1.11. Tensorial properties of local crystal susceptibilities

BY V. E. DMITRIENKO, A. KIRFEL AND E. N. OVCHINNIKOVA

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 2.2.2.15) 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 one. 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 elemental factors. For heavy elements, the anisotropy of the 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 elemental factors. For heavy elements, the anisotropy of the 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 elemental factors. For heavy elements, the anisotropy of the 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 elemental factors. For heavy elements, the anisotropy of the 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 elemental factors. For heavy elements, the anisotropy of the 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 elemental factors.

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...
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 \( G \):

\[
\chi_{ij}(\mathbf{r}) = R_{ik}^{g} R_{jk}^{T} \chi_{mn}(\mathbf{r}'),
\]

where \( R_{ik}^{g} \) is the matrix of the point operation (rotation or mirror reflection), \( r_{k}' = R_{ik}^{g}(r_{k} - a_{k}^{g}) \), 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 \( g \):

\[
\chi_{ij}(\mathbf{r}) = N^{-1} \sum_{g \in G} R_{ik}^{g} R_{jk}^{T} \alpha_{mn}(\mathbf{r}'),
\]

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:

\[
F_{jk}(\mathbf{H}) = -\frac{\pi V}{r_{0} \lambda^{2}} X_{jk}(\mathbf{H}) \equiv -\frac{\pi V}{r_{0} \lambda^{2}} \int \chi_{jk}(\mathbf{r}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}) \, d\mathbf{r},
\]

(1.11.2.3)

where \( r_{0} = e^{2}/me^{2} \) is the classical electron radius, \( \lambda \) 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 \( x, y, z + \frac{1}{2}c \). The corresponding matrix of this symmetry operation changes the sign of \( x \),

\[
R_{jk}^{c} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},
\]

(1.11.2.4)

and the translation vector into \( \mathbf{a'} = (0, 0, \frac{1}{2}c) \). 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 \( 0k\ell \)

\[
F_{jk}(0k\ell) = \exp(-i\pi\ell c) R_{jk}^{c} F_{mn}(0k\ell).
\]

(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 \( \ell \), hence \( F(0k\ell) \) vanishes. This is the well known conventional extinction rule for a 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

\[
F_{jk}(0k\ell; \ell = 2n + 1) = \begin{pmatrix} 0 & F_{1} & F_{2} \\ F_{1} & 0 & 0 \\ F_{2} & 0 & 0 \end{pmatrix}.
\]