

## 1.11. TENSORIAL PROPERTIES OF LOCAL CRYSTAL SUSCEPTIBILITIES

## 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  $f_{ij}^{\text{mag}}$ , 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  $f^{\text{mag}}$  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)

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

$$B_{ijk} = \epsilon_{ijk} - [\epsilon_{ilk}k'_l k'_j - \epsilon_{jlk}k_l k'_i + \frac{1}{2}\epsilon_{ijl}(k'_l k_k + k_l k'_k) - \frac{1}{2}[\mathbf{k} \times \mathbf{k}']_i \delta_{jk} - \frac{1}{2}[\mathbf{k} \times \mathbf{k}']_j \delta_{ik}]/k^2, \quad (1.11.5.2)$$

where  $\epsilon_{ijk}$  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

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

with vectors  $\mathbf{A}$  and  $\mathbf{B}$  given by

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

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

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  $\sigma$ -polarized, *i.e.* the polarization vector is perpendicular to the scattering plane. If due to the orientation of the analysing crystal only the  $\sigma$ -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  $\sigma \rightarrow \pi$  scattering channel.

## 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

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

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

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)

$$\exp(i\mathbf{k} \cdot \mathbf{r}_p) \approx 1 + i\mathbf{k} \cdot \mathbf{r}_p + \frac{1}{2}(i\mathbf{k} \cdot \mathbf{r}_p)^2 + \dots \quad (1.11.6.1)$$

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

$$f_{jk}^{\text{res}} = \sum_c p_a \frac{m\omega_{ca}^3}{\omega} \left\{ \frac{\langle a | R_j | c \rangle \langle c | R_k | a \rangle}{E_a - E_c + \hbar\omega - i\Gamma/2} + \frac{i}{2} \left[ \frac{\langle a | R_j | c \rangle \langle c | R_k R_l R_j | a \rangle}{E_a - E_c + \hbar\omega - i\Gamma/2} - \frac{\langle a | R_j R_l R_j | c \rangle \langle c | R_k | a \rangle}{E_a - E_c + \hbar\omega - i\Gamma/2} \right] + \frac{1}{4} \frac{\langle a | R_j R_l R_l | c \rangle \langle c | R_k R_m R_m | a \rangle}{E_a - E_c + \hbar\omega - i\Gamma/2} \right\} \quad (1.11.6.2)$$

$$= D_{jk} + \frac{i}{2} I_{jkl} k_l - \frac{i}{2} I_{kjl} k'_l + \frac{1}{4} Q_{jklm} k_m k'_l, \quad (1.11.6.3)$$

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 (Sirotnin & Shaskolskaya, 1982) as

$$A_{i_1 \dots i_n} = \gamma r_{i_1 k_1} \dots r_{i_n k_n} A_{k_1 \dots k_n}, \quad (1.11.6.4)$$

where the coefficients  $\gamma = \pm 1$  depend on the kind of tensor (see Table 1.11.6.1) and  $r_{i_1 k_1}$  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,

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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)

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

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

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

and

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

$p'_a = p_a/[\omega - \omega_{ca} - i\Gamma/(2\hbar)]$  and  $p'_a = p_a/[\omega - \omega_{ca} - i\Gamma/(2\hbar)]$ ;  $p_a$  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  $p_a = p_a$  and  $\langle \bar{a}|R_j|\bar{c}\rangle = \langle c|R_k^s|a\rangle$ ; 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)

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

$$\begin{aligned} &= \frac{i}{8} \sum_{ac} \frac{m\omega_{ca}^3}{\hbar\omega} \{ I_{jkl}^{++}(k_l - k'_l) + I_{jkl}^{--}(k_l - k'_l) \\ &\quad + I_{jkl}^{+-}(k_l + k'_l) + I_{jkl}^{-+}(k_l + k'_l) \}, \end{aligned} \quad (1.11.6.9)$$

where

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

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  $\pm$  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  $\text{Cr}_2\text{O}_3$  (Goulon *et al.*, 2002, 2003), and it can be associated with a toroidal moment in a medium possessing magnetoelectric properties. The symmetry properties of magnetoelectric tensors are described well by Sirotni & 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

$$f_{jk}^{qq} = \frac{1}{4} Q_{jklm} k'_l k_m \quad (1.11.6.11)$$

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

$$Q_{jklm} = \sum_{ac} p_a \frac{m\omega_{ca}^3}{\hbar\omega} \frac{\langle a|R_j R_l|c\rangle\langle c|R_k R_m|a\rangle}{\omega - \omega_{ca} - i(\Gamma/2\hbar)}. \quad (1.11.6.12)$$

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

$$Q_{jklm} = Q_{jikm} = Q_{jlmk}. \quad (1.11.6.13)$$

We can define

$$Q_{jklm} = Q_{jklm}^+ + Q_{jklm}^- \quad (1.11.6.14)$$

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

$$\begin{aligned} Q_{jklm}^\pm &= \frac{1}{4} \sum_a (p'_a \pm p'_a) \{ \langle a|R_j R_l|c\rangle\langle c|R_k R_m|a\rangle \\ &\quad \pm \langle a|R_k R_m|c\rangle\langle c|R_j R_l|a\rangle \}. \end{aligned} \quad (1.11.6.15)$$

We see that  $Q_{jklm}^-$  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

$$f_{jk}^{\text{res}} = D_{jk}^+ + iI_{jkl}^+(k'_l - k_l) + iI_{jkl}^-(k'_l + k_l) + Q_{jklm}^+ k'_l k_m + \dots, \quad (1.11.6.16)$$

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  $Q_{jklm}^+$  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),  $D_{jk}$ ,  $I_{jkl}^+$ ,  $I_{jkl}^-$ ,  $Q_{jklm}$ , 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  $f_{jm}^{\text{res}}$  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

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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 an 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  $Q_{jkm}$  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 (Sirotnin & 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  $I_{jkl}^-$ , 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),

$$I_{ijk}^+ = (t_{ijk} + t_{jik})/2, \quad (1.11.6.17)$$

$$I_{ijk}^- = (t_{ijk} - t_{jik})/2, \quad (1.11.6.18)$$

where

$$t_{ijk} = -\frac{1}{2}I_{ijk}^-. \quad (1.11.6.19)$$

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  $I_{ijk}^+$ :

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

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

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

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:

$$I_{123}^- + I_{231}^- + I_{312}^- = 0. \quad (1.11.6.22)$$

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 Sirotnin & Shaskolskaya (1982) and Nye (1985)].

Let us consider two examples, ZnO and anatase, TiO<sub>2</sub>, where the dipole–dipole contributions to forbidden reflections vanish, whereas both the symmetric and antisymmetric dipole–quadrupole terms are in principle 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 3*m* symmetry of the atomic positions imposes the following restrictions on  $t_{ijk}$ :

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

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

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

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

where  $e_{15}$ ,  $e_{31}$ ,  $e_{22}$ ,  $e_{33}$  are energy-dependent complex tensor elements [keeping the notations by Sirotnin & 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

$$I_{131}^+ = I_{232}^+ = (e_{15} + e_{31})/2, \quad (1.11.6.27)$$

$$I_{222}^+ = -I_{121}^+ = -I_{112}^+ = e_{22}, \quad (1.11.6.28)$$

$$I_{113}^+ = I_{223}^+ = e_{15}, \quad (1.11.6.29)$$

$$I_{333}^+ = e_{33} \quad (1.11.6.30)$$

and

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

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

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symmetry; in ZnO, the local coordinations of the Zn positions are only approximately tetrahedral.

In the anatase structure of TiO<sub>2</sub>, 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]:

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

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

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

$$I_{131}^+ = -I_{232}^+ = (e_{15} + e_{31})/2, \quad (1.11.6.34)$$

$$I_{113}^+ = -I_{223}^+ = e_{15} \quad (1.11.6.35)$$

and

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

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  $\partial f_{ij}^{dd}/\partial x_k$ , 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:

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

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

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

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

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;  $o_t \leq 1$  is a site-occupancy factor, and  $W^{tu}(\mathbf{H})$  is the Debye–Waller temperature factor. The tensors of the atomic factors,  $D_{jm}^{tu}$ ,  $I_{jmn}^{tu+}$ ,  $I_{jmn}^{tu-}$ ,  $Q_{jmntp}^{tu}$ , 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  $p'_a \neq p'_a$  if  $p_a \neq p_a$  and/or  $\omega_{ca} \neq \omega_{ca}$  (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  $\epsilon_{jmk}$  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

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

$C_{0s}$ ,  $C_{1s}$  and  $C_{2s}$  are energy-dependent coefficients referring to the  $s$ th 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

## 1.11. TENSORIAL PROPERTIES OF LOCAL CRYSTAL SUSCEPTIBILITIES

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)

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

and

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

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

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

with

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

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  $\Gamma_x/\Gamma$  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 XM $\chi$ D (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

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

and

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

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):

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

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

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 & McMorro (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)

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

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.

# 1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

For  $p = 0$ :

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

For  $p = 1$ :

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

For  $p = 2$ :

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

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

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:

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

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

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

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 ( $1 \rightarrow$  dipole,  $2 \rightarrow$  quadrupole,  $3 \rightarrow$  octupole,  $4 \rightarrow$  hexadecapole) and with the same  $T$  and  $P$  properties. Note that  $P$ -odd  $E1E2$

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

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).

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,  $\Gamma$ , 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 (Tonnerre, 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.