1.11. TENSORIAL PROPERTIES OF LOCAL CRYSTAL SUSCEPTIBILITIES

Table 1.11.2.1. *The indices ℓ of the screw-axis/glide-plane forbidden reflections $(n = 0, \pm 1, \pm 2, \ldots)$ 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	
6_2	$3n\pm 1$	F_1	$\pm iF_1$	0	0	II
6_3	$2n+1$	0	0	0	0	
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	
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:

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

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

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

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

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

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 $a_2(x, y, z)$:

$P23$, $F23$, $I23$:

$$a_1(x, y, z) = a_1(x, \bar{y}, \bar{z}) = a_1(\bar{x}, \bar{y}, z) = a_1(\bar{x}, y, \bar{z}),$$
$$a_2(x, y, z) = a_2(x, \bar{y}, \bar{z}) = -a_2(\bar{x}, \bar{y}, z) = -a_2(\bar{x}, y, \bar{z}).$$
$$(1.11.2.10)$$

$P2_13$, $I2_13$:

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

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

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

Table 1.11.2.2. *The indices of the forbidden reflections and corresponding tensors of structure factors $F_{jk}(hk\ell)$ for the cubic space groups* $(n = 0, \pm 1, \pm 2, \ldots)$

Space group	Indices of reflections	Expressions for $F_{jk}(hk\ell)$ and additional restrictions
$P2_13$	00ℓ: $\ell = 2n+1$	(1.11.2.23)
$Pn\bar{3}$	$0k\ell$: $\ell = 2n+1$	(1.11.2.6); $F_2 = 0$ for 00ℓ
$Fd\bar{3}$	$0k\ell$: $k, \ell = 2n, k + \ell = 4n+2$	(1.11.2.6); $F_2 = 0$ for 00ℓ
$Pa\bar{3}$	$0k\ell$: $k = 2n+1$	(1.11.2.6); $F_2 = 0$ for $0k0$
$Ia\bar{3}$	$0k\ell$: $k, \ell = 2n+1$	(1.11.2.6)
$P4_232$	00ℓ: $\ell = 2n+1$	(1.11.2.24)
$F4_132$	00ℓ: $\ell = 4n+2$	(1.11.2.24)
$P4_332$	00ℓ: $\ell = 4n \pm 1$	(1.11.2.23); $F_2 = \mp iF_1$
	00ℓ: $\ell = 4n+2$	(1.11.2.24)
$P1_332$	00ℓ: $\ell = 4n \pm 1$	(1.11.2.23); $F_2 = \pm iF_1$
	00ℓ: $\ell = 4n+2$	(1.11.2.24)
$I4_132$	00ℓ: $\ell = 4n+2$	(1.11.2.24)
$P\bar{4}3n$	$hh\ell$: $\ell = 2n+1$	(1.11.2.22); $F_2 = 0$ for 00ℓ, $F_1 = F_2 = 0$ for hhh
$F\bar{4}3c$	$hh\ell$: $h, \ell = 2n+1$	(1.11.2.22); $F_1 = F_2 = 0$ for hhh
$I\bar{4}3d$	$hh\ell$: $2h + \ell = 4n+2$	(1.11.2.22); $F_2 = 0$ for 00ℓ, $F_1 = F_2 = 0$ for hhh
$Pn\bar{3}n$	$hh\ell$: $\ell = 2n+1$	(1.11.2.22); $F_1 = F_2 = 0$ for hhh
	$0k\ell$: $k + \ell = 2n+1$	(1.11.2.6); $F_1 = F_2 = 0$ for 00ℓ
$Pm\bar{3}n$	$hh\ell$: $\ell = 2n+1$	(1.11.2.22); $F_1 = F_2 = 0$ for hhh
$Pn\bar{3}m$	$0k\ell$: $k + \ell = 2n+1$	(1.11.2.6); $F_2 = 0$ for 00ℓ
$Fm\bar{3}c$	$hh\ell$: $h, \ell = 2n+1$	(1.11.2.22); $F_1 = F_2 = 0$ for hhh
$Fd\bar{3}m$	$0k\ell$: $k, \ell = 2n, k + \ell = 4n+2$	(1.11.2.6); $F_2 = 0$ for 00ℓ
$Fd\bar{3}c$	$0k\ell$: $k, \ell = 2n, k + \ell = 4n+2$	(1.11.2.6); $F_2 = 0$ for 00ℓ
	$hh\ell$: $h, \ell = 2n+1$	(1.11.2.22); $F_1 = F_2 = 0$ for hhh
$Ia\bar{3}d$	$0k\ell$: $k, \ell = 2n+1$	(1.11.2.6); $F_2 = -F_1$ for $0kk$
	$hh\ell$: $4h + \ell = 4n+2$	(1.11.2.22); hhh: $F_1 = F_2 = 0$, $F_2 = 0$ for 00ℓ

$Pn\bar{3}$: (1.11.2.10) and

$$a_i(x, y, z) = a_i(\tfrac{1}{2} - x, \tfrac{1}{2} - y, \tfrac{1}{2} - z). \qquad (1.11.2.13)$$

$Fd\bar{3}$: (1.11.2.10) and

$$a_i(x, y, z) = a_i(\tfrac{1}{4} - x, \tfrac{1}{4} - y, \tfrac{1}{4} - z). \qquad (1.11.2.14)$$

$Pa\bar{3}$, $Ia\bar{3}$: (1.11.2.11) and (1.11.2.12).
$P432$, $F432$, $I432$: (1.11.2.10) and

$$a_i(x, y, z) = a_i(\bar{x}, \bar{z}, \bar{y}). \qquad (1.11.2.15)$$

$P4_232$: (1.11.2.10) and

$$a_i(x, y, z) = a_i(\tfrac{1}{2} - x, \tfrac{1}{2} - z, \tfrac{1}{2} - y). \qquad (1.11.2.16)$$

$F4_132$, $P4_332$, $I4_132$: (1.11.2.11) and

$$a_i(x, y, z) = a_i(\tfrac{1}{4} - x, \tfrac{1}{4} - z, \tfrac{1}{4} - y). \qquad (1.11.2.17)$$

$P4_132$: (1.11.2.11) and

$$a_i(x, y, z) = a_i(\tfrac{3}{4} - x, \tfrac{3}{4} - z, \tfrac{3}{4} - y). \qquad (1.11.2.18)$$

$P\bar{4}3m$, $F\bar{4}3m$, $I\bar{4}3m$: (1.11.2.10) and

$$a_i(x, y, z) = a_i(x, z, y). \qquad (1.11.2.19)$$

$P\bar{4}3n$, $F\bar{4}3c$: (1.11.2.10) and

$$a_i(x, y, z) = a_i(\tfrac{1}{2} + x, \tfrac{1}{2} + z, \tfrac{1}{2} + y). \qquad (1.11.2.20)$$

$I\bar{4}3d$: (1.11.2.11) and

$$a_i(x, y, z) = a_i(\tfrac{1}{4} + x, \tfrac{1}{4} + z, \tfrac{1}{4} + y). \qquad (1.11.2.21)$$

$Pm\bar{3}m$, $Fm\bar{3}m$, $Im\bar{3}m$: (1.11.2.10), (1.11.2.12) and (1.11.2.19).
$Pn\bar{3}n$: (1.11.2.10), (1.11.2.13) and (1.11.2.15).
$Pm\bar{3}n$, $Fm\bar{3}c$: (1.11.2.10), (1.11.2.12) and (1.11.2.20).
$Pn\bar{3}m$: (1.11.2.10), (1.11.2.13) and (1.11.2.19).

$Fd\bar{3}m$: (1.11.2.10), (1.11.2.14) and (1.11.2.19).
$Fd\bar{3}c$: (1.11.2.10), (1.11.2.13) and (1.11.2.20).
$Ia\bar{3}d$: (1.11.2.11), (1.11.2.12) and (1.11.2.21).

For all $a_i(x, y, z)$, the sets of coordinates are chosen here as in *International Tables for Crystallography* Volume A (Hahn, 2005); the first one being adopted if Volume A offers two alternative origins. The expressions (1.11.2.10) or (1.11.2.11) appear for all space groups because all of them are supergroups of $P23$ or $P2_13$.

The tensor structure factors of forbidden reflections can be further restricted by the cubic symmetry, see Table 1.11.2.2. For the glide plane c, the tensor structure factor of $0k\ell$; $\ell = 2n + 1$ reflections is given by (1.11.2.6), whereas for the diagonal glide plane n, it is given by

$$F_{jk}(hh\ell; \ell = 2n+1) = \begin{pmatrix} F_1 & 0 & F_2 \\ 0 & -F_1 & -F_2 \\ F_2 & -F_2 & 0 \end{pmatrix}, \qquad (1.11.2.22)$$

and additional restrictions on F_1 and F_2 can become effective for $k = \ell$ or $h = \ell$. For forbidden reflections of the 00ℓ type, the tensor structure factor is either

$$F_{jk}(00\ell) = \begin{pmatrix} 0 & 0 & F_1 \\ 0 & 0 & F_2 \\ F_1 & F_2 & 0 \end{pmatrix} \qquad (1.11.2.23)$$

or

$$F_{jk}(00\ell) = \begin{pmatrix} F_1 & F_2 & 0 \\ F_2 & -F_1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \qquad (1.11.2.24)$$

see Table 1.11.2.2.

1.11.3. Polarization properties and azimuthal dependence

There are two important properties that distinguish forbidden reflections from conventional ('allowed') ones: non-trivial polarization effects and strong azimuthal dependence of intensity (and sometimes also of polarization) corresponding to the symmetry of the direction of the scattering vector. The azimuthal dependence means that the intensity and polarization properties of the reflection can change when the crystal is rotated around the direction of the reciprocal-lattice vector, *i.e.* they change with the azimuthal angle of the incident wavevector **k** defined relative to the scattering vector. The polarization and azimuthal properties, both mainly determined by symmetry, are two of the most informative characteristics of forbidden reflections. A third one, energy dependence, is determined by physical interactions, electronic and/or magnetic, where the role of symmetry is indirect but nevertheless also important (*e.g.* in splitting of atomic levels *etc.*, see Section 1.11.4).

In the kinematical theory, usually used for weak reflections, one obtains for unpolarized incident radiation the intensity of a conventional reflection as given by

$$I_{\mathbf{H}} = A_{\mathbf{H}}|F(\mathbf{H})|^2 \left(1 + \cos^2 2\theta\right)/2, \qquad (1.11.3.1)$$

where θ is the Bragg angle, $F(\mathbf{H})$ is the scalar structure factor of reflection $\mathbf{H}$, and $A_{\mathbf{H}}$ is a scale factor, which depends on the incident beam intensity, the sample volume, the geometry of diffraction *etc.* (see *International Tables for Crystallography* Volume B), and can be set to $A_{\mathbf{H}} = 1$ hereafter.