

1.11. TENSORIAL PROPERTIES OF LOCAL CRYSTAL SUSCEPTIBILITIES

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, TiO₂, 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 TiO₂, 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 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

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

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