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 (XMχD) 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:

$$\chi_{jk}(\mathbf{r}) = R^g_{jm} R^{gT}_{nk} \chi_{mn}(\mathbf{r}^g), \tag{1.11.2.1}$$

where R^g_{jk} is the matrix of the point operation (rotation or mirror reflection), $r^g_j = R^g_{kj}(r_k - a^g_k)$, and a^g_k 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:

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

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:

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

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,

$$R^c_{jk} = R^{cT}_{jk} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{1.11.2.4}$$

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 $0k\ell$

$$F_{jk}(0k\ell) = \exp(-i\pi\ell) R^c_{jm} R^{cT}_{nk} F_{mn}(0k\ell). \tag{1.11.2.5}$$

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 $x \to -x$ 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

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