

1.11. Tensorial properties of local crystal susceptibilities

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1.11.1. Introduction

The tensorial characteristics of macroscopic physical properties (as described in Chapters 1.3, 1.4 and 1.6–1.8 of this volume) are determined by the crystal point group, whereas the symmetry of local crystal properties, such as atomic displacement parameters (Chapter 1.9) or electric field gradient tensors (Section 2.2.15) are regulated by the crystal space group. In the present chapter, we consider further examples of the impact of symmetry on local physical properties, particularly both symmetry and physical phenomena that allow and restrict forbidden reflections excited at radiation energies close to X-ray absorption edges of atoms, and reflections caused by magnetic scattering.

We begin with the X-ray dielectric susceptibility, which expresses the response of crystalline matter to an incident X-ray wave characterized by its energy (frequency), polarization and wavevector. The response is a polarization of the medium, finally resulting in a scattered wave with properties generally different from the initial ones. Thus, the dielectric susceptibility plays the role of a scattering amplitude, which relates the scattered wave to the incident wave. This is the basis of the different approaches to X-ray diffraction theories presented in Chapters 1.2 and 5.1 of *International Tables for Crystallography* Volume B (2008). Here, we consider only elastic scattering, *i.e.* the energies of the incident and scattered waves are identical, and the X-ray susceptibility is assumed to comply with the periodicity of the crystalline matter.

It is important that the dielectric susceptibility is (i) a local crystal property and (ii) a tensor physical property, because it relates the polarization vectors of the incident and scattered radiation. Consequently, the symmetry of the tensor is determined by the symmetry of the crystal space group, rather than by that of the point group as in conventional optics. In the vast majority of X-ray applications, this tensor can reasonably be assumed to be given by the product of the unit tensor and a scalar susceptibility, which is proportional to the electron density plus exclusively energy-dependent dispersion corrections as considered in Section 4.2.6 of *International Tables for Crystallography* Volume C (2004). As a result of atomic wavefunction distortions caused by neighbouring atoms, these scalar dispersion corrections can also become anisotropic tensors, namely in the close vicinity (usually less than about 50 eV) of absorption edges of elements. For heavy elements, the anisotropy of the tensor atomic factor can exceed $20 e \text{ atom}^{-1}$. Appropriate references to detailed descriptions of the phenomenon can be found in Brouder (1990), Materlik *et al.* (1994) and in Section 4.2.6 of Volume C (2004).

However, even if the anisotropy of the atomic factor is small, it can be crucial for some effects, for instance the excitation of so-called ‘forbidden’ reflections, which vanish in absence of anisotropy. Indeed, the crystal symmetry imposes strong restrictions on the indices of possible (‘allowed’) reflections. The systematic reflection conditions for the different space groups and for special atomic sites in the unit cell are listed in *International Tables for Crystallography* Volume A (Hahn, 2005). The resulting extinctions are due to (i) the translation symmetry of the non-

primitive Bravais lattices, (ii) the symmetry elements of the space group (glide planes and/or screw axes) and (iii) special sites. The first kind cannot be violated. The other extinctions are obtained if the atomic scattering factor (as the Fourier transform of an independent atom/ion with spherically symmetric electron-density distribution) is an element-specific scalar that depends only on the scattering-vector length and the dispersion corrections. Then the intensities of extinct reflections generally vanish. These reflections are ‘forbidden’, but for different physical reasons not all of their intensities are necessarily strictly zero. Such reflections can appear owing to an asphericity of (i) an atomic electron-density distribution caused by chemical bonding and/or (ii) atomic vibrations (Dawson, 1975) if the atom in question occupies a special site.

In contrast, an anisotropy of the atomic factor affects all reflections and can therefore violate general extinction rules related to glide planes and/or screw axes, *i.e.* symmetry elements with translation components, in nonsymmorphic space groups. Even a very small X-ray anisotropy can be quantitatively studied with this type of forbidden reflections, and yield information about electronic states of crystals or partial structures of resonant scatterers. This was first recognized by Templeton & Templeton (1980), and a detailed theory was developed only a few years later (Dmitrienko, 1983, 1984). The excitation of forbidden reflections caused by anisotropic anomalous scattering was first observed in an NaBrO₃ crystal (Templeton & Templeton, 1985, 1986) and then studied for Cu₂O (Eichhorn & Kirfel, 1988), TiO₂ and MnF₂ (Kirfel & Petcov, 1991), and for many other compounds with different crystal symmetries. Within the dipole approximation, a systematic compilation of ‘forbidden’ reflection properties for all relevant space groups up to tetragonal symmetry and an application to partial-structure analysis followed (Kirfel *et al.*, 1991; Kirfel & Petcov, 1992; Kirfel & Morgenroth, 1993; Morgenroth *et al.*, 1994). Today, there are numerous surveys devoted to this well developed subject, and further details, applications and references can be found therein (Belyakov & Dmitrienko, 1989; Carra & Thole, 1994; Hodeau *et al.*, 2001; Lovesey *et al.*, 2005; Dmitrienko *et al.*, 2005; Altarelli, 2006; Collins *et al.*, 2007; Collins & Bombardi, 2010; Finkelstein & Dmitrienko, 2012). Forbidden reflections of the last type have also been observed (well before corresponding X-ray studies) in diffraction of Mössbauer radiation (Belyakov & Aivazyan, 1969; Belyakov, 1975; Champeney, 1979) and, at optical wavelengths, in the blue phases of chiral liquid crystals (Belyakov & Dmitrienko, 1985; Wright & Mermin, 1989; Seideman, 1990; Crooker, 2001). Similar phenomena have also been reported to exist in chiral smectic liquid crystals (Gleeson & Hirst, 2006; Barois *et al.*, 2012) and, considering neutron diffraction, in crystals with local anisotropy of the magnetic susceptibility (Gukasov & Brown, 2010). All these latter findings are, however, beyond the scope of this chapter.

X-ray polarization phenomena similar to those in visible optics and spectroscopy (birefringence, linear and circular dichroism, the Faraday rotation) have been discussed since the beginning of the 20th century (Hart & Rodrigues, 1981; Templeton & Templeton, 1980, 1982). Experimental studies and applications

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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

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