

## 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 Sirotnin & 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:

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

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

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

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

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,  $D_{jm}^{tu}$ ,  $I_{jmn}^{tu+}$ ,  $I_{jmn}^{tu-}$ ,  $Q_{jmn}^{tu}$ , 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