1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

For $p = 0$:

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

For $p = 1$:

$$F_0^{(1)} = \tfrac{1}{2}(D_{xy} - D_{yx}),$$
$$F_{\pm 1}^{(1)} = \mp \tfrac{1}{2\sqrt{2}}[(D_{yz} - D_{zy} \mp i(D_{xz} - D_{zx})]. \qquad (1.11.6.52)$$

For $p = 2$:

$$F_0^{(2)} = D_{zz} - F_0^{(0)},$$
$$F_{\pm 1}^{(2)} = \mp \tfrac{1}{2}\sqrt{\tfrac{2}{3}}[(D_{xz} + D_{zx} \mp i(D_{yz} + D_{zy})], \qquad (1.11.6.53)$$

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

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:

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

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

$$f^{dq} = \tfrac{1}{2}i\sum_{ijm} e_i'^* e_j (k_m I_{ijm} - k_m' I_{jim})$$

$$= \sum_{p=1}^{3}\sum_{q=-p}^{p}(-1)^{p+q}(X_q^{(p)} F_{-q}^{(p)} + \bar{X}_q^{(p)} \bar{F}_{-q}^{(p)}). \qquad (1.11.6.56)$$

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, Γ, 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 (Tonnere, 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.

references