

## 1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

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

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

$C_{0s}$ ,  $C_{1s}$  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

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):

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

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

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)

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

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.