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Abstract
The relation between the properties of a specific crystallographic site and the properties of the full crystal is discussed by using spherical tensors. The concept of spherical tensors is introduced and the way it transforms under the symmetry operations of the site and from site to site is described in detail. The law of spherical tensor coupling is given and illustrated with the example of the electric dipole and quadrupole transitions in x-ray absorption spectroscopy. The main application of the formalism is the reduction of computation time in the calculation of the properties of crystals by band-structure methods. The general approach is illustrated by the examples of substitutional chromium in spinel and substitutional vanadium in garnet.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

This paper deals with the relation between the properties of specific sites in a crystal and the properties of the crystal itself. We shall discuss in particular the case of x-ray absorption spectroscopy, but many of our results are general.

The aim of this paper is to introduce x-ray physicists, experimentalists and theoreticians, to the use of spherical tensors for analyzing theoretical and experimental spectra. Therefore, our presentation is as pedagogical as we can manage. As the manipulation of spherical tensors can be quite complicated, we have tried to reduce it to the simplest possible rules.

An atom in a crystal generally occupies a crystallographic site that is not unique. If we take the concrete example of a chromium atom substituting for aluminum in spinel ($MgAl_2O_4$), the chromium atom can occupy 16 equivalent trigonal sites in the cubic cell [1]. The (normalized) x-ray absorption spectrum of chromium is the average of the spectra of the chromium atoms occupying the 16 sites. To calculate the spectrum of chromium, we need to put a chromium atom at an aluminum site, relax the environment, carry out a self-consistent band-structure calculation with and without a core hole, and calculate the spectrum of this site. In a straightforward approach, we need then to repeat the procedure for all equivalent sites and take the average spectrum. A considerable amount of time can be saved if we calculate the spectrum of a single site and deduce the spectrum of the other sites by symmetry considerations. The present paper gives all the required tools to do so.

Let us first defend the case of spherical tensors, that will be precisely defined in the next section. Most physical properties are tensors and they are usually considered as Cartesian tensors. Spherical tensors consist of a 'refinement' of Cartesian tensors in the sense that a Cartesian tensor is generally the sum of several spherical tensors. For example, a second-rank Cartesian tensor is the sum a zeroth-rank, a first-rank and a second-rank spherical tensor. This refinement enables us to discard irrelevant contributions. For example, the electric quadrupole contribution to an x-ray absorption spectrum is represented by a symmetric fourth-rank Cartesian tensor with 36 components, whereas it is represented by the sum of a zeroth-rank, a second-rank and a fourth-rank spherical tensor with 15 components altogether. Moreover, the spherical average used to represent powder samples is obtained by taking only one spherical tensor component, whereas it is the sum of 12 Cartesian components. Thus, using spherical tensors can save computing time.

The drawback of the spherical tensor analysis is that some subtleties enter its practical use. One purpose of this paper is to give a detailed presentation of these problems and of their solutions.

In practice, one faces the frustrating task of sorting out the various conventions used by the authors and to determine whether a rotation is active or passive, whether the row index of the Wigner matrix increases from left to right as in a normal matrix or decreases as in [2], which definition of the Wigner matrix is used (seven inequivalent definitions are found in the literature [3]), how tensors transform under complex conjugation, etc.

The paper starts with a presentation of the Cartesian and spherical tensors and a detailed description of our notation. Then, the concept of tensor coupling is introduced and a simple formula is given to change the coupling order. This formula is applied to the calculation of electric dipole and quadrupole transitions. This completes the generalities on spherical tensors. Then, we consider the case of crystals. We show how the symmetry of a crystal site constrains the spherical tensor components in the reference frame of the site and in the reference frame of the crystal. We also give the precise formula relating these reference frames. As an illustration, we treat the example of the Al site in spinel and garnet. Finally, we determine the spherical tensor describing the full crystal from those of the sites. An appendix gathers the formulae that were used to calculate rotation matrices, Wigner matrices and solid harmonics.

2. Cartesian and spherical tensors

A Cartesian tensor is the generalization of a scalar, a vector or a matrix. A three-dimensional vector $\mathbf{r} = (x, y, z) = (\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ is transformed by a rotation R into a vector $\mathbf{r}' = R\mathbf{r}$, so that $\mathbf{r}'_i = \sum_{j=1}^{3} R_{ij}\mathbf{r}_j$. A vector is also called a first-rank tensor. A matrix A defined by $A_{ij} = \mathbf{r}_i \mathbf{r}_j$ transforms under rotation into

$$A'_{ij} = \mathbf{r}'_i \mathbf{r}'_j = \sum_{lm} R_{il} R_{jm} A_{lm}. \tag{1}$$

Any matrix A_{ij} that transforms under rotation as in equation (1) is called a second-rank Cartesian tensor. More generally, an nth-rank Cartesian tensor is a generalized matrix $A_{i_1...i_n}$ that transforms under rotation as in equation (1), but with the product of n matrices R instead of just two. Cartesian tensors are ubiquitous in physics. For example, electric dipole transition amplitudes are described by a first-rank tensor, electric dipole transition intensities and electric quadrupole transition amplitudes by a second-rank tensor, and electric quadrupole transition intensities by a fourth-rank tensor.

Cartesian tensors have very simple transformation rules under rotation, but they suffer from a severe drawback: they are not irreducible. To see what this means, consider a second-rank tensor A_{ij}. Its trace is $t = \sum_{i=1}^{3} A_{ii}$ and transforms under rotation into

$$t' = \sum_{i=1}^{3} A'_{ii} = \sum_{ilm} R_{il} R_{im} A_{lm} = \sum_{lm} \delta_{lm} A_{lm} = t,$$

where we used the fact that $RR^{\mathrm{T}} = \mathrm{Id}$, where R^{T} is the transpose of R. We recover the fact that the trace of a matrix is invariant: it transforms into itself under rotation. A second-order Cartesian tensor gives another interesting object, the

vector $\mathbf{v}$ defined by $\mathbf{v}_i = \sum_{jk} \epsilon_{ijk} A_{jk}$, where j and k run from 1 to 3. The Levi-Civita symbol ϵ_{ijk} is 1 if (i, j, k) is a cyclic permutation of $(1, 2, 3)$, it is -1 if (i, j, k) is another permutation of $(1, 2, 3)$, and it is 0 if two indices are identical. Then, using the identity $\sum_{jk} \epsilon_{ijk} R_{jl} R_{km} = \sum_j R_{ij} \epsilon_{jlm}$, we see that $\mathbf{v}$ transforms under rotation as a vector: $\mathbf{v}' = R\mathbf{v}$. Therefore, from a second-rank Cartesian tensor, we can build a linear combination of its elements (the trace) that is invariant under rotation, and three linear combinations of its elements that transform into each other as the components of a vector. More generally, a tensor is said to be *reducible* when there are linear combinations of its elements that transform into each other under rotation. When a tensor is not reducible, it is called irreducible. Thus, a vector is irreducible but a second-rank Cartesian tensor is reducible. The irreducible tensors are called *spherical tensors* and will be the main topic of this paper.

The first spherical tensors were the spherical harmonics Y_ℓ^m. For each ℓ, there are $2\ell + 1$ spherical harmonics Y_ℓ^m that transform into each other under rotation. More precisely, for each rotation R, there is a unitary matrix D^ℓ, called a *Wigner matrix* (to be precisely defined in the next section), such that the rotation of Y_ℓ^m by R is

$$RY_\ell^m = \sum_{m'=-\ell}^{\ell} Y_\ell^{m'} D_{m'm}^\ell(R).$$

Spherical tensors are defined in analogy with spherical harmonics. An ℓth-rank spherical tensor, denoted by T^ℓ, is a set of $2\ell + 1$ components, written T_m^ℓ, where $m = -\ell, -\ell + 1, \ldots, \ell - 1, \ell$, that transform under rotation as

$$RT_m^\ell = \sum_{m'=-\ell}^{\ell} T_{m'}^\ell D_{m'm}^\ell(R). \tag{2}$$

This definition is rather abstract, but we shall see how spherical tensors are built in practice. It is an unfortunate but historical fact that the position of ℓ and m is different in the spherical harmonics Y_ℓ^m and the spherical tensors T_m^ℓ.

When many spherical tensors are involved in a formula, we use also the notation P^a, Q^b, etc. For notational convenience, we shall often write $RT^\ell = T^\ell D^\ell(R)$ for equation (2), as for the product of a matrix and a vector. Moreover, the product of two Wigner matrices will be denoted by $D^\ell(R)D^\ell(R')$.

2.1. Further symmetries

A spherical tensor is a basis of an irreducible representation of the rotation group $SO(3)$. A different group leads to a different concept of irreducibility. For example, an irreducible representation of $SO(3)$ is generally reducible for a subgroup of $SO(3)$ (e.g. $SO(2)$ or a point symmetry group). In many applications we have to consider a group larger than $SO(3)$, for example $O(3)$, the direct product of the rotation group and the group $\mathcal{I} = \{1, I\}$, where I is the inversion symmetry operation: $I\mathbf{r} = -\mathbf{r}$. An element of $O(3)$ is called a *rotoinversion*. By definition, for any rotoinversion g, there is a unique rotation R_g such that either $g = R_g$ (g is a pure rotation) or $g = IR_g$ (g contains the inversion). It can be

checked that $R_{gg'} = R_g R_{g'}$ and that $R_{g^{-1}} = R_g^{-1}$. The group $\mathcal{I}$ is of order 2 and commutative. It has two one-dimensional irreducible representations, where the inversion is represented by the factor 1 or -1, respectively. Therefore, according to a general theorem ([4], p 115), spherical tensors become bases of the irreducible representations of $O(3)$ if they are provided with a definite parity: the parity of T^ℓ is even if $I T^\ell = T^\ell$; it is odd if $I T^\ell = -T^\ell$. For instance, the spherical tensor representing electric dipole transition amplitudes is odd; the one representing electric quadrupole transition amplitudes is even. We denote the action of a rotoinversion on a tensor T^ℓ with a definite parity by

$$g T_m^\ell = \epsilon(g) \sum_{m'=-\ell}^{\ell} T_{m'}^\ell D_{m'm}^\ell(g), \tag{3}$$

where $D^\ell(g)$ is a simplified notation for $D^\ell(R_g)$ and where ϵ is the *parity operator* associated with T^ℓ: $\epsilon(g) = -1$ if T^ℓ is odd and g contains the inversion, $\epsilon(g) = 1$ otherwise. We have $\epsilon(gg') = \epsilon(g)\epsilon(g') = \epsilon(g'g)$ and $\epsilon(g^{-1}) = \epsilon(g)$.

Time-reversal symmetry is more subtle because of its anti-unitary nature [5]. It is taken into account by considering that the spherical tensors are built from Hermitian operators (see equation (4), p 61 of [3]):

$$(T_m^\ell)^\dagger = (-1)^m T_{-m}^\ell. \tag{4}$$

In this paper, the only tensors that do not satisfy time-reversal symmetry are those built from the polarization vector ϵ, that can possibly be complex. In this case we have $(T_m^\ell(\epsilon))^\dagger = (-1)^m T_{-m}^\ell(\epsilon^*)$. This happens for instance when T^ℓ is a solid harmonic built from a vector with complex coordinates (see appendix B.2).

3. Notation

The fact that many conventions are found in the literature leads us to precisely describe our notation. We consider *active* rotations, i.e. rotations that move the points and not the reference frame. For example the rotation through an angle ψ about the z-axis is represented by

$$R_z(\psi) = \begin{pmatrix} \cos\psi & -\sin\psi & 0 \\ \sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

After an active rotation R, the coordinates $(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ of the vector $\mathbf{r}$ are transformed into the coordinates $\mathbf{r}_i' = \sum_j R_{ij} \mathbf{r}_j$ of $\mathbf{r}' = R\mathbf{r}$. In a *passive* rotation, the reference frame is rotated: the basis vectors $\mathbf{e}_i$ are transformed into the basis vectors $\mathbf{e}_i' = \sum_j R_{ij} \mathbf{e}_j$. Thus, the coordinates of a point $\mathbf{r}$ are transformed by the inverse matrix: $\mathbf{r}' = R^{-1}\mathbf{r}$.

To describe the transformation of the properties of a crystal under rotation, we consider the case of its charge density $\rho(\mathbf{r})$. After a rotation changing $\mathbf{r}$ into $\mathbf{r}' = R\mathbf{r}$, the charge density ρ is transformed into a 'rotated' charge density ρ' of the rotated crystal. To determine ρ', we require the value of the charge density to be invariant under rotation. More precisely, we want $\rho'(\mathbf{r}') = \rho(\mathbf{r})$. Therefore, the

rotated function ρ' is defined by $\rho'(\mathbf{r}') = \rho(R^{-1}\mathbf{r}')$. For later convenience, we denote the rotated function ρ' by $R\rho$. The use of the same symbol R to denote the rotation of both the vectors and the functions should not bring too much confusion. The presence of the inverse rotation R^{-1} in the definition of $R\rho$ ensures that $R'(R\rho) = (R'R)\rho$ (see [6], p 59).

3.1. Wigner rotation matrices

We denote by $D_{m'm}^\ell(R)$ the Wigner rotation matrix corresponding to the rotation R (see appendix B.3 for a definition). For example, $D_{m'm}^\ell(R_z(\psi)) = \delta_{mm'} e^{-im\psi}$. The Wigner rotation matrices define a unitary representation of the rotation group, so that

$$D_{m'm}^\ell(R^{-1}) = (D_{mm'}^\ell(R))^*, \tag{5}$$

and

$$D_{m'm}^\ell(RR') = \sum_{m''=-\ell}^{\ell} D_{m'm''}^\ell(R) D_{m''m}^\ell(R'). \tag{6}$$

3.2. Spherical harmonics

The spherical harmonics are defined by (see [2], p 68)

$$Y_\ell^m(\theta, \phi) = \sqrt{\frac{2\ell+1}{4\pi}} (D_{m0}^\ell(R_{\theta\phi}))^*, \tag{7}$$

where $R_{\theta\phi}$ is the rotation described by the Euler angles $(\phi, \theta, 0)$ (see appendix B.1.2). For notational convenience, we denote by $\mathbf{n}$ the vector $(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$ and we write $Y_\ell^m(\mathbf{n})$ and $R_{\mathbf{n}}$ for $Y_\ell^m(\theta, \phi)$ and $R_{\theta\phi}$, respectively. This notation is justified by the fact that $Y_\ell^m(\mathbf{n})$ can be defined for any (not necessarily normalized) vector $\mathbf{r}$. The resulting functions are called *solid harmonics* and are described in appendix B.2. Solid harmonics are required, for example, in the case of elliptically polarized x-rays because $\mathbf{n}$ has then complex coordinates. A three-dimensional Cartesian vector $\mathbf{r} = (x, y, z)$ can be turned into a set of three solid harmonics

$$Y_1^{-1}(\mathbf{r}) = \sqrt{\frac{3}{8\pi}} (x - iy), \tag{8}$$

$$Y_1^0(\mathbf{r}) = \sqrt{\frac{3}{4\pi}} z, \tag{9}$$

$$Y_1^1(\mathbf{r}) = -\sqrt{\frac{3}{8\pi}} (x + iy). \tag{10}$$

The definition of spherical harmonics implies

$$Y_\ell^m(R\mathbf{n}) = \sum_{m'} Y_\ell^{m'}(\mathbf{n}) D_{m'm}^\ell(R^{-1}).$$

This relation is proved by noticing that the argument $R\mathbf{n}$ of the spherical harmonics corresponds to the argument $RR_{\mathbf{n}}$ of the Wigner matrix in equation (7). From equation (5), we have $(D_{m0}^\ell(RR_{\mathbf{n}}))^* = D_{0m}^\ell((RR_{\mathbf{n}})^{-1})$. The result follows from $(RR_{\mathbf{n}})^{-1} = R_{\mathbf{n}}^{-1} R^{-1}$ and the group representation property defined by equation (6). The same property is true for solid harmonics. Therefore,

$$(RY_\ell^m)(\mathbf{r}) = Y_\ell^m(R^{-1}\mathbf{r}) = \sum_{m'} Y_\ell^{m'}(\mathbf{r}) D_{m'm}^\ell(R). \tag{11}$$

The presence of the spherical harmonics on the left of the Wigner rotation matrices ensures that $R'(RY_\ell^m) = (R'R)Y_\ell^m$. To show this, equation (11) is multiplied on the left by R':

$$(R'(RY_\ell))(\mathbf{r}) = (R'Y_\ell)(\mathbf{r})D^\ell(R) = Y_\ell(\mathbf{r})D^\ell(R')D^\ell(R)$$
$$= Y_\ell(\mathbf{r})D^\ell(R'R) = (R'R)Y_\ell(\mathbf{r}).$$

In the foregoing proof, we simplified the notation by omitting the component index m, as described at the end of section 2.

4. Building tensor operators

Physical properties can be represented by spherical tensors, that can often be built by coupling lower rank tensors. We illustrate this construction by the example of electric dipole and quadrupole transitions. We shall use the remarkable toolbox for spherical tensor calculations elaborated by Varshalovich *et al* [3].

The basic elements of this construction are first-rank spherical tensors. Any three-dimensional Cartesian vector $\mathbf{v} = (x, y, z)$ can be turned into a first-rank spherical tensor $\mathbf{v}^1$ by defining

$$\mathbf{v}_{-1}^1 = (x - \mathrm{i}y)/\sqrt{2},$$
$$\mathbf{v}_0^1 = z, \qquad (12)$$
$$\mathbf{v}_1^1 = -(x + \mathrm{i}y)/\sqrt{2}.$$

Note that solid harmonics $Y_\ell^m(\mathbf{v})$ are also spherical tensors built from $\mathbf{v}$ and that $\mathbf{v}^1 = Y_1(\mathbf{v})\sqrt{4\pi/3}$. However, the factor $\sqrt{4\pi/3}$ is cumbersome and the definition $\mathbf{v}^\ell = Y_\ell(\mathbf{v})\sqrt{4\pi/(2\ell+1)}$ is often preferred.

An ath-rank spherical tensor P^a can be *coupled* to a bth-rank spherical tensor Q^b into a cth-rank spherical tensor, denoted by $\{P^a \otimes Q^b\}^c$, and defined by

$$\{P^a \otimes Q^b\}_\gamma^c = \sum_{\alpha=-a}^{a} \sum_{\beta=-b}^{b} (a\alpha b\beta|c\gamma) P_\alpha^a Q_\beta^b.$$

The symbol $(a\alpha b\beta|c\gamma)$ denote Clebsch–Gordan coefficients [2, 3], which are zero when $\gamma \neq \alpha + \beta$ or when c does not satisfy the triangle relation $|a - b| \leqslant c \leqslant a + b$. For example, the coupling of two vectors (i.e. $a = b = 1$) gives a zeroth-rank, a first-rank and a second-rank spherical tensor (i.e. $c = 0, 1, 2$). The zeroth-rank tensor obtained by coupling two vectors is proportional to the scalar product of these vectors: $\{\mathbf{u}^1 \otimes \mathbf{v}^1\}^0 = -\mathbf{u} \cdot \mathbf{v}/\sqrt{3}$, because $(1\alpha 1 - \alpha|00) = -(-1)^\alpha/\sqrt{3}$. More generally, we define the *scalar product* of two spherical tensors P^a and Q^a of the same rank to be (see [3], p 64 and 65)

$$P^a \cdot Q^a = \sum_{\alpha=-a}^{a} (-1)^\alpha P_{-\alpha}^a Q_\alpha^a = (-1)^a\sqrt{2a+1}\{P^a \otimes Q^a\}^0. \qquad (13)$$

If we consider the group $O(3)$, then let ϵ_P and ϵ_Q be the parity operators of P^a and Q^b, respectively. The parity operator ϵ_T of the coupled tensor $T^c = \{P^a \otimes Q^b\}^c$ is defined by $\epsilon_T(g) = \epsilon_P(g)\epsilon_Q(g)$.

It is often necessary to modify the coupling order of the tensors. For example, to evaluate electric dipole transition

intensities, we have to calculate $|\langle f|\epsilon \cdot \mathbf{r}|i\rangle|^2$, where $\mathbf{r}$ is coupled to ϵ by the scalar product, and the result is multiplied by its complex conjugate. As we shall see in the next section, it is more convenient from the physical point of view to directly couple the x-ray polarization vectors ϵ and ϵ^*. For this purpose, we use the recoupling identity

$$\{P^a \otimes Q^a\}^0 \cdot \{R^d \otimes S^d\}^0 = \sum_g (-1)^g \frac{\{P^a \otimes R^d\}^g \cdot \{Q^a \otimes S^d\}^g}{\sqrt{(2a+1)(2d+1)}}, \qquad (14)$$

where g runs from $|a - d|$ to $a + d$ by the triangle relation. This identity is proved in appendix C.

In the next two sections, we illustrate the recoupling methods with the calculation of electric dipole and quadrupole transitions. Similar methods were used to investigate the interference of electric and quadrupole transitions [7–10] or to calculate x-ray scattering cross-sections [11].

4.1. Dipole

The electric dipole transition amplitudes are given by the formula $T_{fi} = \langle f|\epsilon \cdot \mathbf{r}|i\rangle$. If we denote $\langle f|\mathbf{r}|i\rangle$ by $\mathbf{r}_{fi}$, equation (13) gives us $T_{fi} = \epsilon \cdot \mathbf{r}_{fi} = -\sqrt{3}\{\epsilon^1 \otimes \mathbf{r}_{fi}^1\}^0$. For notational convenience, we remove the exponent 1 in the spherical tensors ϵ^1 and $\mathbf{r}_{fi}^1$. This should not bring confusion: if a vector takes part in a coupling, it is a first-rank spherical tensor. Using the recoupling identity (14), we find the expression of the dipole transition intensity

$$|T_{fi}|^2 = 3\{\epsilon^* \otimes \mathbf{r}_{fi}^*\}^0\{\epsilon \otimes \mathbf{r}_{fi}\}^0$$
$$= \sum_{a=0}^{2} (-1)^a\{\epsilon^* \otimes \epsilon\}^a \cdot \{\mathbf{r}_{fi}^* \otimes \mathbf{r}_{fi}\}^a. \qquad (15)$$

Note that, for elliptic polarization, ϵ is complex. Each term of a decomposition over spherical tensors often has a clear physical meaning. In equation (15), the variables concerning the incident x-ray (i.e. ϵ and ϵ^*) are gathered in $\{\epsilon^* \otimes \epsilon\}^a$; the variables concerning the crystal are in $\{\mathbf{r}_{fi}^* \otimes \mathbf{r}_{fi}\}^a$. Thus, we can easily investigate the influence of a rotation R of the crystal on the absorption cross-section

$$R|T_{fi}|^2 = \sum_{a=0}^{2} (-1)^a\{\epsilon^* \otimes \epsilon\}^a \cdot (R\{\mathbf{r}_{fi}^* \otimes \mathbf{r}_{fi}\}^a)$$
$$= \sum_{a=0}^{2} (-1)^a\{\epsilon^* \otimes \epsilon\}^a \cdot (\{\mathbf{r}_{fi}^* \otimes \mathbf{r}_{fi}\}^a D^a(R)),$$

where we used equation (2) and the fact that $\{\mathbf{r}_{fi}^* \otimes \mathbf{r}_{fi}\}^a$ is an ath-rank spherical tensor. In particular, the spectrum of a powder sample is given by the average over all orientations, i.e. over all rotations R. This average is very simple when performed with spherical tensors: $\langle D^a(R)\rangle = \delta_{a,0}$. Thus, the term $a = 0$ gives the spectrum of a powder, called the isotropic spectrum.

$$\langle|T_{fi}|^2\rangle = \{\epsilon^* \otimes \epsilon\}^0 \cdot \{\mathbf{r}_{fi}^* \otimes \mathbf{r}_{fi}\}^0 = \frac{1}{3}(\epsilon^* \cdot \epsilon)(\mathbf{r}_{fi}^* \cdot \mathbf{r}_{fi}) = \frac{|\mathbf{r}_{fi}|^2}{3},$$

where we used equation (13) and $|\epsilon|^2 = 1$.

To interpret the term $a = 1$, we use the relation between vectors $\mathbf{u}$, $\mathbf{v}$ and the corresponding first-rank spherical tensors

$\mathbf{u}^1$, $\mathbf{v}^1$ (we restore the tensor rank in $\mathbf{u}^1$, $\mathbf{v}^1$ for clarity): according to equation (C.1), $\{\mathbf{u}^1 \otimes \mathbf{v}^1\}^1$ is the first-rank tensor corresponding to the vector $(\mathrm{i}/\sqrt{2})\mathbf{u} \times \mathbf{v}$. Therefore,

$$\{\boldsymbol{\epsilon}^* \otimes \boldsymbol{\epsilon}\}^1 \cdot \{\mathbf{r}_{fi}^* \otimes \mathbf{r}_{fi}\}^1 = -\tfrac{1}{2}(\boldsymbol{\epsilon}^* \times \boldsymbol{\epsilon}) \cdot (\mathbf{r}_{fi}^* \times \mathbf{r}_{fi}).$$

The first cross-product is related to the rate of circular polarization P_c and to the wavevector direction $\hat{k}$ of the incident x-ray by $\boldsymbol{\epsilon}^* \times \boldsymbol{\epsilon} = -\mathrm{i}P_c\hat{k}$ [8]. Moreover, the second cross-product is zero for a non-magnetic sample because time-reversal symmetry implies $\mathbf{r}_{fi}^* = \mathbf{r}_{fi}$. Therefore, the term $a = 1$ describes magnetic circular dichroism.

The term $a = 2$ describes the linear dichroism of x-ray spectra. The number of non-zero components of $\{\mathbf{r}_{fi}^* \otimes \mathbf{r}_{fi}\}^2$ depends on the symmetry of the crystal [12]. We shall determine this number in the case of spinel and garnet.

4.2. Quadrupole

We consider the case of electric quadrupole transitions. We start from the quadrupole transition operator $T = \boldsymbol{\epsilon} \cdot \mathbf{r}\, \mathbf{k} \cdot \mathbf{r}$ and we rewrite it in terms of spherical tensors using equation (C.2): $T = 3\{\{\boldsymbol{\epsilon} \otimes \mathbf{r}\}^0 \otimes \{\mathbf{k} \otimes \mathbf{r}\}^0\}^0$. In this expression $\boldsymbol{\epsilon}$ is coupled with $\mathbf{r}$, and $\mathbf{k}$ with $\mathbf{r}$. As in the case of electric dipole transitions, we want to gather all the terms concerning the crystal into a single tensor. For this purpose, we use equation (14) with the sum over g changed into a sum over a

$$T = \sum_{a=0}^{2} (-1)^a \{\boldsymbol{\epsilon} \otimes \mathbf{k}\}^a \cdot \{\mathbf{r} \otimes \mathbf{r}\}^a.$$

The term $a = 0$ is zero because, according to equation (13), $\{\boldsymbol{\epsilon} \otimes \mathbf{k}\}^0 = -(1/\sqrt{3})\boldsymbol{\epsilon} \cdot \mathbf{k} = 0$ since the polarization and wavevectors are perpendicular. The term $a = 1$ is zero because equation (C.1) gives us $\{\mathbf{r} \otimes \mathbf{r}\}^1 = (\mathrm{i}/\sqrt{2})\mathbf{r} \times \mathbf{r} = 0$. Thus, T is reduced to the single term

$$T = \{\boldsymbol{\epsilon} \otimes \mathbf{k}\}^2 \cdot \{\mathbf{r} \otimes \mathbf{r}\}^2 = \sqrt{5}\{\{\boldsymbol{\epsilon} \otimes \mathbf{k}\}^2 \otimes \{\mathbf{r} \otimes \mathbf{r}\}^2\}^0.$$

The tensor $\{\mathbf{r} \otimes \mathbf{r}\}^2$ can be expressed in terms of spherical harmonics (equation (23), p 67 of [3])

$$\{\mathbf{r} \otimes \mathbf{r}\}_m^2 = \sqrt{\frac{8\pi}{15}} Y_2^m(\mathbf{r}) = \sqrt{\frac{8\pi}{15}} r^2 Y_2^m(\theta, \phi),$$

where r, θ and ϕ are the spherical coordinates of $\mathbf{r}$. For completeness, we give the components of $\{\boldsymbol{\epsilon} \otimes \mathbf{k}\}^2$:

$$\{\boldsymbol{\epsilon} \otimes \mathbf{k}\}_{\pm 2}^2 = \frac{(\epsilon_x \pm \mathrm{i}\epsilon_y)(k_x \pm \mathrm{i}k_y)}{2},$$

$$\{\boldsymbol{\epsilon} \otimes \mathbf{k}\}_{\pm 1}^2 = \mp\frac{(\epsilon_x \pm \mathrm{i}\epsilon_y)k_z + \epsilon_z(k_x \pm \mathrm{i}k_y)}{2},$$

$$\{\boldsymbol{\epsilon} \otimes \mathbf{k}\}_0^2 = \frac{3\epsilon_z k_z - \boldsymbol{\epsilon} \cdot \mathbf{k}}{\sqrt{6}} = \sqrt{\frac{3}{2}}\epsilon_z k_z.$$

The electric quadrupole transition intensities are proportional to $|T_{fi}|^2$, where the transition amplitude is $T_{fi} = \langle f|T|i\rangle$. Therefore, $|T_{fi}|^2 = 5\{P^2 \otimes Q^2\}^0\{R^2 \otimes S^2\}^0$, with

$P^2 = \{\boldsymbol{\epsilon}^* \otimes \mathbf{k}\}^2$, $Q^2 = \langle f|\{\mathbf{r} \otimes \mathbf{r}\}^2|i\rangle^*$, $R^2 = \{\boldsymbol{\epsilon} \otimes \mathbf{k}\}^2$ and $S^2 = \langle f|\{\mathbf{r} \otimes \mathbf{r}\}^2|i\rangle$. The recoupling identity gives us

$$
\begin{aligned}
|T_{fi}|^2 &= 5\{P^2 \otimes Q^2\}^0 \{R^2 \otimes S^2\}^0 \\
&= \sum_{a=0}^{4} (-1)^a \{P^2 \otimes R^2\}^a \cdot \{Q^2 \otimes S^2\}^a.
\end{aligned} \tag{16}
$$

The apparent simplicity of this calculation is essentially due to the powerful tools given in [3]. A straightforward approach is quite heavy [12].

As in the electric dipole case, the term $a = 0$ corresponds to the isotropic spectrum obtained by measuring a powder. Equation (C.3) gives us $\{P^2 \otimes R^2\}^0 = k^2/(2\sqrt{5})$ and the isotropic spectrum is

$$\langle |T_{fi}|^2 \rangle = k^2 \frac{\{Q^2 \otimes S^2\}^0}{2\sqrt{5}}.$$

The calculation of this average in Cartesian coordinates is discussed in appendix A.

If $P^2 = R^2$ (i.e. the x-rays are linearly polarized) or $Q^2 = S^2$ (i.e. the sample is non-magnetic), then the terms $a = 1$ and $a = 3$ are zero. More generally, for any tensor T^a with integer rank a, $\{T^a \otimes T^a\}^c$ is zero if c is odd. This is due to the symmetry of the Clebsch–Gordan coefficients [2, 3] $(b\beta a\alpha|c\gamma) = (-1)^{a+b-c}(a\alpha b\beta|c\gamma)$:

$$
\begin{aligned}
\{T^a \otimes T^a\}_\gamma^c &= \sum_{\alpha,\beta} (a\alpha a\beta|c\gamma) T_\alpha^a T_\beta^a \\
&= (-1)^{2a-c} \sum_{\beta,\alpha} (a\alpha a\beta|c\gamma) T_\beta^a T_\alpha^a \\
&= (-1)^c \{T^a \otimes T^a\}_\gamma^c,
\end{aligned}
$$

where we first exchanged the summation variables α and β, then used the symmetry of the Clebsch–Gordan coefficients, the commutativity of T_α^a and T_β^a, and the fact that a is an integer.

Therefore, if we consider the case of linearly polarized x-rays or non-magnetic samples, only the terms $a = 0$, 2 and 4 are possibly non-zero. The number of independent components depends on the crystal symmetry and is tabulated in [12]. The spherical tensors of [12] are related to the present spherical tensors by

$$\sigma^D(\ell, m) = -4\pi^2\alpha_0\hbar\omega \sum_f \frac{\{\mathbf{r}_{fi} \otimes \mathbf{r}_{fi}\}_m^\ell}{\sqrt{3}} \delta(E_f - E_i - \hbar\omega),$$

$$\sigma^Q(\ell, m) = \pi^2\alpha_0\hbar\omega k^2 \sum_f \frac{\{Q^2 \otimes S^2\}_m^\ell}{2\sqrt{5}} \delta(E_f - E_i - \hbar\omega),$$

where α_0 is the fine-structure constant.

5. Site symmetry

We now describe how to calculate the spherical tensor of a crystallographic site, assuming that it is invariant under the symmetry of the site. We recall that the symmetry group of a site consists of the operations of the space group that leave the site invariant. In a reference frame where the site is the origin, the symmetry group is isomorphic to a point group (i.e. a group of rotoinversions). We can work in a

reference frame corresponding either to the site symmetry or to the crystal symmetry. If we take the example of spinel ($MgAl_2O_4$), the crystal symmetry is cubic and a natural crystal frame is defined by three orthonormal vectors along the edges of the conventional cubic unit cell of the lattice. In spinel, the aluminum site with reduced coordinates $(0, 1/4, 3/4)$ has a threefold symmetry axis along the $(-1, 1, 1)$ direction. Therefore, it is natural to take the unit basis vector $\mathbf{e}'_3$ of the site frame along this direction. The unit basis vector $\mathbf{e}'_2$ is along the $(1, 1, 0)$ direction, which is a twofold symmetry axis of the site. The three vectors $\mathbf{e}'_1 = \mathbf{e}'_2 \times \mathbf{e}'_3$, $\mathbf{e}'_2$ and $\mathbf{e}'_3$ define the orthonormal site frame. In general, the orthonormal reference frames naturally associated with the crystal and with a specific site are different. Symmetrized tensors usually have fewer non-zero components in the site frame, but they are easier to calculate in the crystal frame. We shall describe the way to go from one reference frame to the other. Two examples are treated in detail: a spinel and a garnet.

5.1. Symmetrized tensor

If G is the space group of the crystal, then a site has a symmetry group G', which is a subgroup of G. The number of elements of G' is denoted by $|G'|$. To know the form of a spherical tensor invariant under the site symmetry, we start from an arbitrary spherical tensor T^ℓ (having the parity of the property we investigate) and we calculate the symmetrized tensor $\langle T^\ell \rangle$ by using the classical formula [6]

$$\langle T^\ell_m \rangle = \frac{1}{|G'|} \sum_g \epsilon(g) \sum_{m'=-\ell}^{\ell} T^\ell_{m'} D^\ell_{m'm}(g), \qquad (17)$$

where g runs over the rotoinversion parts of the symmetry operations of the subgroup G'. In this section, the arguments g or h of D^ℓ and ϵ stand for the rotoinversion parts of the space group operations g and h.

From the physical point of view, equation (17) means that the tensor $\langle T^\ell \rangle$ is obtained by averaging over all the symmetry operations that leave the site invariant. From the mathematical point of view, we project onto the subspace that is invariant under any symmetry operation of G'. To check this, take any operation g in G' and evaluate the action of g on the symmetrized tensor. Using equation (17), where the elements of G' are now denoted by h, we find

$$g\langle T^\ell_m \rangle = \frac{1}{|G'|} \sum_h \epsilon(h)\epsilon(g) \sum_{m'm''} T^\ell_{m''} D^\ell_{m''m'}(g) D^\ell_{m'm}(h)$$
$$= \frac{1}{|G'|} \sum_h \epsilon(gh) \sum_{m''} T^\ell_{m''} D^\ell_{m''m}(gh) = \langle T^\ell_m \rangle.$$

Indeed, G' being a group, the set of operations gh where h runs over G' is the same as the set of operations of G'.

5.2. Site and crystal frames

The rotoinversions g can be expressed either in the site frame or in the crystal frame. We shall see in our two examples that symmetrized tensors are simpler when expressed in the site frame. Moreover, some computer programs need to be used in

the site frame[1]. However, the action of the rotoinversions on a vector $\mathbf{r}$ is easier to determine in the crystal frame, because they belong to the tabulated symmetry operations of the crystal [18]. Both cases will be treated in the examples of the following sections.

It is also necessary to describe precisely how to go from one reference frame to the other. If $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$ are the orthonormal axes of the crystal frame and $\mathbf{e}'_1$, $\mathbf{e}'_2$, $\mathbf{e}'_3$ those of the site frame, there is an orthogonal matrix M such that $\mathbf{e}'_i = \sum_j M_{ij}\mathbf{e}_j$. This matrix defines a rotoinversion g by $(g\mathbf{r})_i = \sum_j M_{ij}\mathbf{r}_j$. If we take the example of spinel discussed at the beginning of section 5, if $\mathbf{e}_i$ are the orthonormal axes of the cubic unit cell and $\mathbf{e}'_i$ are the orthonormal axes of the site frame, then M is the rotation matrix representing the pure rotation g with Euler angles $(0, \arccos(1/\sqrt{3}), \pi/4)$. It is the inverse of the rotation matrix of equation (B.2). It can be checked that $\mathbf{e}'_3 = (-\mathbf{e}_1 + \mathbf{e}_2 + \mathbf{e}_3)/\sqrt{3}$ (i.e. the threefold axis is the z-axis of the site along the $(-1, 1, 1)$ direction of the cube) and $\mathbf{e}'_2 = (\mathbf{e}_1 + \mathbf{e}_2)/\sqrt{2}$ (i.e. the y axis of the site is along the $(1, 1, 0)$ direction of the cube). If h is a symmetry operation in the (cubic) crystal frame leaving the site invariant, the basis change formula of linear algebra implies that ghg^{-1} is the same symmetry operation in the (trigonal) site frame. A spherical tensor T^ℓ will be denoted by $T^\ell(3)$ when expressed in the trigonal site frame and by $T^\ell(4)$ when expressed in the cubic crystal frame. The arguments 3 and 4 mean that the z axis is along a threefold axis for a trigonal basis and a fourfold axis for a cubic basis. The relation between $T^\ell(3)$ and $T^\ell(4)$ is given by the formula

$$T^\ell_m(4) = \sum_{m'} T^\ell_{m'}(3) D^\ell_{m'm}(g). \qquad (18)$$

We now give two examples.

5.3. The example of spinel

We illustrate this method with the example of the aluminum site in spinel $MgAl_2O_4$, which is the prototype of the spinel structural family. The spinel structure is derived from a face-centered-cubic close-packing of oxygen atoms with a space group symmetry $Fd\bar{3}m$. The conventional cubic cell contains eight formula units, i.e. 32 oxygen atoms with 24 cations in tetrahedral and pseudo-octahedral interstices. With origin choice 2 [18], the Mg^{2+} cations occupy eight tetrahedral sites, which are located at the special 8a Wyckoff positions $(1/8, 1/8, 1/8)$, with $\bar{4}3m$ (T_d) point symmetry. The Al^{3+} cations occupy 16 pseudo-octahedral sites at the special 16d Wyckoff positions $(0, 1/4, 3/4)$, with $\bar{3}m$ (D_{3d}) point symmetry. This symmetry corresponds to a small elongation of the octahedron along the trigonal axis, arising from a small departure of the position of the oxygen atoms from the perfect fcc arrangement. The O^{2-} ions are located at the Wyckoff positions 32e (u, u, u) with point symmetry $3m$.

---

[1] The most prominent example is the package of multiplet programs written by Cowan, Butler, Thole, Ogasawara and Searle [13–17].

5.3.1. The site frame. The simplest expressions are obtained when the reference frame of the site is used. The point group of the site we consider is D_{3d}. The group D_{3d} has six pure rotations and the same six rotations multiplied by the inversion. We assume that the property we investigate is represented by an even tensor, so that we only have to consider the six pure rotations. It is natural to take the z-axis along the threefold axis and the y axis along one of the C_2 axes. The formulae do not depend on which C_2 axis is chosen. However, they would be different if the y axis were chosen, for example, between two C_2 axes. The six pure rotations are the unit, the C_3 rotation about the z-axis through the angle $2\pi/3$, its square C_3^2, the C_2 rotation about the y-axis through the angle π and the other two rotations C_3C_2 and $C_3^2C_2$. These rotations have Euler angles $(0, 0, 0)$, $(0, 0, 2\pi/3)$, $(0, 0, 4\pi/3)$, $(0, \pi, 0)$, $(0, \pi, 4\pi/3)$ and $(0, \pi, 2\pi/3)$, respectively. These rotations will be denoted by $R_1, \ldots, R_6$, respectively.

To calculate the symmetrized tensors for this site, we use equation (17). The special cases given in appendix B.3.1 enable us to show that $D_{m'm}^\ell(R_1) = \delta_{m'm}$, $D_{m'm}^\ell(R_2) = \delta_{m'm}e^{-2mi\pi/3}$ and $D_{m'm}^\ell(R_3) = \delta_{m'm}e^{-4mi\pi/3}$. Therefore, the sum $\sum_{j=1}^3 D_{m'm}^\ell(R_j)$ is $3\delta_{m'm}$ if m is an integer multiple of 3, and zero otherwise. We calculate the Wigner matrices for the other three rotations and we obtain

$$\frac{1}{|G'|}\sum_{R'} D_{m'm}^\ell(R') = \frac{1}{6}\sum_{j=1}^6 D_{m'm}^\ell(R_j)$$

$$= \frac{\delta_{m'm} + (-1)^{\ell-m}\delta_{m,-m'}}{2}$$

if m and m' are integer multiples of 3, and zero otherwise. Equation (17) is then applied to a general fourth-rank tensor $T_m^4(3)$, where the argument (3) denotes the trigonal axes, and we obtain the non-zero components of the symmetrized tensor $\langle T_m^4(3)\rangle$,

$$\langle T_0^4(3)\rangle = T_0^4(3),$$

$$\langle T_3^4(3)\rangle = -\langle T_{-3}^4(3)\rangle = \frac{T_3^4(3) - T_{-3}^4(3)}{2}.$$

For the second-rank tensor, all symmetrized components are zero, except for $\langle T_0^2(3)\rangle = T_0^2(3)$. Of course, we also have the relation $\langle T_0^0(3)\rangle = T_0^0(3)$, which is valid for any group. We now show that time-reversal symmetry implies that the symmetrized tensors are real. According to equation (4) $(T_0^\ell)^* = T_0^\ell$, so that T_0^ℓ is real. Still, by equation (4) we have $(T_3^\ell)^* = -T_{-3}^\ell$. Thus, $\langle T_3^4(3)\rangle^* = (-T_{-3}^4(3) + T_3^4(3))/2 = \langle T_3^4(3)\rangle$ is real as well.

In x-ray absorption spectra, the symmetrized tensors are spectral functions depending on the photon energy. For the example of the electric quadrupole transitions we take, for each energy $\hbar\omega$,

$$T^\ell = \pi^2\alpha_0\hbar\omega$$
$$\times \sum_f \{\langle f|\{\mathbf{r}\otimes\mathbf{r}\}^2|i\rangle^*\otimes\langle f|\{\mathbf{r}\otimes\mathbf{r}\}^2|i\rangle\}^\ell \delta(E_f - E_i - \hbar\omega),$$

where α_0 is the fine-structure constant and E_i and E_f the energies of the initial and final states. The symmetrized tensors $\langle T^\ell(3)\rangle$ can be calculated by multiplet programs. The value of these tensors for a chromium atom substituting for aluminium in spinel is given in figure 1 (see [1] for more details).
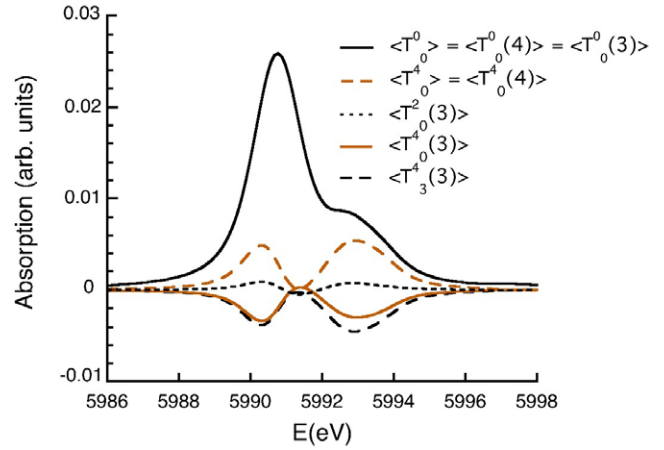

Figure 1. The symmetrized tensors $\langle T_0^0(3)\rangle$, $\langle T_0^2(3)\rangle$, $\langle T_0^4(3)\rangle$ and $\langle T_3^4(3)\rangle$ in the site frame, for the electric quadrupole transitions of the K edge of a chromium atom substituting for aluminium in spinel. After averaging over the sites, only the symmetrized tensors $\langle T_0^0\rangle$ and $\langle T_0^4\rangle$ remain as independent parameters.

5.3.2. The crystal frame. We consider now the same average in the crystal frame. The Al site with reduced coordinates $(0, 1/4, 3/4)$ has a threefold axis along the $(-1, 1, 1)$ direction and a twofold axis along the $(0, 1, 0)$ direction. Therefore, the six pure rotations of D_{3d} are now (i) the identity, denoted by (x, y, z), (ii) a C_3 rotation about $(-1, 1, 1)$, denoted by $(-y, z, -x)$, (iii) its square $(-z, -x, y)$, (iv) a rotation of π about $(1, 1, 0)$ denoted by $(y, x, -z)$, (v) a rotation of π about $(1, 0, 1)$ denoted by $(z, -y, x)$ and (vi) a rotation of π about $(0, 1, -1)$ denoted by $(-x, -z, -y)$. The notation used for the rotations is the result of the operation $R\mathbf{r}$ in the cubic axes. For example, the C_3 rotation gives

$$R\mathbf{r} = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -y \\ z \\ -x \end{pmatrix}.$$

The corresponding Euler angles are $(0, 0, 0)$, $(\pi/2, \pi/2, 0)$, $(\pi, \pi/2, \pi/2)$, $(0, \pi, \pi/2)$, $(0, \pi/2, \pi)$ and $(3\pi/2, \pi/2, 3\pi/2)$.

We apply again equation (17) to the general second-rank tensor $T_m^2(4)$, where the argument (4) stands for the cubic axes. This gives us the symmetrized tensor $\langle T^2(4)\rangle$

$$\langle T_0^2(4)\rangle = 0,$$

$$\langle T_{-2}^2(4)\rangle = \langle T_2^2(4)\rangle^* = -i\lambda, \qquad (19)$$

$$\langle T_{-1}^2(4)\rangle = -\langle T_1^2(4)\rangle^* = (1 + i)\lambda,$$

with

$$\lambda = \frac{\text{Im}\, T_2^2(4) - \text{Re}\, T_1^2(4) + \text{Im}\, T_1^2(4)}{3},$$

where we have used time-reversal symmetry as in equation (4).

Note that λ is real. For the tensor $\langle T^4(4)\rangle$,

$$\langle T_0^4(4)\rangle = \sqrt{\tfrac{14}{5}}\langle T_4^4(4)\rangle = \sqrt{\tfrac{14}{5}}\langle T_{-4}^4(4)\rangle^* = \xi,$$

$$\langle T_{-3}^4(4)\rangle = -\langle T_3^4(4)\rangle^* = (1-i)\sqrt{7}\zeta,$$

$$\langle T_{-2}^4(4)\rangle = \langle T_2^4(4)\rangle^* = 2i\sqrt{2}\zeta, \qquad (20)$$

$$\langle T_{-1}^4(4)\rangle = -\langle T_1^4(4)\rangle^* = (1+i)\zeta,$$

with

$$\xi = \frac{7T_0^4(4) + \sqrt{70}\,\mathrm{Re}\,T_4^4(4)}{12},$$

$$\zeta = -\{\sqrt{7}(\mathrm{Re}\,T_3^4(4) + \mathrm{Im}\,T_3^4(4)) + 2\sqrt{2}\,\mathrm{Im}\,T_2^4(4)$$
$$+ \mathrm{Re}\,T_1^4(4) - \mathrm{Im}\,T_1^4(4)\}/24.$$

Note that ξ and ζ are real.

5.3.3. From site to crystal frame. From this example, it is clear that the symmetrized tensor $\langle T^\ell(3)\rangle$ in the site frame is much simpler than the same tensor $\langle T^\ell(4)\rangle$ in the crystal frame. The relation between the trigonal and cubic axes is worked out in appendix B.4.

To go from one to the other we apply equation (18) and we obtain the relations

$$\langle T_0^4(4)\rangle = -\frac{7\langle T_0^4(3)\rangle + 2\sqrt{70}\langle T_3^4(3)\rangle}{18}, \qquad (21)$$

$$\langle T_{-2}^4(4)\rangle = i\frac{\sqrt{10}\langle T_0^4(3)\rangle - \sqrt{7}\langle T_3^4(3)\rangle}{9}. \qquad (22)$$

We recover equations (20) with

$$\zeta = \frac{2\sqrt{5}\langle T_0^4(3)\rangle - \sqrt{14}\langle T_3^4(3)\rangle}{36},$$

$$\xi = -\frac{7\langle T_0^4(3)\rangle + 2\sqrt{70}\langle T_3^4(3)\rangle}{18}.$$

For the second-rank tensor we find equations (19) with $\lambda = -\langle T_0^2(3)\rangle/\sqrt{6}$. For the zeroth-rank tensor we have obviously $\langle T_0^0(4)\rangle = \langle T_0^0(3)\rangle$.

5.4. The example of garnet

We consider now the Al site in garnet with the example of grossular $Ca_3Al_2(SiO_3)_4$, which is a cubic mineral with the space group $Ia\bar{3}d$. The conventional cubic cell contains 96 oxygen, 24 calcium, 24 silicium and 16 aluminum atoms. The Al^{3+} cations are at the 16a Wyckoff positions. We put vanadium at the Al site $(1/2, 1/2, 0)$, which is a slightly distorted octahedron, with a small elongation along the $(-1, 1, 1)$ axis of the cube, and has the $\bar{3}$ (C_{3i}) point symmetry.

We calculate the symmetrized tensor in the site frame as for spinel, but with the smaller symmetry group C_{3i}.

We find that the non-zero tensor components are [12] $\langle T_{-3}^4(3)\rangle$, $\langle T_0^4(3)\rangle$, $\langle T_3^4(3)\rangle$, $\langle T_0^2(3)\rangle$ and $\langle T_0^0(3)\rangle$, as illustrated in figure 2 (see [19] for more details).

It would not be very illuminating to calculate directly the symmetrized tensor in the crystal frame. It is more
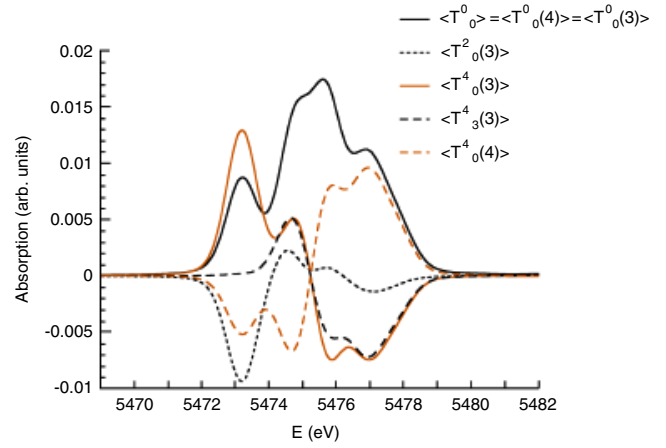

Figure 2. The symmetrized tensors $\langle T_0^0(3)\rangle$, $\langle T_0^2(3)\rangle$, $\langle T_0^4(3)\rangle$ and $\langle T_3^4(3)\rangle$ in the site frame, as well as $\langle T_3^4(4)\rangle$ (for $\alpha = 0$) in the crystal frame, for the electric quadrupole transitions at the K edge of a vanadium atom substituting for aluminum in grossular garnet.

interesting to rotate the tensor. Indeed, when the site has a C_{3i} symmetry group, the z-axis of the orthonormal site frame is specified by the rotation axis, but the y-axis is arbitrary in the plane perpendicular to the rotation axis. This arbitrariness can be quite useful. For instance, the parametrization of the crystal-field Hamiltonian is simplified by choosing the y-axis so that a crystal-field parameter is set to zero (see [14] p 184). This simplifies the calculation of the eigenstates but the parameter reappears as the angle α between the y-axis and the $(1, 1, 0)$ direction of the cube in the plane perpendicular to the $(-1, 1, 1)$ direction.

The corresponding rotation matrix is

$$R = \sqrt{\tfrac{2}{3}}\begin{pmatrix} \cos(\alpha + \pi/3) & \cos(\alpha + 2\pi/3) & \cos\alpha \\ \sin(\alpha + \pi/3) & \sin(\alpha + 2\pi/3) & \sin\alpha \\ -1/\sqrt{2} & 1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix}.$$

The Euler angles are α, $\beta = \arccos(1/\sqrt{3})$ and $\gamma = \pi/4$. The angle α describes a rotation about the axis $(-1, 1, 1)$. Therefore, the α dependence of the result is very simple: $T_m^\ell(\alpha) = T_m^\ell(0)e^{-mi\alpha}$, because the corresponding Wigner matrix is $D_{m'm}^\ell = \delta_{mm'}e^{-im\alpha}$.

To calculate the symmetrized tensor $\langle T_m^4(4)\rangle$ in the cubic axes, we use equation (18), we put $s = \langle T_0^4(3)\rangle$, $t_r + it_i = e^{-3i\alpha}\langle T_3^4(3)\rangle$ and we obtain

$$\langle T_{-4}^4(4)\rangle = \langle T_4^4(4)\rangle^* = -\frac{\sqrt{70}s + 20t_r - 12i\sqrt{3}t_i}{36},$$

$$\langle T_{-3}^4(4)\rangle = -\langle T_3^4(4)\rangle^* = (1-i)\frac{2\sqrt{35}s - 7\sqrt{2}t_r + 3i\sqrt{6}t_i}{36},$$

$$\langle T_{-2}^4(4)\rangle = \langle T_2^4(4)\rangle^* = i\frac{\sqrt{10}s - \sqrt{7}t_r}{9},$$

$$\langle T_{-1}^4(4)\rangle = -\langle T_1^4(4)\rangle^* = (1+i)\frac{2\sqrt{5}s - \sqrt{14}t_r + 3i\sqrt{42}t_i}{36},$$

$$\langle T_0^4(4)\rangle = -\frac{7s + 2\sqrt{70}t_r}{18}. \qquad (23)$$

The symmetrized second-rank tensor in the cubic crystal frame is

$$\langle T_0^2(4) \rangle = 0,$$

$$\langle T_{-2}^2(4) \rangle = \langle T_2^2(4) \rangle^* = -i\lambda,$$

$$\langle T_{-1}^2(4) \rangle = -\langle T_1^2(4) \rangle^* = (1+i)\lambda,$$

where $\lambda = -\langle T_0^2(3) \rangle / \sqrt{6}$ is real.

The effect of the angle α on the experimental spectrum can be considerable, as is illustrated in figure 3.

6. From site symmetry to crystal symmetry

We consider in this section another type of problem. We assume that we have calculated a symmetrized tensor $\langle T^\ell \rangle$ for a certain site A. We want to know the value of the same tensor for all the sites equivalent to A. In the first section, we describe how this can be done. In an x-ray absorption measurement, we measure the average of the signals coming from all sites of the crystal. We present two ways to calculate the average spectrum: the coset method and the brute force method. Finally, we treat the examples of spinel and garnet.

6.1. Changing site

In general, the symmetry of the crystal generates several equivalent sites. Assume that we have calculated a physical property described by a spherical tensor T^ℓ for a given site A. We want to calculate the same property for the equivalent site B.

If $\mathbf{r}_A$ and $\mathbf{r}_B$ are the position vectors of sites A and B, there is a symmetry operation g of the space group such that $\mathbf{r}_B = g\mathbf{r}_A$. If we denote by G_A and G_B the symmetry groups of sites A and B, then any rotoinversion h of G_A is transformed by g into the rotoinversion ghg^{-1} of G_B. A word of caution is in order here. There are two ways to consider h. If it is an element of the space group, it is generally not written as a rotoinversion because it can contain a translation when site A is not at $(0, 0, 0)$. If the origin of the crystal frame is translated to A, then h is a rotoinversion but g contains now an additional translation. In practice, we can drop the translation of g and keep only its rotoinversion part. This will be done implicitly in the following (i.e. h and g stand for the rotoinversion parts of the space group operations h and g).

The tensor $T^\ell(B)$ at site B is related to the tensor $T^\ell(A)$ at site A by the relation

$$T_m^\ell(B) = \epsilon(g) \sum_{m'=-\ell}^{\ell} T_{m'}^\ell(A) D_{m'm}^\ell(g^{-1}). \tag{24}$$

We are now facing a typical subtlety of crystal symmetry. From equation (18), we could have expected the argument of the Wigner matrix to be g instead of g^{-1}. This is actually not the case because, by moving the atoms of the crystal, the operation g transports the reference frame of the site. Therefore, we are in the passive point of view and we need to use g^{-1} since our convention uses the active point of view.
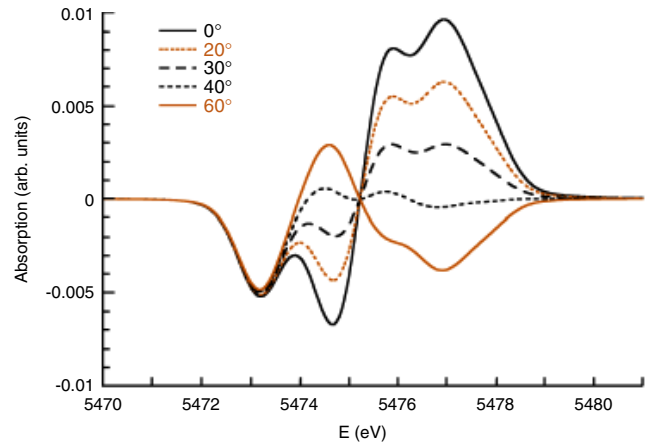

Figure 3. The symmetrized tensor $\langle T_0^4(4) \rangle$ in the crystal frame as a function of α, for the electric quadrupole transitions at the K edge of a vanadium atom substituting for aluminum in grossular garnet.

To check this, we calculate the symmetrized tensor around B.

$$\langle T_m^\ell(B) \rangle = \frac{1}{|G_B|} \sum_{h_B \in G_B} \epsilon(h_B) \sum_{m'=-\ell}^{\ell} T_{m'}^\ell(B) D_{m'm}^\ell(h_B).$$

Now, we can use the fact that, for each rotoinversion h_B of G_B there is a unique rotoinversion h_A of G_A such that $h_B = gh_Ag^{-1}$. Therefore,

$$\langle T_m^\ell(B) \rangle = \frac{1}{|G_A|} \sum_{h_A \in G_A} \epsilon(gh_Ag^{-1})$$
$$\times \sum_{m'=-\ell}^{\ell} T_{m'}^\ell(B) D_{m'm}^\ell(gh_Ag^{-1}),$$

where we used $|G_A| = |G_B|$, a consequence of the isomorphism between G_A and G_B. We see that this is only compatible with the transformations $T^\ell(B) = \epsilon(g)T^\ell(A)D^\ell(g^{-1})$ and $\langle T^\ell(B) \rangle = \epsilon(g)\langle T^\ell(A) \rangle D^\ell(g^{-1})$.

6.2. Changing the x-ray beam

If we have calculated the spectrum of site A for a given incident x-ray beam, it is possible to obtain the spectrum of any site equivalent to A by calculating the spectrum of site A for a rotated x-ray beam. This is physically clear because, if you rotate both the crystal and the x-ray, the spectrum does not change. Thus, if site A is measured with a polarization ϵ and a wavevector $\mathbf{k}$, the spectrum obtained by applying the rotoinversion g on the crystal around A is same as the spectrum of the crystal in its original position, measured with a polarization $g^{-1}\epsilon$ and a wavevector $g^{-1}\mathbf{k}$. To show this, we prove more generally that, if P^a and Q^a are two ath-rank tensors, then $P^a \cdot (gQ^a) = \epsilon_P(g)\epsilon_Q(g)(g^{-1}P^a) \cdot Q^a$. Equations (3) and (13) give us

$$P^a \cdot (gQ^a) = \epsilon_Q(g)P^a \cdot (Q^a D^a(g))$$
$$= \epsilon_Q(g) \sum_{\alpha\beta} (-1)^\alpha P_{-\alpha}^a Q_\beta^a D_{\beta\alpha}^a(g).$$

The symmetry relation (see [3], p 79) $D^a_{\beta\alpha}(g) = (-1)^{\beta-\alpha} D^a_{-\alpha-\beta}(g^{-1})$ enables us to write

$$P^a \cdot (gQ^a) = \epsilon_Q(g) \sum_{\alpha\beta} (-1)^\beta P^a_{-\alpha} D^a_{-\alpha-\beta}(g^{-1}) Q^a_\beta$$
$$= \epsilon_Q(g) \sum_\beta (-1)^\beta (P^a D^a(g^{-1}))_{-\beta} Q^a_\beta$$
$$= \epsilon_Q(g) \epsilon_P(g) (g^{-1} P^a) \cdot Q^a,$$

because $g^{-1}P^a = \epsilon(g^{-1})P^a D^a(g^{-1})$ and $\epsilon(g)\epsilon(g^{-1}) = 1$.

For the example of the electric dipole transition probability (15) we find

$$\{\boldsymbol{\epsilon}^*\otimes\boldsymbol{\epsilon}\}^a \cdot g(\{\mathbf{r}^*_{fi}\otimes\mathbf{r}_{fi}\}^a) = g^{-1}(\{\boldsymbol{\epsilon}^*\otimes\boldsymbol{\epsilon}\}^a) \cdot \{\mathbf{r}^*_{fi}\otimes\mathbf{r}_{fi}\}^a. \quad (25)$$

It remains to prove that the rotation of $\{\boldsymbol{\epsilon}^*\otimes\boldsymbol{\epsilon}\}^a$ corresponds to the rotation of $\boldsymbol{\epsilon}^*$ and $\boldsymbol{\epsilon}$. This is done by using the following identity:

$$g\{P^a\otimes Q^b\}^c = \{(gP^a)\otimes(gQ^b)\}^c.$$

To demonstrate the latter identity, we write the action of a rotoinversion g in terms of the parity operators and the Wigner matrices, and we write the coupled tensor in terms of the Clebsch–Gordan coefficients:

$$g\{P^a\otimes Q^b\}^c_\gamma = \epsilon_P(g)\epsilon_Q(g) \sum_{\alpha\beta\gamma'} (a\alpha b\beta|c\gamma') P^a_\alpha Q^b_\beta D^c_{\gamma'\gamma}(g). \quad (26)$$

The classical identity (C.4) transforms this expression into

$$g\{P^a\otimes Q^b\}^c_\gamma = \epsilon_P(g)\epsilon_Q(g)$$
$$\times \sum_{\alpha\beta\alpha'\beta'} (a\alpha'b\beta'|c\gamma) P^a_\alpha Q^b_\beta D^a_{\alpha\alpha'}(g) D^b_{\beta\beta'}(g)$$
$$= \sum_{\alpha'\beta'} (a\alpha'b\beta'|c\gamma)(gP)^a_{\alpha'}(gQ)^b_{\beta'} = \{(gP^a)\otimes(gQ^b)\}^c_\gamma.$$

Equations (25) and (26) yield

$$\{\boldsymbol{\epsilon}^*\otimes\boldsymbol{\epsilon}\}^a \cdot g(\{\mathbf{r}^*_{fi}\otimes\mathbf{r}_{fi}\}^a) = \{(g^{-1}\boldsymbol{\epsilon}^*)\otimes(g^{-1}\boldsymbol{\epsilon})\}^a \cdot \{\mathbf{r}^*_{fi}\otimes\mathbf{r}_{fi}\}^a.$$

In other words, transforming the crystal by g gives the same result as transforming the x-ray beam by g^{-1}. The same result is true for the electric quadrupole transition probabilities, except for the fact that $\mathbf{k}$ is rotated by g^{-1} as well.

6.3. The coset method

The coset method is a powerful way to calculate the tensor averaged over the crystal from the tensor symmetrized over a single site. However, to make it work, we first need to modify the space group G. For this purpose, we choose a (not necessarily primitive) unit cell of the crystal. There is a group of translations T such that the action of T on the unit cell generates the crystal. We also assume that the group T is invariant under the operations of the point group of G (i.e. the set of rotoinversion parts of the operations of G). If we take the example of spinel, we can choose as a unit cell the conventional cubic cell, which is not primitive. The group T is generated by the pure translations along three orthogonal edges of the cube. If we choose the primitive rhombohedral cell, the group T will be generated by the rhombohedral axes.

To define the *reduced space group* $\overline{G}$, we first consider an equivalence relation where two space group operations are equivalent if their translational parts differ by an element of T. Then, the elements of $\overline{G}$ are the equivalence classes of G under this equivalence relation. We assume that the group T is invariant under the operations of the point group of the space group G. Thus, the product in G induces a product in $\overline{G}$ and $\overline{G}$ is a group. More intuitively, the operations of $\overline{G}$ can be obtained from the operations of G by applying periodic boundary conditions to the unit cell. Consider for instance the symmetry operation $g\mathbf{r} = (y + 1/4, x + 3/4, -z + 1/2)$. We have $g^2\mathbf{r} = (x + 1, y + 1, z)$ in G but $g^2\mathbf{r} = (x, y, z)$ in $\overline{G}$ because of the periodic boundary conditions. The group $\overline{G}$ has a very handy property: it is finite [4].

6.3.1. Mathematical aspects. We first introduce some mathematical concepts [6]. If g is an element of a group G and H a subgroup of G, the set $gH = \{gh : h \in H\}$ is called a *coset*. If we take two elements g and g' of G, then gH and $g'H$ are either identical or disjoint (i.e. they have no element in common). The number of different cosets is $n = |G|/|H|$ (it is an integer by the Euler–Lagrange theorem [6]), and the number of elements in each coset is $|H|$. Moreover, every element of G belongs to one and only one coset. Therefore, if we pick up an arbitrary element g_i in each coset, we have $G = g_1 H \cup \cdots \cup g_n H$ and each g_i is called a *representative* of its coset.

6.3.2. Cosets in a crystal. We now apply these concepts to a crystal. We take the crystal symmetry group to be $\overline{G}$. By definition, the symmetry group of a site A is the set of operations of the space group G that leave site A invariant. It is the same as the set of operations of $\overline{G}$ that leave A invariant [4]. More precisely, if $\mathbf{r}_A$ is the coordinate vector of site A, then $G_A = \{g \in \overline{G}|g(\mathbf{r}_A) = \mathbf{r}_A\}$. It is clear that G_A is isomorphic to a subgroup of $\overline{G}$. In the unit cell, the number of sites equivalent to A is $n = |\overline{G}|/|G_A|$. The group $\overline{G}$ is partitioned into n cosets $g_1 G_A, \ldots, g_n G_A$. All the elements of a given coset send site A to the *same* equivalent site.

The symmetrized tensor $\langle T^\ell \rangle_X$ over the full crystal is obtained from the site-symmetrized tensor $\langle T^\ell \rangle_A$ by the operation

$$\langle T^\ell \rangle_X = \frac{1}{n} \sum_{i=1}^n \epsilon(g_i) \langle T^\ell \rangle_A D^\ell(g_i^{-1}). \quad (27)$$

Equation (27) can be described by saying that, starting from the average over the symmetry of site A, we go to all equivalent sites with g_i and we average over the symmetry of these other sites.

We show now that equation (27) gives the same result as an average over all crystal symmetry operations. We already know that

$$\langle T^\ell \rangle_A = \frac{1}{|G_A|} \sum_{h \in G_A} \epsilon(h) T^\ell D^\ell(h)$$
$$= \frac{1}{|G_A|} \sum_{h \in G_A} \epsilon(h) T^\ell D^\ell(h^{-1}),$$

because the sum over the elements of a group is the same as the sum over the inverse elements of this group and $\epsilon(h^{-1}) = \epsilon(h)$. Therefore

$$
\begin{aligned}
\langle T^\ell \rangle_X &= \frac{1}{n|G_A|} \sum_{i=1}^{n} \sum_{h \in G_A} \epsilon(h)\epsilon(g_i) T^\ell D^\ell(h^{-1}) D^\ell(g_i^{-1}) \\
&= \frac{1}{|\overline{G}|} \sum_{i=1}^{n} \sum_{h \in G_A} \epsilon(hg_i) T^\ell D^\ell(h^{-1}g_i^{-1}) \\
&= \frac{1}{|\overline{G}|} \sum_{i=1}^{n} \sum_{h \in G_A} \epsilon(g_i h) T^\ell D^\ell((g_i h)^{-1}) \\
&= \frac{1}{|\overline{G}|} \sum_{g \in \overline{G}} \epsilon(g) T^\ell D^\ell(g),
\end{aligned}
$$

where we used $(g_i h)^{-1} = h^{-1} g_i^{-1}$ and $|\overline{G}| = n|G_A|$. Note that the proof holds because we defined cosets to be $g_i G_A$ (i.e. left cosets) and not $G_A g_i$ (i.e. right cosets).

In other words, the average over the site symmetry followed by the average over the sites gives the average over the crystal symmetry. This can be considered as a factorization of the average, because $\sum_g = \sum_h \sum_{g_i^{-1}}$. It can be checked that the result of equation (27) is the same if we replace g_i by any g_i' in $g_i G_A$. We illustrate the coset method with our two favorite examples, spinel and garnet.

6.3.3. The example of spinel. We call the site $(0, 1/4, 3/4)$ of the spinel structure site A. The reduced space group $\overline{G}$ has 192 operations[2]. Twelve of them leave site A invariant: (x, y, z), $(-z+3/4, -x+1/4, y+1/2)$, $(-y+1/4, z-1/2, -x+3/4)$, $(y-1/4, x+1/4, -z+3/2)$, $(-x, 1-z, 1-y)$, $(z-3/4, -y+1/2, x+3/4)$, $(-x, -y+1/2, -z+3/2)$, $(z-3/4, x+1/4, 1-y)$, $(y-1/4, 1-z, x+3/4)$, $(-y+1/4, -x+1/4, z)$, $(x, z-1/2, y+1/2)$, and $(-z+3/4, y, -x+3/4)$. This set of 12 operations defines a group isomorphic to D_{3d}. The isomorphism φ is described explicitly as follows. If $\mathbf{r}_A$ is the coordinate vector of site A, for any operation g of the set, we define the operation $\varphi(g)$ by $\varphi(g)(\mathbf{r}) = g(\mathbf{r} + \mathbf{r}_A) - \mathbf{r}_A$. In practice, $\varphi(g)$ is obtained by removing the translation of g. The map φ is an isomorphism because $\varphi(g'g) = \varphi(g')\varphi(g)$:

$$
\begin{aligned}
\varphi(g')\varphi(g)(\mathbf{r}) &= \varphi(g')(g(\mathbf{r} + \mathbf{r}_A) - \mathbf{r}_A) \\
&= (g'g)(\mathbf{r} + \mathbf{r}_A) - \mathbf{r}_A = \varphi(g'g)(\mathbf{r}),
\end{aligned}
$$

and it can be checked that the images by φ of the first six operations are the rotations listed in section 5.3.2, the images of the other six operations are the same rotations multiplied by the inversion. The space group operations g are selected by the condition that the site is fixed: $g(\mathbf{r}_A) = \mathbf{r}_A$. Thus, the origin is a fixed point of $\varphi(g)$: $\varphi(g)(0) = g(\mathbf{r}_A) - \mathbf{r}_A = 0$.

There are 16 sites equivalent to A because the ratio $|Fd\bar{3}m|/|D_{3d}|$ is 16. However, each site is equivalent to three other sites by pure lattice translations with translation vectors $(1/2, 1/2, 0)$, $(1/2, 0, 1/2)$ and $(0, 1/2, 1/2)$. The x-ray spectrum of these sites will be equal because their orientations with respect to the x-ray beam are the same. Therefore, we are left with four equivalent sites: A itself and the sites with

---

[2] This is because we use the conventional cubic unit cell [18]. Using a primitive (rhombohedral) unit cell reduces this number to 48.

coordinates $(1/4, 3/4, 0)$, $(3/4, 0, 1/4)$ and $(1/2, 1/2, 1/2)$. A representative of the coset corresponding to each of these sites is (y, z, x), (z, x, y) and $(-x + 1/2, y + 1/4, z - 1/4)$.

6.3.4. The example of garnet. We consider now site A as the Al site in grossular garnet with coordinates $(1/2, 1/2, 0)$. It is invariant by the following six operations: identity, (x, y, z); rotation through $2\pi/3$ about the $(-1, 1, 1)$ axis, $(1 - y, z + 1/2, -x + 1/2)$; rotation through $4\pi/3$ about the $(-1, 1, 1)$ axis, $(-z + 1/2, 1 - x, y - 1/2)$; and the same operations multiplied by the inversion, $(1 - x, 1 - y, -z)$, $(y, -z + 1/2, x - 1/2)$ and $(z + 1/2, x, -y + 1/2)$. This group is C_{3i}. The number of cosets (i.e. the number of sites equivalent to A) is $|Ia\bar{3}d|/|C_{3i}| = 16$. If we remove the lattice translation $(1/2, 1/2, 1/2)$ we are left with eight equivalent sites.

The approach in terms of cosets is quite powerful in practice because it completely avoids the explicit description of the sites and of the geometric operations that transform a specific site into another one. Many programs compute the symmetry operations of the sites (for example Quantum-ESPRESSO [20]). It is thus enough to take one of these sites, to choose any representative g_i in each coset and to calculate the contribution of all equivalent sites by the formula $\epsilon(g_i)\langle T^\ell \rangle_A D^\ell(g_i^{-1})$. The average over the crystal is then obtained with equation (27).

6.4. The brute force method

If one is not interested in the contribution of each site to the spectrum of the crystal, a still simpler solution is to take the average of $\langle T^\ell \rangle_A$ over all the symmetry operations of the crystal. This is not very clever because the site operations have already been taken into account and we average over them a second time, but this method can simplify the computer implementation.

We show now that averaging the site-symmetrized tensor over all the symmetry operations of the crystal gives the same result as the coset method.

$$
\begin{aligned}
\frac{1}{|\overline{G}|} \sum_{g \in \overline{G}} &\epsilon(g)\langle T^\ell \rangle_A D^\ell(g) \\
&= \frac{1}{|G_A||\overline{G}|} \sum_{h \in G_A} \sum_{g \in \overline{G}} \epsilon(h)\epsilon(g) T^\ell D^\ell(h) D^\ell(g) \\
&= \frac{1}{n|G_A|^2} \sum_{h,h' \in G_A} \sum_i \epsilon(h)\epsilon(h')\epsilon(g_i) \\
&\quad \times T^\ell D^\ell(h) D^\ell(h') D^\ell(g_i^{-1}) \\
&= \frac{1}{n|G_A|} \sum_{h \in G_A} \sum_i \epsilon(h)\epsilon(g_i) T^\ell D^\ell(h) D^\ell(g_i^{-1}) \\
&= \langle T^\ell \rangle_X,
\end{aligned}
$$

where we used the identity $\sum_{h,h' \in G_A} \epsilon(hh') D^\ell(hh') = |G_A| \sum_{h \in G_A} \epsilon(h) D^\ell(h)$. This equation is readily established by noting that, in the sum $\sum_{h,h' \in G_A}$, each group element appears exactly $|G_A|$ times.

Therefore, the average over all the symmetry operations of the crystal gives the same result as the average over the sites, irrespective of the number of equivalent sites.

6.5. The case of spinel

We illustrate the coset method with the case of spinel. We first notice that the absorption cross-section is invariant under a translation of the Bravais lattice, because such a translation multiplies the wavefunction by a phase (independent of **r**) that disappears in the square modulus. Therefore, by removing the translations, we can replace the representatives of the four cosets given in section 6.3.3 by the four rotations about the *z*-axis of the crystal through angles 0, $\pi/2$, π and $3\pi/2$. For a fourth-rank tensor, the average over these coset operations is rather drastic. The only non-zero elements of the matrix $M = (1/4)\sum_i D^4(g_i^{-1})$ are $M(-4,-4) = M(0,0) = M(4,4) = 1$. Therefore, the crystal-averaged fourth-rank tensor is $\langle T^4\rangle_X = \langle T^4(4)\rangle M$:

$$\langle T_0^4\rangle_X = \sqrt{\tfrac{14}{5}}\langle T_4^4\rangle_X = \sqrt{\tfrac{14}{5}}\langle T_{-4}^4\rangle_X = \langle T_0^4(4)\rangle.$$

The relation between $\langle T_0^4(4)\rangle$ and the site-symmetrized tensor in the trigonal axes is given by equation (21).

For a second-rank tensor, the matrix $M = (1/4)\sum_i D^2(g_i^{-1})$ has a single non-zero element: $M(0,0) = 1$. Therefore $\langle T_0^2\rangle_X = 0$, as expected [12].

6.6. The case of garnet

To calculate the spherical tensor of garnet, we use the brute force method and calculate $M = (1/48)\sum_g D^\ell(g)$, where the sum runs over all the symmetry operations of the cube and the tensor is assumed to be even.

For $\ell = 4$, the only non-zero matrix elements are

$$M(4,4) = M(-4,4) = M(4,-4) = M(-4,-4) = \tfrac{5}{24},$$

$$M(4,0) = M(0,4) = M(0,-4) = M(-4,0) = \tfrac{\sqrt{70}}{24},$$

$$M(0,0) = \tfrac{7}{12}.$$

Therefore, the only non-zero components of a fourth-rank tensor are

$$\langle T_0^4\rangle_X = \sqrt{\frac{14}{5}}\langle T_4^4\rangle_X = \sqrt{\frac{14}{5}}\langle T_{-4}^4\rangle_X = \langle T_0^4(4)\rangle$$
$$= -\frac{7s + 2\sqrt{70}t_r}{18},$$

where we recall that $s = \langle T_0^4(3)\rangle$ and $t_r = (1/2)(e^{-3i\alpha}\langle T_3^4(3)\rangle + e^{3i\alpha}\langle T_3^4(3)\rangle^*)$.

7. Conclusion

We have tried to provide the main tools required for the calculation of a site-dependent property in a crystal. Although most of these methods are probably known to the expert, we were not able to find them presented in a systematic and pedagogical way. These tools proved quite efficient for the calculation of the x-ray absorption spectra of impurities in crystals [1]. The computation time was approximately divided by the number of equivalent sites of the crystal. Moreover, the group theoretical methods were useful to determine the properties of the spectra, for example the fact that the spectra of two sites have to be equal for a specific direction of the polarization vector.

The property we considered (x-ray absorption spectrum) is relatively simple because translations do not play any role. A similar calculation for x-ray scattering would require an explicit treatment of translations. The tools provided here can be extended to this case.

Appendix A. Spherical average

In Cartesian coordinates, the electric dipole absorption cross-section can be written, for linearly polarized x-rays, as

$$\sigma^D(\epsilon) = \sum_{ij}\epsilon_i\epsilon_j\sigma_{ij},$$

with

$$\sigma_{ij} = 4\pi^2\alpha_0\hbar\omega\sum_f\langle i|\mathbf{r}_i|f\rangle\langle f|\mathbf{r}_j|i\rangle\delta(E_f - E_i - \hbar\omega).$$

It is well known that the absorption spectrum of a powder is given by the spherical average

$$\langle\sigma^D(\epsilon)\rangle = \tfrac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}).$$

For electric quadrupole transitions, the average is more complicated. If we write the electric quadrupole absorption cross-section for linearly polarized x-rays

$$\sigma(\epsilon,\mathbf{k}) = \sum_{ijlm}\epsilon_i k_j\epsilon_l k_m\sigma_{ijlm}, \tag{A.1}$$

with

$$\sigma_{ijlm} = \pi^2\alpha_0\hbar\omega\sum_f\langle i|\mathbf{r}_i\mathbf{r}_j|f\rangle\langle f|\mathbf{r}_l\mathbf{r}_m|i\rangle\delta(E_f - E_i - \hbar\omega), \tag{A.2}$$

the absorption by a powder is given by the spherical average

$$\langle\sigma(\epsilon,\mathbf{k})\rangle = \frac{k^2}{30}(2\sigma_{xxxx} + 2\sigma_{yyyy} + 2\sigma_{zzzz} + 6\sigma_{xyxy} + 6\sigma_{xzxz}$$
$$+ 6\sigma_{yzyz} - \sigma_{xxyy} - \sigma_{xxzz} - \sigma_{yyxx} - \sigma_{zzxx}$$
$$- \sigma_{yyzz} - \sigma_{zzyy}).$$

This average was obtained by substituting the second and third columns of the rotation matrix (B.1) for the unit vectors ϵ and $\mathbf{k}/k$ in the absorption cross-section (A.1) and by averaging over all angles α, β and γ. The result was then simplified by using the symmetries of the tensor σ_{ijlm} that can be read from equation (A.2). If the system is non-magnetic, then $\sigma_{iijj} = \sigma_{jjii}$ and the average further simplifies

$$\langle\sigma(\epsilon,\mathbf{k})\rangle = \frac{k^2}{15}(\sigma_{xxxx} + \sigma_{yyyy} + \sigma_{zzzz} + 3\sigma_{xyxy} + 3\sigma_{xzxz}$$
$$+ 3\sigma_{yzyz} - \sigma_{xxyy} - \sigma_{xxzz} - \sigma_{yyzz}).$$

Appendix B. Formulae

B.1. Rotation matrix

In this section we give several expressions for the rotation matrices.

B.1.1. Axis and angle.
The rotation through an angle ψ about the direction $\mathbf{n}$ (a unit vector) is represented by the rotation matrix $R = \mathrm{Id} + \sin\psi\, N + (1 - \cos\psi) N^2$, where N is the skew-symmetric matrix with matrix elements $N_{ij} = -\sum_k \epsilon_{ijk} n_k$, so that $(N^2)_{ij} = n_i n_j - \delta_{ij}$ (see [2], p 10).

Conversely, the rotation angle ψ and the rotation axis $\mathbf{n}$ are determined from the rotation matrix R by the relations $\cos\psi = (\mathrm{tr}\,R - 1)/2$, $n_1 \sin\psi = (R_{32} - R_{23})/2$, $n_2 \sin\psi = (R_{13} - R_{31})/2$ and $n_3 \sin\psi = (R_{21} - R_{12})/2$. This is a corrected version of the relation given in [2] p 20.

B.1.2. Euler angles.
The rotation matrix can be expressed in terms of the Euler angles α, β and γ (see [2], p 24)

$$R = \begin{pmatrix} c_\alpha c_\beta c_\gamma - s_\alpha s_\gamma & -c_\alpha c_\beta s_\gamma - s_\alpha c_\gamma & c_\alpha s_\beta \\ s_\alpha c_\beta c_\gamma + c_\alpha s_\gamma & -s_\alpha c_\beta s_\gamma + c_\alpha c_\gamma & s_\alpha s_\beta \\ -s_\beta c_\gamma & s_\beta s_\gamma & c_\beta \end{pmatrix}, \quad \text{(B.1)}$$

where $0 \leqslant \alpha < 2\pi$, $0 \leqslant \beta \leqslant \pi$ and $0 \leqslant \gamma < 2\pi$, $c_\alpha = \cos\alpha$, $s_\alpha = \sin\alpha$ etc. There is a one-to-one correspondence between rotations and parameters in this range, except for the cases $\beta = 0$ and π, which describe the rotation through the angle $\alpha + \gamma$ and $\alpha - \gamma$, respectively, about the axis $(0, 0, 1)$.

B.1.3. Euler–Rodrigues parameters.
Although the Euler angles are more common, the Euler–Rodrigues parameters have the advantage that the relation between these parameters and the rotation matrix elements does not involve trigonometric functions. Thus, they are convenient to derive analytical expressions. From the rotation axis $\mathbf{n}$ and angle ψ, we define the Euler–Rodrigues parameters $\alpha_0 = \cos(\psi/2)$, $\alpha_i = \sin(\psi/2) n_i$ ([2], p 54). In terms of these parameters, the rotation matrix is

$$R = \begin{pmatrix} \alpha_0^2 + \alpha_1^2 - \alpha_2^2 - \alpha_3^2 & 2\alpha_1\alpha_2 - 2\alpha_0\alpha_3 & 2\alpha_1\alpha_3 + 2\alpha_0\alpha_2 \\ 2\alpha_1\alpha_2 + 2\alpha_0\alpha_3 & \alpha_0^2 + \alpha_2^2 - \alpha_3^2 - \alpha_1^2 & 2\alpha_2\alpha_3 - 2\alpha_0\alpha_1 \\ 2\alpha_1\alpha_3 - 2\alpha_0\alpha_2 & 2\alpha_2\alpha_3 + 2\alpha_0\alpha_1 & \alpha_0^2 + \alpha_3^2 - \alpha_1^2 - \alpha_2^2 \end{pmatrix}.$$

Conversely, the Euler–Rodrigues parameters can be obtained from the rotation matrix R ([2], p 54). If $\mathrm{tr}\,R \neq -1$, then $\alpha_0 = \sqrt{\mathrm{tr}\,R + 1}/2$, $\alpha_1 = (R_{32} - R_{23})/(4\alpha_0)$, $\alpha_2 = (R_{13} - R_{31})/(4\alpha_0)$, and $\alpha_3 = (R_{21} - R_{12})/(4\alpha_0)$. If $\mathrm{tr}\,R = -1$, then $\alpha_0 = 0$ and $\alpha_i = (\mathrm{sign}\,\alpha_i)\sqrt{(1 + R_{ii})/2}$ for $i = 1, 2, 3$, with $\mathrm{sign}\,\alpha_1 = 1$, $\mathrm{sign}\,\alpha_2 = \mathrm{sign}\,R_{12}$, and $\mathrm{sign}\,\alpha_3 = \mathrm{sign}\,R_{13}$.

B.2. Solid harmonics

For a vector $\mathbf{r} = (x, y, z)$, the solid harmonics $Y_\ell^m(\mathbf{r})$ are defined by (see [2], p 71)

$$Y_\ell^m(\mathbf{r}) = \sqrt{\frac{(2\ell + 1)(\ell + m)!(\ell - m)!}{4\pi}}$$
$$\times \sum_k \frac{(-x - \mathrm{i}y)^{k+m}(x - \mathrm{i}y)^k z^{\ell - 2k - m}}{2^{2k+m}(k + m)! k! (l - m - 2k)!},$$

where k runs from $\max(0, -m)$ to the integer part of $(\ell - m)/2$. The most important example of solid harmonics is

$$Y_1(\mathbf{r}) = \sqrt{\frac{3}{4\pi}} \begin{pmatrix} \frac{x - \mathrm{i}y}{\sqrt{2}} \\ z \\ -\frac{x + \mathrm{i}y}{\sqrt{2}} \end{pmatrix},$$

where the upper component is $Y_1^{-1}(\mathbf{r})$.

B.3. Wigner matrices

There are several representations of the Wigner rotation matrices. We present here the expressions in terms of Euler angles and of Euler–Rodrigues parameters. Other formulae have been derived, for example the recent invariant spinor representation [21].

B.3.1. Euler angles.
For a rotation R expressed in terms of Euler angles α, β, γ, the Wigner matrix is ([2], p 46)

$$D_{m'm}^\ell(R) = \mathrm{e}^{-\mathrm{i}m'\alpha} d_{m'm}^\ell(\beta) \mathrm{e}^{-\mathrm{i}m\gamma}.$$

Various expressions exist for the reduced Wigner matrix $d_{m'm}^\ell(\beta)$. The following formula (valid for half-integer ℓ) is particularly convenient for computers, because it (almost) avoids the presence of singular terms ([2], p 50, [3], p 78):

$$d_{m'm}^\ell(\beta) = (-1)^\lambda \sqrt{\frac{k!(2\ell - k)!}{(k + \mu)!(k + \nu)!}}$$
$$\times \left(\sin\frac{\beta}{2}\right)^\mu \left(\cos\frac{\beta}{2}\right)^\nu P_k^{(\mu,\nu)}(\cos\beta),$$

where $\mu = |m - m'|$, $\nu = |m + m'|$, $k = \ell - (\mu + \nu)/2$ and $\lambda = 0$ if $m \geqslant m'$, $\lambda = m - m'$ if $m < m'$. In this expression, the only possible numerical difficulty occurs with 0^0, that should be set to unity. The Jacobi polynomials $P_k^{(\mu,\nu)}(x)$ are given by the formula

$$P_k^{(\mu,\nu)}(x) = \sum_{i=0}^k \binom{k + \mu}{i}\binom{k + \nu}{k - i}\left(\frac{x - 1}{2}\right)^{k-i}\left(\frac{x + 1}{2}\right)^i.$$

For example, the Wigner matrix for first-rank tensors is

$$D^1 = \begin{pmatrix} \frac{\cos\beta + 1}{2}\mathrm{e}^{\mathrm{i}(\alpha+\gamma)} & \frac{\sin\beta}{\sqrt{2}}\mathrm{e}^{\mathrm{i}\alpha} & \frac{1 - \cos\beta}{2}\mathrm{e}^{\mathrm{i}(\alpha-\gamma)} \\ -\frac{\sin\beta}{\sqrt{2}}\mathrm{e}^{\mathrm{i}\gamma} & \cos\beta & \frac{\sin\beta}{\sqrt{2}}\mathrm{e}^{-\mathrm{i}\gamma} \\ \frac{1 - \cos\beta}{2}\mathrm{e}^{\mathrm{i}(\gamma-\alpha)} & -\frac{\sin\beta}{\sqrt{2}}\mathrm{e}^{-\mathrm{i}\alpha} & \frac{\cos\beta + 1}{2}\mathrm{e}^{-\mathrm{i}(\alpha+\gamma)} \end{pmatrix},$$

where the upper left matrix element is D_{-1-1}^1. Two useful special cases are $d_{m'm}^\ell(0) = \delta_{mm'}$ and $d_{m'm}^\ell(\pi) = (-1)^{\ell-m}\delta_{m',-m}$.

B.3.2. Euler–Rodrigues parameters.
In terms of the Euler–Rodrigues parameters, the Wigner rotation matrix is ([2], p 54)

$$D_{m'm}^\ell(R) = \sqrt{(\ell + m')!(\ell - m')!(\ell + m)!(\ell - m)!}$$
$$\times \sum_k \{(\alpha_0 - \mathrm{i}\alpha_3)^{\ell+m-k}(-\mathrm{i}\alpha_1 - \alpha_2)^{m'-m+k}$$
$$\times (-\mathrm{i}\alpha_1 + \alpha_2)^k (\alpha_0 + \mathrm{i}\alpha_3)^{\ell-m'-k}\}$$
$$\times \{(\ell + m - k)!(m' - m + k)! k! (\ell - m' - k)!\}^{-1},$$

where k runs from $\max(0, m - m')$ to $\min(\ell + m, \ell - m')$.

B.4. Butler's orientation

The powerful multiplet program developed by Thole and colleagues is based on Butler's conventions. For the calculation of trigonal sites in cubic crystals, it is necessary to know precisely the relation between the cubic and trigonal reference frames, which is not clearly stated in Butler's book. To determine it, we combine Butler's tables pp 522, 527 and 549 of [14]. This shows that the transition between spherical harmonics $|1m\rangle_3$ in the trigonal axes (i.e. in the O–D_3–C_3 basis) and spherical harmonics $|1m\rangle_4$ in the cubic axes (i.e. in the O–D_4–C_4 basis) is

$$|1-1\rangle_3 = |1-1\rangle_4 \frac{(1-i)(\sqrt{3}+1)}{\sqrt{24}} + |10\rangle_4 \frac{1}{\sqrt{3}}$$
$$+ |11\rangle_4 \frac{(1+i)(\sqrt{3}-1)}{\sqrt{24}},$$

$$|10\rangle_3 = |1-1\rangle_4 \frac{-1+i}{\sqrt{6}} + |10\rangle_4 \frac{1}{\sqrt{3}} + |11\rangle_4 \frac{1+i}{\sqrt{6}},$$

$$|11\rangle_3 = |1-1\rangle_4 \frac{(1-i)(\sqrt{3}-1)}{\sqrt{24}} + |10\rangle_4 \frac{-1}{\sqrt{3}}$$
$$+ |11\rangle_4 \frac{(1+i)(\sqrt{3}+1)}{\sqrt{24}}.$$

This can be rewritten

$$|1m\rangle_3 = \sum_{m'=-1}^{1} |1m'\rangle_4 D^1_{m'm}(R),$$

for the rotation R corresponding to the Euler angles $\alpha = 3\pi/4$, $\beta = \beta_0 = \arccos(1/\sqrt{3})$ and $\gamma = \pi$. This corresponds to the C_{3z} axis of D_3 along the $(-1, 1, 1)$ direction of the cube and the C_{2y} axis of D_3 along the $(1, 1, 0)$ direction of the cube (see figure 11.6 of [14], p 204). The inverse rotation has Euler angles $(0, \beta_0, \pi/4)$. More precisely, the rotation

$$R = R(3\pi/4, \beta_0, \pi) = \begin{pmatrix} 1/\sqrt{6} & 1/\sqrt{2} & -1/\sqrt{3} \\ -1/\sqrt{6} & 1/\sqrt{2} & 1/\sqrt{3} \\ \sqrt{2/3} & 0 & 1/\sqrt{3} \end{pmatrix},$$
(B.2)

transforms any symmetry operation R' in the D_{3d} axes into the symmetry operation $RR'R^{-1}$ in the cubic axes.

Appendix C. Coupling identities

We gather some useful coupling formulae. If **a**, **b**, **c** and **d** are vectors, we denote by $\mathbf{a}^1$, $\mathbf{b}^1$, $\mathbf{c}^1$ and $\mathbf{d}^1$ the corresponding first-rank spherical tensors. Then, according to [3] p 66 and 67,

$$\{\mathbf{a}^1 \otimes \mathbf{b}^1\}^1 = \frac{i}{\sqrt{2}}(\mathbf{a} \times \mathbf{b})^1.$$
(C.1)

$$\{\{\mathbf{a}^1 \otimes \mathbf{b}^1\}^0 \otimes \{\mathbf{c}^1 \otimes \mathbf{d}^1\}^0\}^0 = \frac{1}{3}(\mathbf{a} \cdot \mathbf{b})(\mathbf{c} \cdot \mathbf{d}).$$
(C.2)

$$\{\{\mathbf{a}^1 \otimes \mathbf{b}^1\}^2 \otimes \{\mathbf{c}^1 \otimes \mathbf{d}^1\}^2\}^0 = \frac{1}{\sqrt{5}}(\frac{1}{2}(\mathbf{a} \cdot \mathbf{c})(\mathbf{b} \cdot \mathbf{d}) + \frac{1}{2}(\mathbf{a} \cdot \mathbf{d})(\mathbf{b} \cdot \mathbf{c})$$
$$- \frac{1}{3}(\mathbf{a} \cdot \mathbf{b})(\mathbf{c} \cdot \mathbf{d})).$$
(C.3)

To prove equation (14), we start from the identity

$$\{P^a \otimes Q^b\}^c \cdot \{R^d \otimes S^e\}^c = (-1)^{2a+b-d} \sum_g (2c+1)$$

$$\times \begin{Bmatrix} a & b & c \\ e & d & g \end{Bmatrix} \{P^a \otimes R^d\}^g \cdot \{Q^b \otimes S^e\}^g,$$

where g runs from $\max(|a-d|, |b-e|)$ to $\min(a+d, b+e)$ (see equation (13), p 70 of [3]). Equation (14) corresponds to the case $c = 0$ because of the special value of the $6j$-symbol (equation (1), p 299 of [3]),

$$\begin{Bmatrix} a & b & 0 \\ e & d & g \end{Bmatrix} = (-1)^{a+d+g} \frac{\delta_{ab}\delta_{de}}{\sqrt{(2a+1)(2d+1)}}.$$

The interplay between Wigner matrices and Clebsch–Gordan coefficients is described by the following identity (equation (5), p 85 of [3]):

$$\sum_\gamma (a\alpha b\beta|c\gamma)D^c_{\gamma\gamma'}(R) = \sum_{\alpha'\beta'}(a\alpha' b\beta'|c\gamma')D^a_{\alpha\alpha'}(R)D^b_{\beta\beta'}(R).$$
(C.4)

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