

## 1.11. TENSORIAL PROPERTIES OF LOCAL CRYSTAL SUSCEPTIBILITIES

kind of X-ray dichroism is also influenced by the crystal field (Thole *et al.*, 1986; van der Laan *et al.*, 1986).

The coefficients  $C_{0s}$ ,  $C_{1s}$  and  $C_{2s}$  involved in (1.11.6.41) may be represented in terms of spherical harmonics. Using the relations (Berestetskii *et al.*, 1982; Hannon *et al.*, 1988)

$$\begin{aligned} & [\mathbf{e}^* \cdot \mathbf{Y}_{1\pm 1}(\mathbf{k}') \mathbf{Y}_{1\pm 1}^*(\mathbf{k}) \cdot \mathbf{e}] \\ &= \frac{3}{16\pi} [(\mathbf{e}^* \cdot \mathbf{e}) \mp i[\mathbf{e}^* \times \mathbf{e}] \cdot \mathbf{m}_s - (\mathbf{e}^* \cdot \mathbf{m}_s)(\mathbf{e} \cdot \mathbf{m}_s)] \end{aligned} \quad (1.11.6.42)$$

and

$$[\mathbf{e}^* \cdot \mathbf{Y}_{10}(\mathbf{k}') \mathbf{Y}_{10}^*(\mathbf{k}) \cdot \mathbf{e}] = \frac{3}{8\pi} (\mathbf{e}^* \cdot \mathbf{m}_s)(\mathbf{e} \cdot \mathbf{m}_s) \quad (1.11.6.43)$$

for  $L = 1$ ,  $M = \pm 1$  and  $L = 0$ ,  $M = 0$ , respectively, one obtains

$$\begin{aligned} f^{dd} = -\frac{3}{4k} & \left[ (\mathbf{e}^* \cdot \mathbf{e})(F_{11} + F_{1-1}) - i[\mathbf{e}^* \times \mathbf{e}] \cdot \mathbf{m}_s(F_{11} - F_{1-1}) \right. \\ & \left. + (\mathbf{e}^* \cdot \mathbf{m}_s)(\mathbf{e} \cdot \mathbf{m}_s)(2F_{10} - F_{11} - F_{1-1}) \right] \end{aligned} \quad (1.11.6.44)$$

with

$$F_{LM}(\omega) = \sum_{a,c} p_a p_{ac} \frac{\Gamma_x(aMc; EL)}{E_c - E_a - \hbar\omega - i\Gamma/2}, \quad (1.11.6.45)$$

where  $p_a$  is the probability of the initial state  $a$ ,  $p_{ac}$  is that for the transition from state  $a$  to a final state  $c$ , and  $\Gamma_x/\Gamma$  is the ratio of the partial line width of the excited state due to a pure  $2^L$  ( $EL$ ) radiative decay and the width due to all processes, both radiative and non-radiative (for example, the Auger decay).

Magnetic ordering is frequently accompanied by a local anisotropy in the crystal. In this case, both kinds of local anisotropies exist simultaneously and must be taken into account in, for example, XMLD (van der Laan *et al.*, 1986) and XM $\chi$ D (Goulon *et al.*, 2002). In resonant X-ray scattering experiments, simultaneous existence of forbidden reflections provided by spin and orbital ordering (Murakami *et al.*, 1998) as well as magnetic and crystal anisotropy (Ji *et al.*, 2003; Paolasini *et al.*, 2002, 1999) have been observed. The explicit Cartesian form of the tensor atomic factor in the presence of both a magnetic moment and crystal anisotropy has been proposed by Blume (1994). When the symmetry of the atomic site is high enough, *i.e.* the atom lies on an  $n$ -order axis ( $n > 2$ ), then the tensors  $D^+$  and  $D^-$  can be represented as

$$\begin{aligned} D_{jk}^+ = & (z_j z_k - \frac{1}{3} \delta_{jk}) [a_1 + b_1 (\mathbf{z} \cdot \mathbf{m})^2] + c_1 (m_j m_k - \frac{1}{3} m^2 \delta_{jk}) \\ & + d_1 [z_j m_k + z_k m_j - \frac{2}{3} (\mathbf{z} \cdot \mathbf{m}) \delta_{jk}] (\mathbf{z} \cdot \mathbf{m}) \end{aligned} \quad (1.11.6.46)$$

and

$$D_{jk}^- = i \epsilon_{jkl} [a_2 m_l + b_2 z_l (\mathbf{z} \cdot \mathbf{m})], \quad (1.11.6.47)$$

where  $a_i$  and  $b_i$  depend on the energy, and  $\mathbf{z}$  is a unit vector along the symmetry axis under consideration. One can see that the atomic tensor factor is given by a sum of three terms: the first is due to the symmetry of the local crystal anisotropy, the second describes pure magnetic scattering, and the last ('combined') term is induced by interference between magnetic and non-magnetic resonant scattering. This issue was first discussed by Blume (1994) and later in more detail by Ovchinnikova & Dmitrienko (1997, 2000). All the terms can give rise to forbidden reflections, *i.e.* sets of pure resonant forbidden magnetic and non-magnetic reflections can be observed for the same crystal, see Ji *et al.*

(2003) and Paolasini *et al.* (2002, 1999). Only reflections caused by the 'combined' term (Ovchinnikova & Dmitrienko, 1997) have not been observed yet.

Neglecting the crystal field, an explicit form of the fourth-rank tensors describing the quadrupole–quadrupole  $E2E2$  events in magnetic structures was proposed by Hannon *et al.* (1988) and Blume (1994):

$$\begin{aligned} Q_{ijkm}^- = & a_1 \{ \epsilon_{ikl} m_l \delta_{jm} + \epsilon_{jml} m_l \delta_{ik} + \epsilon_{iml} m_l \delta_{jk} + \epsilon_{jkl} m_l \delta_{im} \} \\ & + b_2 \{ \epsilon_{ikl} m_l m_j m_m + \epsilon_{jml} m_l m_i m_k + \epsilon_{iml} m_l m_j m_k \\ & + \epsilon_{jkl} m_l m_i m_m \}, \end{aligned} \quad (1.11.6.48)$$

$$\begin{aligned} Q_{ijkm}^+ = & a_2 \delta_{ij} \delta_{km} + b_2 \{ \delta_{ik} \delta_{jm} + \delta_{im} \delta_{jk} \} \\ & + c_2 \{ \delta_{ik} m_j m_m + \delta_{im} m_j m_k + \delta_{jm} m_i m_k + \delta_{jk} m_i m_m \} \\ & + d_2 \{ \delta_{ij} m_k m_m + \delta_{km} m_i m_j \} + e_2 m_i m_j m_k m_m \\ & + f_2 \{ \epsilon_{ikl} \epsilon_{jmp} m_l m_p + \epsilon_{iml} \epsilon_{jkp} m_l m_p \}. \end{aligned} \quad (1.11.6.49)$$

Then, being convoluted with polarization vectors, the scattering amplitude of the quadrupole transition ( $L = 2$ ) can be written as a sum of 13 terms belonging to five orders of magnetic moments (Hannon *et al.*, 1988; Blume, 1994). The final expression that gives the quadrupole contribution to the magnetic scattering amplitude in terms of individual spin components is rather complicated and can be found, for example, in Hill & McMorro (1996). In the presence of both a magnetic moment and local crystal anisotropy, the fourth-rank tensor describing  $E2E2$  events depends on both kinds of anisotropy and can include the 'combined' part in explicit form, as found by Ovchinnikova & Dmitrienko (2000).

## 1.11.6.6. Tensor atomic factors (spherical tensor representation)

Another representation of the scattering amplitude is widely used in the scientific literature (Hannon *et al.*, 1988; Luo *et al.*, 1993; Carra *et al.*, 1993; Lovesey & Collins, 1996) for the description of resonant multipole transitions. In order to obtain the scattering amplitude and intensity for a resonant process described by some set of spherical tensor components, the tensor that describes the atomic scattering must be contracted by a tensor of the same rank and inversion/time-reversal symmetry which describes the X-ray probe, so that the result would be a scalar. There are well known relations between the components of the atomic factor tensor, both in Cartesian and spherical representations. For the dipole–dipole transition, the resonant scattering amplitude can be written as (Hannon *et al.*, 1988; Collins *et al.*, 2007; Paolasini, 2012; Joly *et al.*, 2012)

$$f^{dd} \sim \sum_{jm} e_j^* e_m D_{jm} = \sum_{p=0}^2 \sum_{q=-p}^p (-1)^{p+q} X_q^{(p)} F_{-q}^{(p)}, \quad (1.11.6.50)$$

where  $D_{jm}$  are the Cartesian tensor components,  $X_q^{(p)}$  depends only on the incident and scattered radiation and the polarization vectors, and  $F_{-q}^{(p)}$  is associated with the tensor properties of the absorbing atom and can be represented in terms of a multipole expansion.

It is convenient to decompose each tensor into its irreducible parts. For example, an  $E1E1$  tensor containing nine Cartesian components can be represented as a sum of three irreducible tensors with ranks  $p = 0$  (one component),  $p = 1$  (three components) and  $p = 2$  (five components). This decomposition is unique.

# 1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

For  $p = 0$ :

$$F_0^{(0)} = \frac{1}{3}(D_{xx} + D_{yy} + D_{zz}). \quad (1.11.6.51)$$

For  $p = 1$ :

$$\begin{aligned} F_0^{(1)} &= \frac{1}{2}(D_{xy} - D_{yx}), \\ F_{\pm 1}^{(1)} &= \mp \frac{1}{2\sqrt{2}}[(D_{yz} - D_{zy} \mp i(D_{xz} - D_{zx})]. \end{aligned} \quad (1.11.6.52)$$

For  $p = 2$ :

$$\begin{aligned} F_0^{(2)} &= D_{zz} - F_0^{(0)}, \\ F_{\pm 1}^{(2)} &= \mp \frac{1}{2}\sqrt{\frac{3}{2}}[(D_{xz} + D_{zx} \mp i(D_{yz} + D_{zy})], \end{aligned} \quad (1.11.6.53)$$

$$F_{\pm 2}^{(2)} = \frac{1}{6}[2D_{xx} - 2D_{yy} \pm i(D_{xy} + D_{yx})]. \quad (1.11.6.54)$$

It follows from (1.11.6.14) that the fourth-rank tensor describing the quadrupole–quadrupole X-ray scattering can also be divided into two parts: the time-reversal part,  $Q_{jklm}^+$ , and the non-time-reversal part,  $Q_{jklm}^-$ . Both can be explicitly represented by (1.11.6.3) and (1.11.6.2), in which all these tensors are parity-even. The explicit form of the fourth-rank tensors is suitable for the analysis of possible effects in resonant X-ray absorption and scattering. Nevertheless, sometimes the following representation of the scattering amplitude as a product of spherical tensors is preferable:

$$f^{qq} = \frac{1}{4} \sum_{ijmn} e_i^* e_m k_j' k_n Q_{ijmn} = \sum_{p=0}^4 \sum_{q=-p}^p (-1)^{p+q} X_q^{(p)} F_{-q}^{(p)}. \quad (1.11.6.55)$$

Here, the dipole–quadrupole tensor atomic factor given by (1.11.6.10) is represented by a sum over several tensors with different symmetries. All tensors are parity-odd, but the tensors  $I_{jml}^-$  and  $I_{jml}^+$  are also non-time-reversal. The scattering amplitude corresponding to the dipole–quadrupole resonant X-ray scattering can be represented as

$$\begin{aligned} f^{dq} &= \frac{1}{2} i \sum_{ijm} e_i^* e_j (k_m I_{ijm} - k_m' I_{ijm}) \\ &= \sum_{p=1}^3 \sum_{q=-p}^p (-1)^{p+q} (X_q^{(p)} F_{-q}^{(p)} + \bar{X}_q^{(p)} \bar{F}_{-q}^{(p)}). \end{aligned} \quad (1.11.6.56)$$

The explicit form of  $F_{-q}^{(p)}$  can be found in Marri & Carra (2004). Various parts of  $F_{-q}^{(p)}$  possess different symmetry with respect to the reversal of space  $P$  and time  $T$ .

The spherical representation of the tensor atomic factor allows one to analyse its various components, as they possess different symmetries with respect to rotations or space and time inversion. For each  $p$ ,  $F_{-q}^{(p)}$  is related to a specific term of the multipole expansion of the system. Multipole expansions of electric and magnetic fields generated by charges and permanent currents are widely used in characterizing the electromagnetic state of a physical system (Berestetskii *et al.*, 1982). The transformation rules for electric and magnetic multipoles of both parities under space inversion and time reversal are of great importance for electromagnetic effects in crystals. The correspondence between the  $F_{-q}^{(p)}$  and electromagnetic multipoles is shown in Table 1.11.6.2. In this table, the properties of the tensors  $F_{-q}^{(p)}$  under time reversal and space inversion on one side are identified with multipole terms describing the physical system on the other. In fact, for any given tensor of rank  $p = 1, 2, 3, 4$  there is one electromagnetic multipole of the same rank ( $1 \rightarrow$  dipole,  $2 \rightarrow$  quadrupole,  $3 \rightarrow$  octupole,  $4 \rightarrow$  hexadecapole) and with the same  $T$  and  $P$  properties. Note that  $P$ -odd  $E1E2$

Table 1.11.6.2. Identification of properties under time inversion  $T$  and space inversion  $P$  of tensors associated with multipole expansion

After Di Matteo *et al.* (2005) and Paolasini (2012).

Rank of tensor	Resonant process	$T$	$P$	Type	Multipole
0	$E1E1$	+	+	charge	monopole
0	$E2E2$	+	+	charge	monopole
1	$E1E1$	–	+	magnetic	dipole
1	$E2E2$	–	+	magnetic	dipole
1	$E1E2$	+	–	electric	dipole
1	$E1E2$	–	–	polar toroidal	dipole
2	$E1E1$	+	+	electric	quadrupole
2	$E2E2$	+	+	electric	quadrupole
2	$E1E2$	+	–	axial toroidal	quadrupole
2	$E1E2$	–	–	magnetic	quadrupole
3	$E2E2$	–	+	magnetic	octupole
3	$E1E2$	+	–	electric	octupole
3	$E1E2$	–	–	polar toroidal	octupole
4	$E2E2$	+	+	electric	hexadecapole

tensors have both  $T$ -odd (–) and  $T$ -even (+) terms for any  $p$ , whereas  $P$ -even tensors (both  $E1E1$  and  $E2E2$ ) are  $T$ -odd for odd rank and  $T$ -even for even rank, respectively (Di Matteo *et al.*, 2005).

An important contribution of Luo *et al.* (1993) and Carra *et al.* (1993) consisted of expressing the amplitude coefficients in terms of experimentally significant quantities, electron spin and orbital moments. This procedure is valid within the fast-collision approximation, when either the deviation from resonance,  $\Delta E = E_c - E_a - \hbar\omega$ , or the width,  $\Gamma$ , is large compared to the splitting of the excited-state configuration. The approximation is expected to hold for the  $L_2$  and  $L_3$  edges of the rare earths and actinides, as well as for the  $M_4$  and  $M_5$  edges of the actinides. In this energy regime, the resonant factors can be summed independently, leaving amplitude coefficients that may be written in terms of multipole moment operators, which are themselves single-particle operators summed over the valence electrons in the initial state.

Magnetic scattering has become a powerful method for understanding magnetic structures (Tonnerre, 1996; Paolasini, 2012), particularly as it is suitable even for powder samples (Collins *et al.*, 1995). Since the first studies (Gibbs *et al.*, 1988), resonant magnetic X-ray scattering has been observed at various edges of transition metals and rare earths. The studies include magnetics and multiferroics with commensurate and incommensurate modulation (Walker *et al.*, 2009; Kim *et al.*, 2011; Ishii *et al.*, 2006; Partzsch *et al.*, 2012; Lander, 2012; Beale *et al.*, 2012; Lovesey *et al.*, 2012; Mazzoli *et al.*, 2007) as well as multi- $k$  magnetic structures (Bernhoeft *et al.*, 2012), and structures with orbital ordering (Murakami *et al.*, 1998) and higher-order multipoles (Princep *et al.*, 2011). It has also been shown that effects can be measured not only at the edges of magnetic atoms [ $K$  edges of transition metals,  $L$  edges of rare-earth elements and  $M$  edges of actinides (Vettier, 2001, 2012)], but also at the edges of non-magnetic atoms (Mannix *et al.*, 2001; van Veenendaal, 2003).

Thus, magnetic and non-magnetic resonant X-ray diffraction clearly has the potential to be an important working tool in modern materials research. The advantage of polarized X-rays is their sensitivity to both the local atomic environments of resonant atoms and their partial structures. The knowledge of the local and global crystal symmetries and of the interplay of their effects is therefore of great value for a better understanding of structural, electronic and magnetic features of crystalline condensed matter.