1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

dipole–quadrupole events can exist only for atoms at positions without inversion symmetry.

It is convenient to separate the time-reversible and time-non-reversible terms in the contributions to the atomic tensor factor (1.11.6.3). The dipole–dipole contribution to the resonant atomic factor can be represented as a sum of an isotropic, a symmetric and an antisymmetric part, written as (Blume, 1994)

$$D_{jk} = D_0^{\text{res}}\delta_{jk} + D_{jk}^+ + D_{jk}^-, \qquad (1.11.6.5)$$

where $D_0^{\text{res}} = (1/3)(\text{Tr}D)$,

$$D_{jk}^+ = \frac{1}{2}(D_{jk} + D_{kj}) - \frac{1}{3}(\text{Tr}D)\delta_{jk}$$

$$= \frac{1}{4}\sum_{a,c}\frac{m\omega_{ca}^3}{\hbar\omega}(p_a' + p_{\bar a}')(\langle a|R_j|c\rangle\langle c|R_k|a\rangle + \langle a|R_k|c\rangle\langle c|R_j|a\rangle)$$

$$\qquad (1.11.6.6)$$

and

$$D_{jk}^- = \frac{1}{2}(D_{jk}^- - D_{kj}^-)$$

$$= \frac{1}{4}\sum_{a,c}\frac{m\omega_{ca}^3}{\hbar\omega}(p_a' - p_{\bar a}')(\langle a|R_j|c\rangle\langle c|R_k|a\rangle - \langle a|R_k|c\rangle\langle c|R_j|a\rangle),$$

$$\qquad (1.11.6.7)$$

$p_a' = p_a/[\omega - \omega_{ca} - i\Gamma/(2\hbar)]$ and $p_{\bar a}' = p_a/[\omega - \omega_{c\bar a} - i\Gamma/(2\hbar)]$; $p_{\bar a}$ means the probability of the time-reversed state $|\bar a\rangle$. If, for example, $|a\rangle$ has a magnetic quantum number m, then $|\bar a\rangle$ has a magnetic quantum number $-m$.

In non-magnetic crystals, the probability of states with $\pm m$ is the same, so that $p_{\bar a} = p_a$ and $\langle \bar a|R_j^s|\bar c\rangle = \langle c|R_k^s|a\rangle$; in this case D_{jk} is symmetric under permutation of the the indices.

Similarly, the dipole–quadrupole atomic factor can be represented as (Blume, 1994)

$$f_{jk}^{dq} = \frac{i}{2}\sum_{ac}p_a\frac{m\omega_{ca}^3}{\hbar\omega} \times \{\langle a|R_j|c\rangle\langle c|R_kR_l|a\rangle k_l$$

$$- \langle a|R_jR_l|c\rangle\langle c|R_k|a\rangle k_l'\} \qquad (1.11.6.8)$$

$$= \frac{i}{8}\sum_{ac}\frac{m\omega_{ca}^3}{\hbar\omega}\{I_{jkl}^{++}(k_l - k_l') + I_{jkl}^{--}(k_l - k_l')$$

$$+ I_{jkl}^{-+}(k_l + k_l') + I_{jkl}^{+-}(k_l + k_l')\}, \qquad (1.11.6.9)$$

where

$$I_{jkl}^{\mu\nu} = \sum_{ac}(p_a' + \mu p_{\bar a}')\{\langle a|R_j|c\rangle\langle c|R_kR_l|a\rangle k_l$$

$$+ \nu\langle a|R_jR_l|c\rangle\langle c|R_k|a\rangle k_l'\} \qquad (1.11.6.10)$$

with $\mu, \nu = \pm 1$. In (1.11.6.10) the first plus ($\mu = 1$) corresponds to the non-magnetic case (time reversal) and the minus ($\mu = -1$) corresponds to the time-non-reversal magnetic term, while the second $\pm$ corresponds to the symmetric and antisymmetric parts of the atomic factor. We see that $I_{jkl}^{--}(k_l - k_l')$ can contribute only to scattering, while $I_{jkl}^{-+}(k_l + k_l')$ can contribute to both resonant scattering and resonant X-ray propagation. The latter term is a source of the so-called magnetochiral dichroism, first observed in Cr_2O_3 (Goulon *et al.*, 2002, 2003), and it can be associated with a toroidal moment in a medium possessing magnetoelectric properties. The symmetry properties of magnetoelectic tensors are described well by Sirotin & Shaskolskaya (1982), Nye (1985) and Cracknell (1975). Which magnetoelectric properties can be studied using X-ray scattering are widely discussed by Marri &

Carra (2004), Matsubara *et al.* (2005), Arima *et al.* (2005) and Lovesey *et al.* (2007).

It follows from (1.11.6.8) and (1.11.6.10) that $I_{jkl} = I_{jlk}$ and the dipole–quadrupole term can be represented as a sum of the symmetric $I_{jkl}^+ = I_{kjl}^+$ and antisymmetric $I_{jkl}^- = -I_{kjl}^-$ parts. From the physical point of view, it is useful to separate the dipole–quadrupole term into I_{jkl}^+ and I_{jkl}^-, because only I_{jkl}^- works in conventional optics where $\mathbf{k}' = \mathbf{k}$. The dipole–quadrupole terms are due to the hybridization of excited electronic states with different spacial parities, *i.e.* only for atomic sites without an inversion centre.

The pure quadrupole–quadrupole term in the tensor atomic factor is equal to

$$f_{jk}^{qq} = \tfrac{1}{4}Q_{jlkm}k_l'k_m \qquad (1.11.6.11)$$

with the fourth-rank tensor Q_{jklm} given by

$$Q_{jlkm} = \sum_{ac}p_a\frac{m\omega_{ca}^3}{\hbar\omega}\frac{\langle a|R_jR_l|c\rangle\langle c|R_kR_m|a\rangle}{\omega - \omega_{ca} - i(\Gamma/2\hbar)}. \qquad (1.11.6.12)$$

This fourth-rank tensor Q_{ijkm} has the following symmetries:

$$Q_{jlkm} = Q_{ljkm} = Q_{jlmk}. \qquad (1.11.6.13)$$

We can define

$$Q_{jlkm} = Q_{jlkm}^+ + Q_{jlkm}^- \qquad (1.11.6.14)$$

with $Q_{jlkm}^\pm = \pm Q_{kmjl}$, where

$$Q_{jlkm}^\pm = \tfrac{1}{4}\sum_a(p_a' \pm p_{\bar a}')(\langle a|R_jR_l|c\rangle\langle c|R_kR_m|a\rangle$$

$$\pm \langle a|R_kR_m|c\rangle\langle c|R_jR_l|a\rangle). \qquad (1.11.6.15)$$

We see that Q_{jlkm}^- vanishes in time-reversal invariant systems, which is true for non-magnetic structures.

1.11.6.2. *Tensor atomic factors (non-magnetic case)*

In time-reversal invariant systems, equation (1.11.6.3) can be rewritten as

$$f_{jk}^{\text{res}} = D_{jk}^+ + iI_{jkl}^+(k_l' - k_l) + iI_{jkl}^-(k_l' + k_l) + Q_{jlkm}^+k_l'k_m + \dots, \qquad (1.11.6.16)$$

where D_{jk}^+ corresponds to the symmetric part of the dipole–dipole contribution, I_{jkl}^+ and I_{jkl}^- mean the symmetric and antisymmetric parts of the third-rank tensor describing the dipole–quadrupole term, and Q_{jlkm}^+ denotes a symmetric quadrupole–quadrupole contribution. From the physical point of view, it is useful to separate the dipole–quadrupole term into I_{jkl}^+ and I_{jkl}^-, because in conventional optics, where $\mathbf{k}' = \mathbf{k}$, only I_{jkl}^- is relevant.

The tensors contributing to the atomic factor in (1.11.6.16), $D_{jk}, I_{jkl}^+, I_{jkl}^-, Q_{jlkm}$, are of different ranks and must obey the site symmetry of the atomic position. Generally, the tensors can be different, even for crystallographically equivalent positions, but all tensors of the same rank can be related to one of them, because all are connected through the symmetry operations of the crystal space group. In contrast, the scattering amplitude tensor f_{jm}^{res} does not necessarily comply with the point symmetry of the atomic position, because this symmetry is usually violated considering the arbitrary directions of the radiation wavevectors $\mathbf{k}$ and $\mathbf{k}'$.

Equation (1.11.6.16) is also frequently considered as a phenomenological expression of the tensor atomic factor where

each tensor possesses internal symmetry (with respect to index permutations) and external symmetry (with respect to the atomic environment of the resonant atom). For instance, the tensor D_{jk} is symmetric, the rank-3 tensor has a symmetric and a antisymmetric part, and the rank-4 tensor is symmetric with respect to the permutation of each pair of indices. The external symmetry of D_{jk} coincides with the symmetry of the dielectric susceptibility tensor (Chapter 1.6). Correspondingly, the third-rank tensors I^-_{jkl} and I^+_{jkl} are similar to the gyration susceptibility and electro-optic tensors (Chapter 1.6), and Q_{jlkm} has the same tensor form as that for elastic constants (Chapter 1.3). The symmetry restrictions on these tensors (determining the number of independent elements and relationships between tensor elements) are very important and widely used in practical work on resonant X-ray scattering. Since they can be found in Chapters 1.3 and 1.6 or in textbooks (Sirotin & Shaskolskaya, 1982; Nye, 1985), we do not discuss all possible symmetry cases in the following, but consider in the next section one specific example for X-ray scattering when the symmetries of the tensors given by expression (1.11.6.3) do not coincide with the most general external symmetry that is dictated by the atomic environment.

1.11.6.3. *Hidden internal symmetry of the dipole–quadrupole tensors in resonant atomic factors*

It is fairly obvious from expressions (1.11.6.3) and (1.11.6.16) that in the non-magnetic case the symmetric and antisymmetric third-rank tensors, I^+_{jkl} and I^-_{jlk}, which describe the dipole–quadrupole contribution to the X-ray scattering factor, are not independent: the antisymmetric part, which is also responsible for optical-activity effects, can be expressed *via* the symmetric part (but not *vice versa*). Indeed, both of them can be described by a symmetric third-rank tensor $t_{ijk} = t_{ikj}$ resulting from the second-order Born approximation (1.11.6.3),

$$I^+_{ijk} = (t_{ijk} + t_{jik})/2, \qquad (1.11.6.17)$$

$$I^-_{ijk} = (t_{ijk} - t_{jik})/2, \qquad (1.11.6.18)$$

where

$$t_{ijk} = -\tfrac{1}{2} I_{ijk}. \qquad (1.11.6.19)$$

From equation (1.11.6.17), one can infer that the symmetry restrictions for I^+_{ijk} and t_{ijk} are the same. Then it can be seen that I^-_{ijk} can be expressed *via* I^+_{ijk}.

For any symmetry, I^+_{ijk} and t_{ijk} have the same number of independent elements (with a maximum 18 for site symmetry 1). Thus, one can reverse equation (1.11.6.17) and express t_{ijk} directly in terms of I^+_{ijk}:

$$t_{111} = I^+_{111}, \quad t_{211} = 2I^+_{121} - I^+_{112}, \quad t_{311} = 2I^+_{311} - I^+_{113},$$
$$t_{122} = 2I^+_{122} - I^+_{221}, \quad t_{222} = I^+_{222}, \quad t_{322} = 2I^+_{232} - I^+_{223},$$
$$t_{133} = 2I^+_{313} - I^+_{331}, \quad t_{233} = 2I^+_{233} - I^+_{332}, \quad t_{333} = I^+_{333},$$
$$t_{123} = I^+_{123} + I^+_{312} - I^+_{231}, \quad t_{223} = I^+_{223}, \quad t_{332} = I^+_{332},$$
$$t_{113} = I^+_{113}, \quad t_{231} = I^+_{231} + I^+_{123} - I^+_{312}, \quad t_{331} = I^+_{331},$$
$$t_{112} = I^+_{112}, \quad t_{221} = I^+_{221}, \quad t_{312} = I^+_{312} + I^+_{231} - I^+_{123}.$$
$$(1.11.6.20)$$

Using equations (1.11.6.18) and (1.11.6.20), one can express all nine elements of I^-_{ijk} through I^+_{ijk}:

$$I^-_{231} = I^+_{123} - I^+_{312}, \quad I^-_{232} = I^+_{223} - I^+_{232}, \quad I^-_{233} = I^+_{233} - I^+_{332},$$
$$I^-_{311} = I^+_{311} - I^+_{113}, \quad I^-_{312} = I^+_{231} - I^+_{123}, \quad I^-_{313} = I^+_{331} - I^+_{313},$$
$$I^-_{121} = I^+_{112} - I^+_{121}, \quad I^-_{122} = I^+_{122} - I^+_{221}, \quad I^-_{123} = I^+_{312} - I^+_{231},$$
$$(1.11.6.21)$$

according to which the antisymmetric part of the dipole–quadrupole term is a linear function of the symmetric one [however, not *vice versa*: equations (1.11.6.21) cannot be reversed].

Note that the equations (1.11.6.21) impose an additional restriction on I^-_{ijk}, which applies to all atomic site symmetries:

$$I^-_{123} + I^-_{231} + I^-_{312} = 0. \qquad (1.11.6.22)$$

This is, in fact, a well known result: the pseudo-scalar part of I^-_{ijk} vanishes in the dipole–quadrupole approximation used in equation (1.11.6.3). Thus, for point symmetry 1, I^-_{ijk} has only eight independent elements rather than nine. This additional restriction works in all cases of higher symmetries provided the pseudo-scalar part is allowed by the symmetry (*i.e.* point groups 2, 3, 4, 6, 222, 32, 422, 622, 23 and 432). All other symmetry restrictions on I^-_{ijk} arise automatically from equation (1.11.6.21) taking into account the symmetry of I^+_{ijk} [symmetry limitations on I^+_{ijk} and I^-_{ijk} for all crystallographic point groups can be found in Sirotin & Shaskolskaya (1982) and Nye (1985)].

Let us consider two examples, ZnO and anatase, TiO$_2$, where the dipole–dipole contributions to forbidden reflections vanish, whereas both the symmetric and antisymmetric dipole-quadrupole terms are in principal allowed. In these crystals, the dipole–quadrupole terms have been measured by Goulon *et al.* (2007) and Kokubun *et al.* (2010).

In ZnO, crystallizing in the wurtzite structure, the $3m$ symmetry of the atomic positions imposes the following restrictions on t_{ijk}:

$$t_{131} = t_{223} = e_{15}, \qquad (1.11.6.23)$$

$$t_{222} = -t_{112} = -t_{211} = e_{22}, \qquad (1.11.6.24)$$

$$t_{311} = t_{322} = e_{31}, \qquad (1.11.6.25)$$

$$t_{333} = e_{33}, \qquad (1.11.6.26)$$

where e_{15}, e_{31}, e_{22}, e_{33} are energy-dependent complex tensor elements [keeping the notations by Sirotin & Shaskolskaya (1982), the x axis is normal to the mirror plane, the y axis is normal to the glide plane and the z axis corresponds to the c axis of ZnO]. If we suppose these restrictions for Zn at $\frac{1}{3}, \frac{2}{3}, z$, then for the other Zn at $\frac{2}{3}, \frac{1}{3}, z + \frac{1}{2}$, which is related to the first site by the glide plane, there is the following set of elements: $e_{15}, e_{31}, -e_{22}, e_{33}$. Therefore, the structure factors of the glide-plane forbidden reflections are proportional to e_{22}.

For the symmetric and antisymmetric parts one obtains from equations (1.11.6.17) and (1.11.6.18) the non-zero components

$$I^+_{131} = I^+_{232} = (e_{15} + e_{31})/2, \qquad (1.11.6.27)$$

$$I^+_{222} = -I^+_{121} = -I^+_{112} = e_{22}, \qquad (1.11.6.28)$$

$$I^+_{113} = I^+_{223} = e_{15}, \qquad (1.11.6.29)$$

$$I^+_{333} = e_{33} \qquad (1.11.6.30)$$

and

$$I^-_{232} = -I^-_{311} = I^+_{113} - I^+_{131} = (e_{15} - e_{31})/2. \qquad (1.11.6.31)$$

Physically, we can expect that $|e_{15} + e_{31}| \gg |e_{15} - e_{31}|$ because $e_{15} + e_{31}$ survives even for tetrahedral symmetry $\bar{4}3m$, whereas $e_{15} - e_{31}$ is non-zero owing to a deviation from tetrahedral