

## 1.11. TENSORIAL PROPERTIES OF LOCAL CRYSTAL SUSCEPTIBILITIES

 Table 1.11.2.1. The indices  $\ell$  of the screw-axis/glide-plane forbidden reflections ( $n = 0, \pm 1, \pm 2, \dots$ ) and independent components of their tensorial structure factors  $F_{jk}^H$ 

Other components:  $F_{yy}^H = -F_{xx}^H$ ,  $F_{zz}^H = 0$ ,  $F_{jk}^H = F_{kj}^H$ . 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	$\ell$	$F_{xx}^H$	$F_{xy}^H$	$F_{xz}^H$	$F_{yz}^H$	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  $\ell$ . 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  $00\ell$ ;  $\ell = 2n + 1$  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

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