Vettier, C. (1988). *Polarization and resonance properties of magnetic X-ray scattering in holmium. Phys. Rev. Lett.* **61**, 1241–1244.

Gleeson, H. & Hirst, L. (2006). *Resonant X-ray scattering: a tool for structure elucidation in liquid crystals. Chem. Phys. Chem.* **7**, 321–328.

Goulon, J., Jaouen, N., Rogalev, A., Wilhelm, F., Goulon-Ginet, C., Brouder, C., Joly, Y., Ovchinnikova, E. N. & Dmitrienko, V. E. (2007). *Vector part of optical activity probed with X-rays in hexagonal ZnO. J. Phys. Condens. Matter*, **19**, 156201.

Goulon, J., Rogalev, A., Wilhelm, F., Goulon-Ginet, C. & Carra, P. (2002). *X-ray magnetochiral dichroism: a new spectroscopic probe of parity nonconserving magnetic solids. Phys. Rev. Lett.* **88**, 237401.

Goulon, J., Rogalev, A., Wilhelm, F., Goulon-Ginet, C., Carra, P., Marri, I. & Brouder, C. (2003). *X-ray optical activity: application of sum rules. J. Exp. Theor. Phys.* **97**, 402–431.

Gukasov, A. & Brown, P. J. (2010). *Determination of atomic site susceptibility tensors from neutron diffraction data on polycrystalline samples. J. Phys. Condens. Matter*, **22**, 502201.

Hagiwara, K., Kanazawa, M., Horie, K., Kokubun, J. & Ishida, K. (1999). *Measurements of ATS scattering from magnetite near the Fe K-absorption edge in the temperature range 290 K–80 K. J. Phys. Soc. Jpn*, **68**, 1592–1597.

Hahn, Th. (2005). Editor. *International Tables for Crystallography*, Volume A, *Space-Group Symmetry*, 5th ed. Heidelberg: Springer.

Hannon, J. P., Trammell, G. T., Blume, M. & Gibbs, D. (1988). *X-ray resonance exchange scattering. Phys. Rev. Lett.* **61**, 1245–1248.

Hart, M. & Rodriques, A. R. D. (1981). *Optical activity and the Faraday effect at X-ray frequencies. Philos. Mag. B*, **43**, 321–332.

Hill, J. P. & McMorrow, D. F. (1996). *Resonant exchange scattering: polarization dependence and correlation function. Acta Cryst.* A**52**, 236–244.

Hodeau, J.-L., Favre-Nicolin, V., Bos, S., Renevier, H., Lorenzo, E. & Bérar, J.-F. (2001). *Resonant diffraction. Chem. Rev.* **101**, 1843–1867.

International Tables for Crystallography (2004). Volume C, *Mathematical, Physical and Chemical Tables*, 3rd ed., edited by E. Prince. Dordrecht: Kluwer.

International Tables for Crystallography (2008). Volume B, *Reciprocal Space*, 3rd ed., edited by U. Shmueli. Heidelberg: Springer.

Ishii, K., Kuzushita, K., Murakami, Y., Haga, Y., Yamamoto, E. & Onuki, Y. (2006). *Resonant magnetic X-ray scattering study of UPd$_2$Al$_3$. J. Phys. Soc. Jpn*, **75S**, 102–104.

Ji, S., Song, C., Koo, J., Lee, K.-B., Park, Y. J., Kim, J. Y., Park, J.-H., Shin, H. J., Rhyee, J. S., Oh, B. H. & Cho, B. K. (2003). *Interference of magnetic and ATS reflections in resonant X-ray scattering of GdB$_4$. Phys. Rev. Lett.* **91**, 257205.

Joly, Y., Di Matteo, S. & Bunau, O. (2012). *Resonant X-ray diffraction: basic theoretical principles. Eur. Phys. J. Spec. Top.* **208**, 21–38.

Kim, M. G., Kreyssig, A., Lee, Y. B., McQueeney, R. J., Harmon, B. N. & Goldman, A. I. (2011). *Fe K-edge X-ray resonant magnetic scattering from Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ superconductors. Phys. Rev. B*, **83**, 134522.

Kirfel, A. & Morgenroth, W. (1993). *Anisotropy of anomalous scattering in X-ray diffraction. III. 'Forbidden' axial reflections in space groups up to orthorhombic symmetry. Acta Cryst.* A**49**, 35–45.

Kirfel, A. & Petcov, A. (1991). *Anisotropy of anomalous dispersion. An application to partial structure determination. Z. Kristallogr.* **195**, 1–15.

Kirfel, A. & Petcov, A. (1992). *Anisotropy of anomalous scattering in X-ray diffraction. II. Combining polarization-dependent transmission and diffraction, and an application to partial-structure analysis. Acta Cryst.* A**48**, 247–259.

Kirfel, A., Petcov, A. & Eichhorn, K. (1991). *Anisotropy of anomalous dispersion in X-ray diffraction. Acta Cryst.* A**47**, 180–195.

Kokubun, J., Sawai, H., Uehara, M., Momozawa, N., Ishida, K., Kirfel, A., Vedrinskii, R. V., Novikovskii, N., Novakovich, A. A. & Dmitrienko, V. E. (2010). *Pure dipole–quadrupole resonant scattering induced by the p–d hybridization of atomic orbitals in anatase TiO$_2$. Phys. Rev. B*, **82**, 205206.

Kolpakov, A. V., Bushuev, V. A. & Kuz'min, R. N. (1978). *Dielectric permittivity in the X-ray region. Sov. Phys. Usp.* **21**, 959–977.

Laan, G. van der, Arenholz, E., Chopdekar, R. V. & Suzuki, Y. (2008). *Influence of crystal field on anisotropic X-ray magnetic linear dichroism at the Co^{2+} $L_{2,3}$ edges. Phys. Rev. B*, **77**, 064407.

Laan, G. van der, Thole, B. T., Sawatzky, G., Goedkoop, J. B., Fuggle, J. C., Esteva, J.-M., Karnatak, R., Remeika, J. P. & Dabkowska, H. A. (1986). *Experimental proof of magnetic X-ray dichroism. Phys. Rev. B*, **34**, 6529–6531.

Lander, G. H. (2012). *Resonant elastic X-ray scattering from 5f systems. Eur. Phys. J. Spec. Top.* **208**, 129–132.

Lovesey, S. W., Balcar, E., Knight, K. S. & Fernández-Rodríguez, J. (2005). *Electronic properties of crystalline materials observed in X-ray diffraction. Phys. Rep.* **411**, 233–289.

Lovesey, S. W. & Collins, S. P. (1996). *X-ray Scattering and Absorption by Magnetic Materials*. Oxford: Clarendon Press.

Lovesey, S. W., Detlefs, C. & Rodríguez-Fernández, A. (2012). *Neptunium multipoles and resonant X-ray Bragg diffraction by neptunium dioxide (NpO$_2$). J. Phys. Condens. Matter*, **24**, 256009.

Lovesey, S. W., Fernández-Rodríguez, J., Blanco, J. A., Sivia, D. S., Knight, K. S. & Paolasini, L. (2007). *Vanadium magnetoelectric multipoles in V$_2$O$_3$. Phys. Rev. B*, **75**, 014409.

Luo, J., Trammell, G. T. & Hannon, J. P. (1993). *Scattering operator for elastic and inelastic resonant X-ray scattering. Phys. Rev. Lett.* **71**, 287–290.

Mannix, D., Stunault, A., Bernhoeft, N., Paolasini, L., Lander, G. H., Vettier, C., de Bergevin, F., Kaczorowski, D. & Czopnik, A. (2001). *Resonant enhancements at nonmagnetic ions: new possibilities for magneic X-ray scattering. Phys. Rev. Lett.* **86**, 4128–4131.

Marri, I. & Carra, P. (2004). *Scattering operators for E1–E2 X-ray resonant diffraction. Phys. Rev. B*, **69**, 113101.

Materlik, G., Sparks, C. J. & Fischer, K. (1994). Editors. *Resonant Anomalous X-ray Scattering. Theory and Applications*. Amsterdam: North-Holland.

Matsubara, M., Shimada, Y., Arima, T., Taguchi, Y. & Tokura, Y. (2005). *Observation of nonreciprocal magnetoelectric X-ray scattering in magnetite*. *Phys. Rev. B*, **72**, 220404.

Mazzoli, C., Fabrizi, F., Di Matteo, S., Paolasini, L., de Bergevin, F., Bombardi, A., Ghigna, P. & Caciuffo, R. (2007). *Resonant magnetic X-ray scattering study of $KCuF_3$*. *J. Magn. Magn. Mater.* **310**, 796–797.

Morgenroth, W., Kirfel, A. & Fischer, K. (1994). *Anisotropy of anomalous scattering in X-ray diffraction. 'Forbidden' axial reflections in tetragonal space groups*. *Z. Kristallogr.* **209**, 124–131.

Murakami, Y., Kawada, H., Kawata, H., Tanaka, M., Arima, T., Moritomo, Y. & Tokura, Y. (1998). *Direct observation of charge and orbital ordering in $La_{0.5}Sr_{1.5}MnO_4$*. *Phys. Rev. Lett.* **80**, 1932–1935.

Natoli, C. R., Brouder, C., Sainctavit, P., Goulon, J., Goulon-Ginet, C. & Rogalev, A. (1998). *Calculation of X-ray natural circular dichroism*. *Eur. Phys. J. B*, **4**, 1–11.

Nazarenko, E., Lorenzo, J. E., Joly, Y., Hodeau, J. L., Mannix, D. & Marin, C. (2006). *Resonant X-ray diffraction studies on the charge ordering in magnetite*. *Phys. Rev. Lett.* **97**, 056403.

Nye, J. F. (1985). *Physical Properties of Crystals: Their Representation by Tensors and Matrices*. Oxford University Press.

Ovchinnikova, E. N. & Dmitrienko, V. E. (1997). *Combined effects of magnetic structure and local crystal fields in anisotropic X-ray anomalous scattering*. *Acta Cryst.* A**53**, 388–395.

Ovchinnikova, E. N. & Dmitrienko, V. E. (2000). *Resonant X-ray scattering in the presence of several anisotropic factors*. *Acta Cryst.* A**56**, 2–10.

Paolasini, L. (2012). *Magnetism in condensed matter: resonant and magnetic scattering by synchrotron radiation*. In *Italian School on Magnetism, Pavia 2012*, pp. 1–83. Universita di Pavia.

Paolasini, L., Caciuffo, R., Sollier, A., Ghigna, P. & Altarelli, M. (2002). *Coupling between spin and orbital degrees of freedom in $KCuF_3$*. *Phys. Rev. Lett.* **88**, 106403.

Paolasini, L., Vettier, C., de Bergevin, F., Yakhou, F., Mannix, D., Stunault, A., Neubeck, W., Altarelli, M., Fabrizio, M., Metcalf, P. & Honig, J. (1999). *Orbital occupancy order in V_2O_3: resonant X-ray scattering results*. *Phys. Rev. Lett.* **82**, 4718–4722.

Partzsch, S., Wilkins, S. B., Schierle, E., Hamann-Borrero, J. E., Wadati, H., Soltwisch, V., Hill, J. P., Weschke, E., Souptel, D., Buchner, B. & Geck, J. (2012). *Resonant soft X-ray scattering studies of multiferroic YMn_2O_5*. *Eur. Phys. J. Spec. Top.* **208**, 133–140.

Platzman, P. M. & Tzoar, N. (1970). *Magnetic scattering of X-rays from electrons in molecules and solids*. *Phys. Rev. B*, **2**, 3556–3559.

Princep, A. J., Mulders, A. M., Staub, U., Scagnoli, V., Nakamura, T., Kikkawa, A., Lovesey, S. W. & Balcar, E. (2011). *Triakontadipole and high-order dysprosium multipoles in the antiferromagnetic phase of DyB_2C_2*. *J. Phys. Condens. Matter*, **23**, 266002.

Renevier, H., Joly, Y., García, J., Subías, G., Proietti, M. G., Hodeau, J. L. & Blasco, J. (2001). *Diffraction anomalous fine structure of forbidden Bragg reflections: charge localization and structure of the octahedral site in magnetite*. *J. Synchrotron Rad.* **8**, 390–392.

Rogalev, A., Wilhelm, F., Jaouen, N., Goulon, J. & Kappler, J.-P. (2006). *X-ray magnetic circular dichroism: historical perspective and recent highlights*. *Lecture Notes in Physics*, Vol. 697, pp. 71–89. Heidelberg: Springer.

Schütz, G., Wagner, W., Wilhelm, W., Kenle, P., Zeller, R., Frahm, R. & Materlik, G. (1987). *Absorption of circularly polarized X-rays in iron*. *Phys. Rev. Lett.* **58**, 737–740.

Seideman, T. (1990). *The liquid-crystalline blue phases*. *Rep. Prog. Phys.* **53**, 659–705.

Sirotin, Y. & Shaskolskaya, M. P. (1982). *Fundamentals of Crystal Physics*. Moscow: Mir.

Strange, P. (1994). *Magnetic absorption dichroism and sum rules in itinerant magnets*. *J. Phys. Condens. Matter*, **6**, L491–L495.

Subías, G., García, J., Blasco, J., Herrero-Martín, J., Sánchez, M. C., Orna, J. & Morellón, L. (2012). *Structural distortion, charge modulation and local anisotropies in magnetite below the Verwey transition using resonant X-ray scattering*. *J. Synchrotron Rad.* **19**, 159–173.

Tanaka, Y., Collins, S. P., Lovesey, S. W., Matsumami, M., Moriwaki, T. & Shin, S. (2010). *Determination of the absolute chirality of tellurium using resonant diffraction with circularly polarized X-rays*. *J. Phys. Condens. Matter*, **22**, 122201.

Tanaka, Y., Kojima, T., Takata, Y., Chainani, A., Lovesey, S. W., Knight, K. S., Takeuchi, T., Oura, M., Senba, Y., Ohashi, H. & Shin, S. (2010). *Determination of structural chirality of berlinite and quartz using resonant X-ray diffraction with circularly polarized X-rays*. *Phys. Rev. B*, **81**, 144104.

Tanaka, Y., Takeuchi, T., Lovesey, S. W., Knight, K. S., Chainani, A., Takata, Y., Oura, M., Senba, Y., Ohashi, H. & Shin, S. (2008). *Right handed or left handed? Forbidden X-ray diffraction reveals chirality*. *Phys. Rev. Lett.* **100**, 145502.

Templeton, D. H. & Templeton, L. K. (1980). *Polarized X-ray absorption and double refraction in vanadyl bisacetylacetonate*. *Acta Cryst.* A**36**, 237–241.

Templeton, D. H. & Templeton, L. K. (1982). *X-ray dichroism and polarized anomalous scattering of the uranyl ion*. *Acta Cryst.* A**38**, 62–67.

Templeton, D. H. & Templeton, L. K. (1985). *Tensor X-ray optical properties of the bromate ion*. *Acta Cryst.* A**41**, 133–142.

Templeton, D. H. & Templeton, L. K. (1986). *X-ray birefringence and forbidden reflections in sodium bromate*. *Acta Cryst.* A**42**, 478–481.

Thole, B. T., Carra, P., Sette, F. & van der Laan, G. (1992). *X-ray circular dichroism as a probe of orbital magnetization*. *Phys. Rev. Lett.* **68**, 1943–1946.

Thole, B. T., van der Laan, G. & Sawatzky, G. (1986). *Strong magnetic dichroism predicted in the $M_{4,5}$ X-ray absorption spectra of magnetic rare-earth materials*. *Phys. Rev. Lett.* **55**, 2086–2088.

Tonnere, J.-M. (1996). *X-ray magnetic scattering*. In *Magnetism and Synchrotron Radiation. Lectures Notes*, edited by E. Beaurepaire, B. Carriere & J.-P. Kappler, pp. 245-273. Mittelwihr: Les Editions de Physique.

Veenendaal, M. van (2003). *Resonant X-ray magnetic scattering at nonmagnetic ions*. *Phys. Rev. B*, **67**, 134112.

Vettier, C. (2001). *Resonant X-ray scattering in transition metal and rare-earth materials*. *J. Electron Spectrosc. Relat. Phenom.* **117**, 113–128.

Vettier, C. (2012). *Resonant elastic X-ray scattering: Where from? Where to?* *Eur. Phys. J. Spec. Top.* **208**, 3–14.

Walker, H. C., McEwen, K. A., McMorrow, D. F., Bleckmann, M., Lee, J. G. P. S., Iga, F. & Mannix, D. (2009). *X-ray resonant scattering study of the structural and magnetic transitions in PrB_6*. *Phys. Rev. B*, **79**, 054402.

Wright, D. C. & Mermin, N. D. (1989). *Crystalline liquids: the blue phases*. *Rev. Mod. Phys.* **61**, 385–432.