

1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

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 (XM χ D) 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 :

$$\chi_{jk}(\mathbf{r}) = R_{jm}^g R_{nk}^{gT} \chi_{mn}(\mathbf{r}^g), \quad (1.11.2.1)$$

where R_{jk}^g is the matrix of the point operation (rotation or mirror reflection), $r_j^g = R_{kj}^g(r_k - a_k^g)$, and a_k^g 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 :

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

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:

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

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 ,

$$R_{jk}^c = R_{jk}^{cT} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (1.11.2.4)$$

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 $0k\ell$

$$F_{jk}(0k\ell) = \exp(-i\pi\ell) R_{jm}^c R_{nk}^{cT} F_{mn}(0k\ell). \quad (1.11.2.5)$$

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 $x \rightarrow -x$ 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

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

1.11. TENSORIAL PROPERTIES OF LOCAL CRYSTAL SUSCEPTIBILITIES

Table 1.11.2.1. The indices ℓ of the screw-axis/glide-plane forbidden reflections ($n = 0, \pm 1, \pm 2, \dots$) 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	$3n \pm 1$	F_1	$\mp iF_1$	F_2	$\pm iF_2$	II
3_2	$3n \pm 1$	F_1	$\pm iF_1$	F_2	$\mp iF_2$	II
4_1	$4n \pm 1$	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	$4n \pm 1$	0	0	F_1	$\mp iF_1$	I
4_3	$4n + 2$	F_1	F_2	0	0	II
6_1	$6n \pm 1$	0	0	F_1	$\pm iF_1$	I
6_1	$6n \pm 2$	F_1	$\pm iF_1$	0	0	II
6_1	$6n + 3$	0	0	0	0	I
6_2	$3n \pm 1$	F_1	$\pm iF_1$	0	0	II
6_3	$2n + 1$	0	0	0	0	I
6_4	$3n \pm 1$	F_1	$\mp iF_1$	0	0	II
6_5	$6n \pm 1$	0	0	F_1	$\mp iF_1$	I
6_5	$6n \pm 2$	F_1	$\mp iF_1$	0	0	II
6_5	$6n + 3$	0	0	0	0	I
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:

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

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

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

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

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

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 $a_2(x, y, z)$:

$P2_3, F2_3, I2_3$:

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

$P2_13, I2_13$:

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

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

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