research papers

X-ray resonant magnetic scattering: polarization dependence in the non-spherical case

Alessandro Mirone,[a]* Laurence Bouchenoire[b,c] and Simon Brown[b,c]

[a] European Synchrotron Radiation Facility (ESRF), 6 rue Jules Horowitz, BP 220, F-38043 Grenoble CEDEX, France, [b]XMaS, ESRF, 6 rue Jules Horowitz, BP220, F-38043 Grenoble, France, and [c]Department of Physics, University of Liverpool, Oliver Lodge Laboratory, Oxford Street, Liverpool L69 7ZE, UK. Correspondence e-mail: mirone@esrf.fr

A simple tensorial contraction method has been developed to obtain analytical formulae for X-ray resonant magnetic scattering. First, the method has been applied considering electric dipole–dipole and electric quadrupole–quadrupole scattering in the isolated-atom approximation. The results have been compared with previous work. The same method has then been extended to non-spherical systems by deriving new phenomenological formulae.

1. Introduction

X-ray magnetic scattering (XRMS) exhibits enhancement at resonances corresponding to localized electronic states (Gibbs, 1988; Carra & Thole, 1994). Because of its coherent nature, element specificity and polarization dependence, XRMS can be used to determine both the spatial distribution and orientation of matter's magnetization.

To plan experiments and analyse data, there is a strong necessity for simple analytical formulae that directly relate the experimental geometry, sample orientation and photon polarization to the measured scattered intensity. Simple formulae for XRMS amplitude can be found in the literature with the spherical-atom approximation (Hill & McMorrow, 1996). They are composed of a sum of terms, each term being the product of a geometrical expression, containing polarization vectors, multiplied by energy-dependent complex-valued functions. In a phenomenological analysis, where one is interested in separating the different contributions to the spectra, one can take theses functions as free parameters, under the constraint that dispersion relations are satisfied.

These simple formulae for the cross section have been successfully used in the resonant studies of rare-earth compounds (Detlefs et al., 1997; Perry et al., 1998; Dumesnil et al., 2000; Stunault et al., 2002; Kim et al., 2005). However, they cannot account for forbidden reflections arising from the joint effect of magnetic ordering and local crystal field (Ovchinnikova & Dmitrienko, 1997, 2000).

In this paper, we derive a simple and understandable theoretical framework within which we recover previous XRMS formulae and extend them to non-spherical systems. As an example, we show that, for basal-plane spiral holmium, our new expression for the cross section predicts the existence of extra reflections which are otherwise forbidden.

2. Introduction to scattering factors

The resonant scattering of a photon described by a wavevector $\mathbf{k}$ and polarization $\boldsymbol{\varepsilon}$ can be written in terms of electric dipole and quadrupole interactions, disregarding the spin–magnetic field interaction (Blume, 1994):

$$F_{\boldsymbol{\varepsilon}\mathbf{k}\to\boldsymbol{\varepsilon}'\mathbf{k}'} = \frac{m}{\hbar}\sum_n \frac{\omega_n^2 \langle 0|(\boldsymbol{\varepsilon}'\cdot\mathbf{r} - \frac{i}{2}\mathbf{k}'\cdot\mathbf{r}\boldsymbol{\varepsilon}\cdot\mathbf{r})|n\rangle\langle n|(\boldsymbol{\varepsilon}\cdot\mathbf{r} + \frac{i}{2}\mathbf{k}\cdot\mathbf{r}\boldsymbol{\varepsilon}\cdot\mathbf{r})|0\rangle}{\omega - \omega_n + i\delta},$$

(1)

where $\langle n|$ is a complete set of eigenstates of matter, $\langle 0|$ being the initial state, and $\hbar\omega_n$ is the energy difference between $\langle n|$ and $\langle 0|$.

As the atoms are going to be described as spherical entities plus some kind of distortion, one can consider the spherical group and how the angular part of the different terms of equation (1) decomposes on the irreducible representations of such a group. The scalar product $\boldsymbol{\varepsilon}\cdot\mathbf{r}$ can be rewritten as a sum of products of rank 1 spherical harmonic tensor components:

$$\boldsymbol{\varepsilon}\cdot\mathbf{r} = \sum_{q=-1}^{q=+1} \varepsilon_q^{1*} r_q^1,$$

(2)

where, given a Cartesian vector $\mathbf{A}$, its spherical tensor components are

$$\begin{aligned} A_0^1 &= A_z \\ A_1^1 &= -(A_x + iA_y)/2^{1/2} \\ A_{-1}^1 &= (A_x - iA_y)/2^{1/2}. \end{aligned}$$

(3)

The product $(\mathbf{k}\cdot\mathbf{r})(\boldsymbol{\varepsilon}\cdot\mathbf{r})$ can be written as follows:

$$(\mathbf{k}\cdot\mathbf{r})(\boldsymbol{\varepsilon}\cdot\mathbf{r}) = \tfrac{1}{3}(\mathbf{k}\cdot\boldsymbol{\varepsilon})(\mathbf{r}\cdot\mathbf{r}) + \sum_{q=-2}^{q=+2}(k\varepsilon)_q^*(\mathbf{rr})_q,$$

(4)

where, given two Cartesian vectors $\mathbf{A}$ and $\mathbf{B}$, the symbols $(\mathbf{AB})_q$ denote the rank 2 spherical symmetric tensor components of their products, which are:

$$
\begin{aligned}
(\mathbf{AB})_0 &= \frac{1}{6^{1/2}}(2A_zB_z - A_xB_x - A_yB_y) \\
(\mathbf{AB})_{\pm 1} &= \mp\tfrac{1}{2}[A_xB_z + A_zB_x \pm i(A_yB_z + A_zB_y)] \\
(\mathbf{AB})_{\pm 2} &= \tfrac{1}{2}[A_xB_x - A_yB_y \pm i(A_xB_y + A_yB_x)].
\end{aligned} \quad (5)
$$

According to equation (4), spherical tensorial components of the tensor product $\mathbf{k} \otimes \boldsymbol{\varepsilon}$ are coupled to the same rank components of the product $\mathbf{r} \otimes \mathbf{r}$ to form a scalar. As the product $\mathbf{r} \otimes \mathbf{r}$ has no antisymmetric component, the rank 1 components of the product $\mathbf{k} \otimes \boldsymbol{\varepsilon}$ do not appear in equation (4).

The transformations of equations (2) and (5) are used to simplify the scattering-factor expression by choosing the angular moment quantization axis in the most appropriate way.

In the next section, a spherical system is treated as being perturbed by a magnetic exchange interaction. In §4, a non-spherical perturbation term is considered and a phenomenological expression is derived for the magnetic scattering amplitude. We consider the case of holmium as an example. For such a system, the deviation from spherical symmetry contains both a parity even and a parity odd term. We find that the former gives a correction to the dipole–dipole (E1–E1) and quadrupole–quadrupole (E2–E2) scattering amplitudes. That correction merges with the spherical symmetry formulae while the parity odd term gives rise to dipole–quadrupole (E1–E2) Bragg peaks which are otherwise forbidden.

3. Derivation of formulae for the spherical case with a magnetic field perturbation

For a spherical atom perturbed by a magnetic exchange field, the final scattering amplitude expression does not mix dipolar with quadrupolar terms because of parity conservation. We take the angular moment quantization axis $\hat{\boldsymbol{\xi}}$ along the magnetic field. Terms having different quantization number q will not mix. The expression for the scattering amplitudes then assumes the following simple form:

$$
F_{\boldsymbol{\varepsilon}\mathbf{k}\to\boldsymbol{\varepsilon}'\mathbf{k}'} = \frac{3}{2k}\sum_{q=-1}^{q=1} F_{1,q}\varepsilon_q^{1*}\varepsilon_q^1 + \frac{5}{k}\sum_{q=-2}^{q=2} F_{2,q}(k\varepsilon)_q^*(k\varepsilon)_q, \quad (6)
$$

where the prefactors are non-essential but correspond to the definitions used by Hill & McMorrow (1996).

In the spherically symmetric case with no magnetic field, the $F_{1,q}$ and $F_{2,q}$ are independent of q. The introduction of a magnetic field introduces a q dependence in the scattering factors that can be expanded as a polynomial in the quantization number q:

$$
\begin{aligned}
F_{1,q} &= F_1^{0'} + qF_1^{1'} + q^2F_1^{2'} \\
F_{2,q} &= F_2^{0'} + qF_2^{1'} + q^2F_2^{2'} + q^3F_2^{3'} + q^4F_2^{4'},
\end{aligned} \quad (7)
$$

where the coefficients are given by

$$
\begin{aligned}
F_1^{0'} &= F_{1,0} \\
F_1^{1'} &= (F_{1,1} - F_{1,-1})/2 \\
F_1^{2'} &= (2F_{1,0} - F_{1,1} - F_{1,-1})/2 \\
F_2^{0'} &= F_{2,0} \\
F_2^{1'} &= (F_{2,-2} - F_{2,2} + 8F_{2,1} - 8F_{2,-1})/12 \\
F_2^{2'} &= (16F_{2,1} + 16F_{2,-1} - F_{2,-2} - F_{2,2} - 30F_{2,0})/24 \\
F_2^{3'} &= (F_{2,2} - F_{2,-2} + 2F_{2,-1} - 2F_{2,1})/12 \\
F_2^{4'} &= (6F_{2,0} + F_{2,2} + F_{2,-2} - 4F_{2,1} - 4F_{2,-1})/24.
\end{aligned} \quad (8)
$$

In the non-magnetic case, all the terms are zero except the zero-order ones.

We can substitute q in equation (6) by $\hat{\boldsymbol{\xi}} \cdot \mathbf{L}$, where $\mathbf{L}$ is the angular moment operator. Going back to the Cartesian space, equation (6) is then written as

$$
\begin{aligned}
F_{\boldsymbol{\varepsilon}\mathbf{k}\to\boldsymbol{\varepsilon}'\mathbf{k}'} = &\frac{3}{2k}\mathbf{C}\left(\boldsymbol{\varepsilon}' \sum_{n=0}^{n=2}(i\hat{\boldsymbol{\xi}}\times)^n F_1''^n \boldsymbol{\varepsilon}\right) \\
&+ \frac{5}{k}\mathbf{C}\left(\mathbf{k}' \otimes \boldsymbol{\varepsilon}' \sum_{n=0}^{n=4}(i\hat{\boldsymbol{\xi}}\times)^n F_2''^n \mathbf{k} \otimes \boldsymbol{\varepsilon}\right)\bigg/2, \quad (9)
\end{aligned}
$$

where the symbol $\mathbf{C}$ means the sum of all possible contractions of the two vectors $\boldsymbol{\varepsilon}'$ and $\mathbf{k}'$ with the expression to their right. A contraction is realized by coupling in pairs the $2N$ vectors that enter the expression, where $2N$ is the sum of the rank of each tensor. Each vector couple is then contracted to give a scalar product. The N scalar products are multiplied together to give the final result. The contraction of a tensor of defined rank with itself is not considered here. The dipolar scattering amplitude becomes

$$
F_{\boldsymbol{\varepsilon}\mathbf{k}\to\boldsymbol{\varepsilon}'\mathbf{k}'}^{\text{dipolar}} = \frac{3}{2k}[\boldsymbol{\varepsilon}' \cdot \boldsymbol{\varepsilon}F_1'^0 + \boldsymbol{\varepsilon}' \cdot (i\hat{\boldsymbol{\xi}}\times\boldsymbol{\varepsilon})F_1'^1 + \boldsymbol{\varepsilon}' \cdot (i\hat{\boldsymbol{\xi}}\times i\hat{\boldsymbol{\xi}}\times\boldsymbol{\varepsilon})F_1'^2].
$$
(10)

Such a formula can be rearranged in the same form as that presented by Hill & McMorrow (1996):

$$
F_{\boldsymbol{\varepsilon}\mathbf{k}\to\boldsymbol{\varepsilon}'\mathbf{k}'}^{\text{dipolar}} = \frac{3}{2k}[\boldsymbol{\varepsilon}' \cdot \boldsymbol{\varepsilon}(F_1'^0 - F_1'^2) - i\hat{\boldsymbol{\xi}} \cdot (\boldsymbol{\varepsilon}' \times \boldsymbol{\varepsilon})F_1'^1 + (\boldsymbol{\varepsilon}' \cdot \hat{\boldsymbol{\xi}})(\boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{\xi}})F_1'^2].
$$
(11)

For the quadrupolar scattering amplitude, the same procedures apply with some more bookkeeping for the various terms. In detail:

$$
\begin{aligned}
(i\hat{\boldsymbol{\xi}}\times)^0 \boldsymbol{\varepsilon} \otimes \mathbf{k} &= \boldsymbol{\varepsilon} \otimes \mathbf{k} \\
(i\hat{\boldsymbol{\xi}}\times)^1 \boldsymbol{\varepsilon} \otimes \mathbf{k} &= i(\hat{\boldsymbol{\xi}} \times \boldsymbol{\varepsilon}) \otimes \mathbf{k} + i\boldsymbol{\varepsilon} \otimes (\hat{\boldsymbol{\xi}} \times \mathbf{k}) \\
-(\hat{\boldsymbol{\xi}}\times)^2 \boldsymbol{\varepsilon} \otimes \mathbf{k} &= \boldsymbol{\varepsilon}_\perp \otimes \mathbf{k} - 2(\hat{\boldsymbol{\xi}} \times \boldsymbol{\varepsilon}) \otimes (\hat{\boldsymbol{\xi}} \times \mathbf{k}) + \boldsymbol{\varepsilon} \otimes \mathbf{k}_\perp \\
-i(\hat{\boldsymbol{\xi}}\times)^3 \boldsymbol{\varepsilon} \otimes \mathbf{k} &= i(\hat{\boldsymbol{\xi}} \times \boldsymbol{\varepsilon}) \otimes \mathbf{k} + 3i\boldsymbol{\varepsilon}_\perp \otimes (\hat{\boldsymbol{\xi}} \times \mathbf{k}) \\
&\quad + 3i(\hat{\boldsymbol{\xi}} \times \boldsymbol{\varepsilon}) \otimes \mathbf{k}_\perp + i(\hat{\boldsymbol{\xi}} \times \mathbf{k}) \otimes \boldsymbol{\varepsilon} \\
(\hat{\boldsymbol{\xi}}\times)^4 \boldsymbol{\varepsilon} \otimes \mathbf{k} &= \boldsymbol{\varepsilon}_\perp \otimes \mathbf{k} - 8(\hat{\boldsymbol{\xi}} \times \boldsymbol{\varepsilon}) \otimes (\hat{\boldsymbol{\xi}} \times \mathbf{k}) \\
&\quad + 6\boldsymbol{\varepsilon}_\perp \otimes \mathbf{k}_\perp + \mathbf{k}_\perp \otimes \varepsilon. \quad (12)
\end{aligned}
$$

Each term of the above equation must be multiplied by its own $F_2'^q$ and contracted with $\varepsilon' \mathbf{k}'$. The result is

$$
\begin{aligned}
\frac{k}{5} F_{\varepsilon \mathbf{k} \to \varepsilon' \mathbf{k}'}^{\text{quadrupolar}} = {}& (F_2'^0 + 2F_2'^2 + 8F_2'^2) S(\varepsilon' \cdot \varepsilon \mathbf{k}' \cdot \mathbf{k})/4 \\
& + i(-F_2'^1 - 4F_2'^3) S(\mathbf{z} \cdot (\varepsilon' \times \varepsilon) \mathbf{k}' \cdot \mathbf{k})/2 \\
& + (-F_2'^2 - 7F_2'^4) S(\varepsilon' \cdot \mathbf{z} \varepsilon \cdot \mathbf{z} \mathbf{k}' \cdot \mathbf{k})/2 \\
& + (-2F_2'^2 - 8F_2'^4) S(\mathbf{z} \cdot (\varepsilon' \times \varepsilon) \mathbf{z} \cdot (\mathbf{k}' \times \mathbf{k}))/4 \\
& + 3iF_2'^3 S(\varepsilon' \cdot \mathbf{z} \varepsilon \cdot \mathbf{z} \mathbf{z} \cdot (\mathbf{k}' \times \mathbf{k}))/2 \\
& + 6F_2'^4 \varepsilon' \cdot \mathbf{z} \varepsilon \cdot \mathbf{z} \mathbf{k}' \cdot \mathbf{z} \mathbf{k} \cdot \mathbf{z},
\end{aligned} \tag{13}
$$

where $S(t)$ represents the symmetrized expression composed of the term t as well as the other three terms which can be obtained by swapping ε' with $\mathbf{k}'$ and/or ε with $\mathbf{k}$. We have verified that with some lengthy vector algebra our formulae can be recast in the form given by Hill & McMorrow (1996).

4. Non-spherical case

In this section, we develop a phenomenological formalism for XRMS in the non-spherical case. Our starting point is crystal-field theory where the non-sphericity of the atomic environment is represented by a one-particle mean-field potential added to the atomic Hamiltonian. Such an approach, pioneered by the works of Bequerel (1929), Bethe (1929), Kramers (1930) and Van Vleck (1932), was applied for the first time for the calculation of X-ray absorption spectra and scattering factors by van der Laan (1991) and Carra & Thole (1994).

The crystal field T is given by a superposition of spherical tensors:

$$
T = \sum_{l,q} t_{l,q} T_q^l. \tag{14}
$$

The tensor T must be invariant under all operations of the point symmetry group of the system (Carra & Thole, 1994).

The crystal-field correction to the scattering amplitude is treated in a perturbative way in one-particle approximation. We consider here the process where an electron is promoted from a closed-shell state, denoted by $|n_g l_g \frac{1}{2}; J_a j_z\rangle$, to the intermediate states $|n_a l_a m_{az}\rangle |\frac{1}{2}\sigma\rangle$ and $|n_b l_b m_{bz}\rangle |\frac{1}{2}\sigma\rangle$ of two open shells (n_a, l_a) and (n_b, l_b). The perturbation T has matrix elements that mix the two shells.

If some non-essential labels are disregarded, the initial one-electron state can be written as follows:

$$
|J_a j_z\rangle = \sum_\sigma c(j_z, \sigma)|\sigma\rangle |l_g, j_z - \sigma\rangle, \tag{15}
$$

where $c(j_z, \sigma)$ stands for the Clebsch–Gordan coefficient $c(l_g, j_z - \sigma, 1/2, \sigma; J_a, j_z)$.

The electron–photon interaction is represented by the tensors $P' = P(\varepsilon', \mathbf{k}')$ for the outgoing photon and P for the incoming one.

The scattering amplitude at first order in T takes the form

$$
\begin{aligned}
\sum_{m_{gz}} \sum_\sigma c_{(m_{gz}+\sigma,\sigma)}^2 & \sum_{qq'} \langle l_g, m_{gz} | P_b'^* | l_b, m_{gz} + q'\rangle f_{b(m_{gz}+q',\sigma)} \\
& \times \langle l_b, m_{gz} + q' | T | l_a, m_{gz} + q\rangle \\
& \times f_{a(m_{gz}+q,\sigma)} \langle l_a, m_{gz} + q | P_a | l_g, m_{gz}\rangle + [a \leftrightarrow b].
\end{aligned} \tag{16}
$$

In this expression, the factor $f_b(m, \sigma)$, or $f_a(m, \sigma)$, implicitly contains the electron propagator for the spherical atom and accounts also for the orbital occupancies.

Starting from this expression, a contracted form can be derived. In addition to the polarization vectors and the magnetization axis already present in the spherical case, it contains the T tensor expression representing the crystal field and the spherical tensors $T_{m_z}^{l_g}$ representing the core state.

The perturbative process concerns intermediate levels of well defined angular momenta, l_a and l_b. This imposes a restriction on the possible contractions: the transition due to a P tensor from the $L = l_g$ ground state to the $L = l_n$ excited levels implies that exactly $[l_g + \text{rank}(P) - l_n]/2$ contractions must be done between the tensor and the initial ground state. Our one-particle approximation neglects the energy spread of the intermediate states due to many-body effects and is therefore similar to the fast-collision approximation employed by Marri & Carra (2004) for the case of E1–E2 scattering in a magnetoelectric crystal. Moreover, as the $f_b(m, \sigma)$ or $f_a(m, \sigma)$ propagators are diagonal in m and σ, our approach neglects spin–orbit (SO) interaction in the intermediate levels.

One can develop $f_a(q, \sigma)$ and $f_b(q, \sigma)$ in powers of L_z, as in the previous section:

$$
f(q, \sigma) = \sum_n f_{n,\sigma} q^n \to \sum_n f_{n,\sigma} L_z^n. \tag{17}
$$

The scattering amplitude can then be written as follows:

$$
\begin{aligned}
\sum_{m_{gz},\sigma,n_a,n_b} & f_{n_b,\sigma}^b f_{n_a,\sigma}^a c_{(m_{gz}+\sigma,\sigma)}^2 \\
& \times \mathbf{C}(T_{m_z}^{l_g*} P_b'^* |^\leftarrow (i\xi_m \times)^{n_b} T_{m_z}^{l_g} (i\xi_m \times)^{n_a} P_a |^\rightarrow T_{m_z}^{l_g}) + \text{symm.},
\end{aligned} \tag{18}
$$

where the above expression is symmetrized by the following substitutions:

$$
\text{symm.} = [a \leftrightarrow b].
$$

The symbol $|^\leftarrow$ ($|^\rightarrow$) which follows a polarization tensor implies that the number of contractions of such a tensor with the preceding (following) ground-level tensorial object is constrained as discussed above. The $(i\xi_m \times)$ operator acts on all the objects to its right. Note that $(i\xi_m \times)AB = [(i\xi_m \times)A]B + A[(i\xi_m \times)B]$. A formal derivation of these contraction rules is given in Appendix A.

In general, for any edge e, the factors c^2 can be expressed as: $c^2(m_z + \sigma, \sigma) = l_e + 2s_e \sigma m_z$, where l_e and s_e are constants that depend on the edge. For example, at the L_3 edge, we have $l_e = 2/3$ and $s_e = 1/3$ while, at the L_2 edge, $l_e = 1/3$ and $s_e = -1/6$.

It is then useful to rewrite equation (18) as:

$$l_e \sum_{n_a,n_b} \tfrac{2}{3}(f^b_{n_b,1/2}f^a_{n_a,1/2} + f^b_{n_b,-1/2}f^a_{n_a,-1/2})$$

$$\times \sum_{m_{gz}} \mathbf{C}(T^{l_g*}_{m_z}P'^*_b|^{\leftarrow}(i\xi_m\times)^{n_b}T^{l_g}_{m_z}(i\xi_m\times)^{n_a}P_a|^{\rightarrow}T^{l_g}_{m_z})$$

$$+ s_e \sum_{n_a,n_b} \tfrac{1}{3}(f^b_{n_b,1/2}f^a_{n_a,1/2} - f^b_{n_b,-1/2}f^a_{n_a,-1/2})$$

$$\times \sum_{m_{gz}} \mathbf{C}(T^{l_g*}_{m_z}P'^*_b|^{\leftarrow}(i\xi_m\times)^{n_b}T^{l_g}_{m_z}(i\xi_m\times)^{n_a}P_a|^{\rightarrow}(i\xi_m\times)T^{l_g}_{m_z})$$

$$+ \text{symm.} \tag{19}$$

In the second term, the m_z quantization number has been converted into the operator $(i\xi_m\times)$ placed to the left of the core-hole orbitals, $T^{l_g}_{m_z}$. Once contracted, the above formula generally remains a complicated expression. However, for the zero- and first-order terms in $(i\xi_m\times)$, the sum over the core-hole orbitals can be simplified in an elegant way.

The zero-order terms describe the non-sphericity of the crystal field. The first-order terms describe corrections induced by the crystal field to the magnetic scattering.

Concerning the zero-order terms, one can observe that such a sum looks like a trace. In other words, if, in a given contraction diagram, a vector A is contracted with the *ket* ground orbital while another vector B is contracted with the same *bra* core orbital, the result is equivalent to a contraction of A with B because the sum runs over a complete basis of an irreducible subspace.

For the first-order terms, $(i\xi_m\times)$ operates either on the core-hole orbital or on the intermediate tensors (P, P' and crystal-field tensor T). The terms where $(i\xi_m\times)$ operates on the intermediate tensors can be simplified, as in the zero-order case described above.

Now we consider the terms where one $(i\xi_m\times)$ operates on the core-hole orbital. The contraction diagrams arising from these terms can be split into two classes. In the first class, $(i\xi_m\times)$ operates on a core-hole vector and the result is contracted with another core-hole vector. This class gives zero contribution because $(i\xi_m\times)$ is an antisymmetric operator. The second class is given by the remaining terms containing the factor $\mathbf{v}\cdot[(i\xi_m\times)\mathbf{h}]$, where $\mathbf{v}$ and $\mathbf{h}$ are vectors that enter the composition of an intermediate and core-hole tensors, respectively. This factor can be rewritten as $-[(i\xi_m\times)\mathbf{v}]\cdot\mathbf{h}$ and once again the sum over the core-hole orbitals disappears from the final expression.

The general expression for the scattering amplitude up to first order in $(i\xi_m\times)$ is therefore

$$\sum_{n_a,n_b=0}^{n_a+n_b=1} a_{n_a,n_b}\mathbf{C}(P'^*_b(i\xi_m\times)^{n_b}T^{l_g}_{m_z}(i\xi_m\times)^{n_a}P_a) + \text{symm.}, \tag{20}$$

where the a_{n_a,n_b} depends linearly on the f electron propagators. The exact linearity coefficients can be found by working out the contraction diagrams.

For higher-order terms, this simplification is not applicable in the same way. Indeed, when one rewrites $\mathbf{v}\cdot[(i\xi_m\times)^2\mathbf{h}]$ as $[(i\xi_m\times)^2\mathbf{v}]\cdot\mathbf{h}$, the $(i\xi_m\times)^2$ operator cannot be factored out from the tensor composed of v. In fact,

$$(i\xi_m\times)^2(\mathbf{v}_1\mathbf{v}_2) \neq [(i\xi_m\times)^2\mathbf{v}_1]\mathbf{v}_2 + \mathbf{v}_1[(i\xi_m\times)^2\mathbf{v}_2]. \tag{21}$$

The core orbital disappears from the final expression because, in our approximation, our L_3 core state in equation (15) is not coupled to the valence orbitals. Such an approximation is valid for the hard X-rays domain where the core hole is deep.

It is interesting to compare our method to the one established by Ovchinnikova & Dmitrienko (1997, 2000). These authors write a general form for the dielectric tensor and then, by symmetry considerations, they restrict their formulae to the terms that have the right invariance properties. In our method, it is the mechanism of the contraction method that ensures that the final expression has the correct symmetry.

For the sake of simplicity, only the contribution from the zero- and first-order terms is considered in the following example. The general case can be treated with a recently developed computer code (Wood & Mirone, 2006).

5. Example: a case study of holmium

Our method is illustrated here choosing holmium as an example of a non-centrosymmetric system. Holmium has a h.c.p. structure where the atoms are embedded in a local D_{3h} symmetry environment. It is a basal-plane spiral antiferromagnet, where the moments are confined to the *ab* plane in ferromagnetic sheets. The magnetization direction rotates from basal plane to basal plane, creating a spiral structure propagating along the *c* axis. The modulation vector lies along (00*l*). Taking a Cartesian x, y, z frame with x along the h.c.p. a axis, we get

$$T = t_2[3z^2 - (x^2 + y^2 + z^2)] \pm t_3(x^3 - 3xy^2) + \dots, \tag{22}$$

where the first omitted term of the series is a rank 4 component. The $\pm$ signs alternate from one *ab* plane to another.

The contribution from the $(2z^2 - x^2 - y^2)$ term is centrosymmetric. The E1–E1 and the E2–E2 scattering are treated separately. Within the framework of our assumption [equation (20)], we find that the E1–E1 scattering correction is proportional to

$$3\boldsymbol{\varepsilon}'\cdot\mathbf{z}(i\hat{\xi}_m\times\boldsymbol{\varepsilon})\cdot\mathbf{z} - \boldsymbol{\varepsilon}'\cdot(i\hat{\xi}_m\boldsymbol{\varepsilon}) - [\boldsymbol{\varepsilon}'\leftrightarrow\boldsymbol{\varepsilon}]. \tag{23}$$

The second term of this expression merges with the form obtained for the scattering in the spherical approximation [equation (11)]. However, the first term contains two scalar products with the $\mathbf{z}$ axis and adds complexity to the experimental geometry dependence of the amplitude.

Disregarding those terms that can be merged with the spherical formulae, the E2–E2 scattering has the form

$$(\mathbf{k}'\cdot\hat{\mathbf{z}})(\mathbf{k}\cdot\hat{\mathbf{z}})\boldsymbol{\varepsilon}'\cdot(i\hat{\xi}_m\times\boldsymbol{\varepsilon}) + [i\hat{\xi}\times\boldsymbol{\varepsilon}\leftrightarrow\mathbf{k}] + [\mathbf{k}\leftrightarrow\boldsymbol{\varepsilon}]$$

$$+ [[\mathbf{k}'\leftrightarrow\boldsymbol{\varepsilon}']] - [\mathbf{k},\boldsymbol{\varepsilon}\leftrightarrow\mathbf{k}',\boldsymbol{\varepsilon}']. \tag{24}$$

This expression also contains two scalar products with the $\mathbf{z}$ axis, again adding some complexity.

In our system, the E1–E1 and E2–E2 terms contribute to the amplitude of the $2n \pm q$ Bragg-order diffraction peaks, where n is an integer and $\mathbf{q}$ is the modulation vector. In an experiment where several magnetic peaks are measured, the

incidence angle may considerably vary from one order to the next. Consequently, one might think that the inclusion of our correction could improve the agreement between experiment and theory.

However we found that, by fully developing equations (23) and (24), the centrosymmetric part has the same polarization dependence as the spherical contributions, when the in-plane magnetization turns about the z (c) axis. This may explain why these non-spherical contributions have not been detected so far in studies of $l = 2n \pm q$ Bragg reflections.

The scattering-factor contribution from the alternating term $\pm(x^3 - 3xy^2)$ gives diffraction peaks at $l = 2n + 1 \pm mq$, where m is an integer. For simplicity, we consider the magnetization to be in the xy plane and the terms having $n_a = 1$ and $n_b = 0$ in equation (20).

We apply the contraction rules to formula (20), where P' and P are ε and $\mathbf{k} \otimes \varepsilon$ tensors, respectively. In this case, we obtain a scattering amplitude proportional to

$$
\begin{aligned}
&- 6i(\varepsilon' \cdot \hat{\mathbf{x}})(\varepsilon \cdot \hat{\mathbf{x}})\hat{\xi}_m \cdot (\hat{\mathbf{x}} \times \mathbf{k}) + 6i(\varepsilon' \cdot \hat{\mathbf{x}})(\varepsilon \cdot \hat{\mathbf{y}})\hat{\xi}_m \cdot (\hat{\mathbf{y}} \times \mathbf{k}) \\
&+ 6i(\varepsilon' \cdot \hat{\mathbf{y}})(\varepsilon \cdot \hat{\mathbf{x}})\hat{\xi}_m \cdot (\hat{\mathbf{y}} \times \mathbf{k}) + 6i(\varepsilon' \cdot \hat{\mathbf{y}})(\varepsilon \cdot \hat{\mathbf{y}})\hat{\xi}_m \cdot (\hat{\mathbf{x}} \times \mathbf{k}) \\
&+ [\varepsilon \leftrightarrow \mathbf{k}] + [\mathbf{k} \leftrightarrow \mathbf{k}', \varepsilon \leftrightarrow \varepsilon'].
\end{aligned} \tag{25}
$$

For 00l diffraction, we have $\mathbf{k}' \cdot \hat{\mathbf{z}} = -\mathbf{k} \cdot \hat{\mathbf{z}}$. After symmetrization and considering linear polarization, only the $\sigma - \pi$ terms survive in the above expression, where π lies in the scattering plane and σ is perpendicular to it. Decomposing the incoming and outgoing wave into σ and π components and entering them into equation (25), we obtain for the E1–E2 scattering-amplitude matrix:

$$
\begin{pmatrix} F_{\sigma' \leftarrow \sigma}^{dq} & F_{\sigma' \leftarrow \pi}^{dq} \\ F_{\pi' \leftarrow \sigma}^{dq} & F_{\pi' \leftarrow \pi}^{dq} \end{pmatrix}
$$
$$
= 6if \begin{pmatrix} 0 & \cos^2(\theta)\cos(\mathbf{q} \cdot \mathbf{r} + 2\phi) \\ \cos^2(\theta)\cos(\mathbf{q} \cdot \mathbf{r} + 2\phi) & 0 \end{pmatrix},
$$
(26)

where f is an energy-dependent factor, θ is the Bragg angle and ϕ is the azimuthal angle between the scattering plane and the x axis. We have also considered the case of $n_a = 0$ and $n_b = 1$ and found the same form. For an in-plane rotating magnetic field, the scattering amplitude for the $2n + 1 + q$ reflections is proportional to the $\exp(i\mathbf{q} \cdot \mathbf{r})$ component in equation (26) and only exists in $\sigma - \pi$. The azimuthal angle only influences the phase. Consequently, the E1–E2 magnetic intensity is independent of the azimuth for terms up to first order. The E1–E2 scattering would also contribute to the $l = 2n + 1 \pm mq$ with $m > 1$ but such a scattering is due to the higher-order terms ($n_a + n_b > 1$) and is not treated here. The zero-order term only contributes to the $l = 2n + 1$ peaks which have a sixfold azimuthal dependence. To our knowledge, no $l = 2n + 1 \pm mq$ or $l = 2n + 1$ peak has been observed so far in heavy rare-earth metals, except a preliminary experimental study of holmium which has detected the (003) peak and its $\pm q$ satellites (Bouchenoire et al., 2007).

6. Conclusions

We have established a contraction method and obtained phenomenological analytical expressions for the scattering factors. These factors have been expressed in terms of scalar and vector products of the polarization, the magnetization axis and of the vectors defining the crystal field tensor. Using a perturbative approach, we have been able to go beyond the usual SO2 approximation (Hill & McMorrow, 1996) by simultaneously considering the magnetization and a general crystal-field tensor. Our method is a viable diagrammatic technique based on contraction between vectors. With our method, useful formulae can be directly obtained in terms of polarization, crystal-field vectors and magnetization direction. Our formalism accounts for the SO coupling of the core-hole electron. In the intermediate levels, we have considered propagators which are diagonal in m, σ. The introduction of diagonal propagators in the formalism would mix orbital and spin degrees of freedom. We recognize that it would be possible, in this case, to generalize the method by writing the vectors as symmetric products of spinor couples and by operating contractions between spinors instead of between vectors. Our method can be considered a bottom-up alternative to the one developed by Ovchinnikova & Dmitrienko (1997, 2000). In fact, these authors trace down the polarization dependence from a general expression, using symmetry considerations to restrict the possible terms of the dielectric tensor. Our method, instead, expresses first the local non-sphericity by a sum of spherical-harmonic tensors and then the contraction mechanism automatically builds up formulae with the correct dependence. In agreement with these authors, we also find that the joint effect of local non-sphericity and magnetization gives rise to reflections otherwise forbidden. Our treatment is illustrated with the case of holmium, which predicts E1–E2 peaks occurring at $2n + 1 + mq$ reflections.

APPENDIX A
Derivation of contraction rules

The transition amplitude between different atomic levels is in general the product of radial integrals with a spherical integral of a product of spherical harmonic functions. The angular dependence is given by the angular integral while the product of the radial integrals acts like a constant. A spherical harmonic of given rank l can be written as a sum of terms $f(n)$ given by

$$
f(n) = \prod_{i=1}^{i=l} \mathbf{a}_i \cdot \mathbf{n}, \tag{27}
$$

where n denotes the position on the unit sphere surface and $l = 2N$ is the sum of the rank of each spherical harmonic (an even number for a non-zero integral). The product of all the spherical harmonics entering the radial integral is then equal to the sum of terms having $f(n)$ form.

We show in this section how such angular integration over the unit sphere surface can be expressed as a sum of contraction diagrams.

The polynomial integration considered here is

$$\int_S \left(\prod_i^{2N} \mathbf{a}_i \cdot \mathbf{n} \right) dn^2. \tag{28}$$

By multiplying and dividing this expression by $\int \exp(-r^2) r^{2N+2} \, dr$, it can be transformed into an integral over the whole space:

$$\int_S \left(\prod_i^{2N} \mathbf{a}_i \cdot \mathbf{n} \right) dn^2$$

$$= \frac{1}{4\pi} \int \left(\prod_i^{2N} \mathbf{a}_i \cdot \mathbf{r} \right) \exp(-r^2) \, d\mathbf{r}^3 / [\Gamma(N+3/2)/2]$$

$$= \frac{1}{4\pi} \prod_i^{2N} \mathbf{a}_i \cdot \boldsymbol{\partial}_{\mathbf{v}} \left(\int \exp(-r^2 + \mathbf{v} \cdot \mathbf{r}) \, d\mathbf{r}^3 \right) \bigg|_{v=0} \bigg/ [\Gamma(N+3/2)/2]$$

$$= \prod_i^{2N} \mathbf{a}_i \cdot \boldsymbol{\partial}_{\mathbf{v}} \exp(\mathbf{v}^2/4)|_{v=0} \, \Gamma(3/2)/\Gamma(N+3/2). \tag{29}$$

In this expression, only the terms fully contracted remain. Indeed, when $v = 0$, if $\mathbf{a}_i \cdot \boldsymbol{\partial}_{\mathbf{v}}$ takes down a $\mathbf{v}/2$ factor from the exponent, another $\mathbf{a}_m \cdot \boldsymbol{\partial}_{\mathbf{v}}$ must be used to derive this factor to obtain $\mathbf{a}_l \cdot \mathbf{a}_m$. Otherwise a zero contribution is obtained.

The intermediate sum that appears in equation (16) can be considered as a projector p_{l_a} over a tensorial space of definite rank l_a. The projection over definite rank space is obtained through the $|^{\leftarrow}$ and $|^{\rightarrow}$ constraint. When applying contraction rules to expressions formed by tensors of a defined rank, one must bear in mind that, by definition, a defined rank tensor gives zero when contracted with itself.

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