RMP Colloquia

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Anisotropic x-ray anomalous diffraction and forbidden reflections

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In this paper the authors present a general analysis of resonant elastic scattering of x rays. The approach exploits crystal symmetry, scattering geometry, and polarization. Extinction rules, their breaking, and the observation of forbidden reflections are discussed. As an application, a detailed description of the experiment performed by Finkelstein, Shen, and Shastri at the iron K edge in α Fe$_2$O$_3$ (hematite) is reported.

CONTENTS

I. INTRODUCTION

The angular distribution of x rays diffracted by a crystal usually reflects only the crystal's macroscopic dielectric properties, but additional effects emerge when the response of particular atoms or ions in the lattice is boosted by resonances. Such resonances occur when the x-ray photon energy approaches the value required to excite an inner-shell electron to an empty orbital of its atom's valence shell. The atom's elastic-scattering form factor then depends on crystal and/or magnetic orientations with respect to the polarization of the incoming and outgoing photons. This effect has been demonstrated by various authors (Namikawa *et al.*, 1985; Gibbs *et al.*, 1988; Isaacs *et al.*, 1989) for magnetic systems. The relevant intensities can be as large as 1% of the charge peaks (Isaacs *et al.*, 1989); electric dipole and quadrupolar transitions may then contribute to the scattering process with comparable magnitude (Gibbs *et al.*, 1988; Hannon *et al.*, 1988).

The x ray's short wavelength, comparable to the atom-

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ic spacing, causes the aggregate response of all resonant atoms to reflect lattice symmetries that otherwise fail to emerge. Disparate elements—the x-ray polarization, magnetism of the resonant atoms, and lattice features—thus combine to yield a sensitive anisotropy. The combination of such disparate elements provides a basis to illustrate, in this colloquium, an unusual interplay of crystal symmetry elements, x-ray propagation and polarization, diffraction, and single-atom responses in a crystalline setting.

The anisotropy of x-ray "anomalous" diffraction was first observed by Templeton and Templeton (1982), near the uranium L_3 edge in sodium uranyl acetate. Near the same edge of a related uranyl compound, a substantial linear dichroism had also been previously observed (Templeton and Templeton, 1980). Linear dichroism implies a difference in absorption between radiations with linear polarization parallel or perpendicular to a local symmetry axis. Both effects involve a single electronic process: electric dipolar transitions in the presence of a low-symmetry crystalline environment.

The anomalous diffraction anisotropy thus violates screw-axis and glide-plane extinction rules, which hold for isotropic scattering (Dmitrienko, 1983; Templeton and Templeton, 1985, 1986; Kirfel and Morgenroth, 1993, and references therein). Octahedral symmetry reflections, forbidden at the dipolar level, may instead manifest themselves via quadrupolar transitions boosted by resonance, as shown for the K edge of iron in αFe$_2$O$_3$ (hematite) by Finkelstein and co-workers (Finkelstein *et al.*, 1992).

The present authors have recently developed, as have others, a theoretical interpretation of x-ray dichroism and anomalous diffraction in terms of simple sum rules, relating the integral of the observed spectra to the ground-state expectation value of effective spin and orbit

one-electron operators (Thole *et al.*, 1992; Carra, Thole, *et al.*, 1993; Luo *et al.*, 1993). This development provides an opportunity to outline a comprehensive symmetry analysis of the anisotropic x-ray resonant diffraction.

Given an arbitrary point-group symmetry, a set of simple rules identifies the terms in the resonant amplitude that determine observable effects. Taking into account the local symmetry (crystalline as well as magnetic), the scattering geometry, and the polarization yields an effective procedure for inferring which scattered components will receive nonzero intensity. Extinction rules, their breakdown, and the observation of forbidden reflections are all treated in the same framework. As an illustration, Sec. III will discuss the resonant diffraction at the iron K edge of hematite (Finkelstein *et al.*, 1992).

II. THE RESONANT AMPLITUDE

The $\mathbf{p} \cdot \mathbf{A}$ interaction between x rays and matter expands into spherical Bessel functions $g_l(k_i r)$ and spherical harmonics of $\hat{\mathbf{k}}_i$ and $\hat{\mathbf{r}}$: $\mathbf{p} \cdot \mathbf{e}_i g_l(k_i r) \sum_m Y_m^{l*}(\hat{\mathbf{k}}_i) Y_m^l(\hat{\mathbf{r}})$. Here $\mathbf{e}_i$ and $\hat{\mathbf{k}}_i$ denote the polarization and a unit vector in the direction of the photon momentum of the incident beam, respectively. A better formulation[1] is obtained by recoupling $\mathbf{p}$ and $Y^l(\hat{\mathbf{r}})$ to a total L, yielding the term

$$\sum_L [[\mathbf{e}_i, Y^l(\hat{\mathbf{k}}_i)]^L [\mathbf{p}, Y^l(\hat{\mathbf{r}})]^L]^0 g_l(k_i r) ,$$

with the couplings defined by

$$[A^{L'}, B^{L''}]_l^L \equiv \Sigma_{l'l''} A_{l'}^{L'} B_{l''}^{L''} \langle L'L''l'l''|Ll \rangle .$$

The product $g_l(k_i r)[\mathbf{p}, Y^l(\hat{\mathbf{r}})]_M^L$ forms a core of the "current operator" J_M^L that raises an inner-shell electron to empty valence orbitals. The remaining factor $[\mathbf{e}_i, Y^l(\hat{\mathbf{k}}_i)]_M^L$ pertains to the geometry of x-ray scattering. When $L=0$, one obtains

$$[\mathbf{e}_i, Y^1(\hat{\mathbf{k}})]^0 = -\frac{1}{\sqrt{3}} \mathbf{e}_i \cdot \hat{\mathbf{k}} = 0 .$$

Three values of l contribute to any other value of L. In the limit $k_i r \ll 1$, $g_l(k_i r) \sim (k_i r)^l$, and the lowest value $l = L - 1$ yields the largest contribution. This term can be rewritten as

$$[\mathbf{p}, Y^{L-1}(\hat{\mathbf{r}})]_M^L r^{L-1} = \frac{1}{\sqrt{L(2L+1)}} \mathbf{p} \cdot \nabla(r^L Y_M^L) ,$$

reducing to

$$\langle \psi_2 | \mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p} | \psi_1 \rangle \sim \frac{2m(E_2 - E_1)}{i\hbar\sqrt{L(2L+1)}} \langle \psi_2 | r^L Y_M^L(\hat{\mathbf{r}}) | \psi_1 \rangle ,$$

i.e., as an electric multipole matrix element.

The current operator J_M^L and the excited state $\langle I|$ combine with their Hermitian conjugates and the resonance denominator $E_I - E_g - \hbar\omega - i\Gamma/2$ to form the second-order perturbation operator

$$\frac{(J^L)^\dagger |I\rangle \langle I| J^L}{E_I - E_g - \hbar\omega - i\Gamma/2} .$$

Here $\hbar\omega$ represents the resonant photon's energy and Γ the resonance width of the excited state.

For any electric 2^L-pole transition in a spherically symmetric ion, the coupled-multipole expansion for the resonant coherent elastic-scattering amplitude therefore takes the form (Luo *et al.*, 1993)

$$f^{EL}(\omega) = 4\pi\lambda \sum_{\mu=0}^{2L} [T^{(\mu)}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_i, \hat{\mathbf{k}}_i)_{EL}$$
$$\times \langle \psi_g | F^{(\mu)}(\omega)_{EL} | \psi_g \rangle]^0 , \qquad (1)$$

with

$$F_m^{(\mu)}(\omega)_{EL} = \sum_I \frac{1}{2\lambda_{Ig}} \left[\frac{(J^L)^\dagger |I\rangle \langle I| J^L}{E_I - E_g - \hbar\omega - i\frac{\Gamma}{2}} \right]_m^\mu , \qquad (2)$$

$$T_m^{(\mu)}(\mathbf{e}_f^*, \hat{\mathbf{k}}_f; \mathbf{e}_i, \hat{\mathbf{k}}_i)_{EL}$$
$$= \frac{2L+1}{L+1} [[\mathbf{e}_f^* Y^{L-1}(\hat{\mathbf{k}}_f)]^L [\mathbf{e}_i Y^{L-1}(\hat{\mathbf{k}}_i)]^L]_m^\mu , \qquad (3)$$

and the current operator

$$J_M^L = -\frac{4\pi i^L k^L}{(2L+1)!!} \sqrt{(L+1)/L} \sum_j e r_j^L Y_M^L . \qquad (4)$$

This formulation yields the scattering amplitude as a linear combination of pairs of tensors of increasing rank μ, which transform according to the irreducible representations of the spherical group (SO_3); we shall refer to them as μ-irreps. Each pair consists of a polarization response (angular factor) and of the expectation value of a frequency-dependent transition operator (a "spectrum") coupled into a scalar. Equation (1) provides a suitable starting point for determining the form of the amplitude diffracted into any crystal point group.[2] To this end, a simple procedure can be devised.

A. The spectrum

Consider the ground-state matrix element of a transition operator. To yield a nonzero value, the operator has to be totally symmetric. In spherical symmetry only $\mu = 0$ has such a property. The spectrum is necessarily isotropic.

Upon a lowering of the crystal symmetry, from SO_3 down to a specific point group, for example, each μ-irrep

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[1]Here we sketch a simplified derivation, dealing with the electric part only, of the photon wave-function expansion in angular momentum and parity eigenstates—the vector spherical harmonics. Full details can be found in Akhiezer and Berestetsky (1957).

[2]Changing one L into L' generalizes Eq. (1) to include interference effects. An example is the $E1$-$E2$ interference in ordered compounds that display natural optical activity.
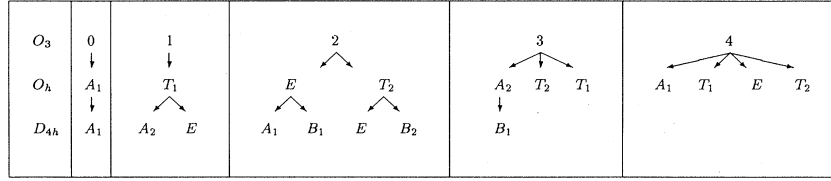
FIG. 1. Representation branchings for the group chain $O_3 \supset O_h \supset D_{4h}$. The subgroup representations are given in Schönflies notation; A_1 denotes the totally symmetric one. (In this case, all $2jm$ phases are unity.)

branches into a number of subgroup irreducible representations. Only those μ-irreps that branch into the totally symmetric representation (usually denoted by A_1) will contribute to the anomalous scattering amplitude. Anisotropy effects are observable for such $\mu > 0$ tensors [$\mu = 0$ is always present; the group-subgroup branchings are tabulated for all crystallographic groups (Butler, 1981), and those that are relevant to our discussion are displayed in Fig. 1].

As an example, consider dipolar transitions (for which $\mu = 0, 1, 2$) in octahedral symmetry. According to Fig. 1, only $\mu = 0$ branches to A_1; again, the spectrum is isotropic and no Templeton effects are detectable. In the case of a tetragonal distortion (D_{4h} symmetry), $\mu = 0$ and 2 must both be taken into account (Fig. 1), yielding observable anisotropy effects.

As a further example, consider a magnetic system with negligible crystal-field effects. In this case the symmetry is SO_2 and all the μ-irreps branch to 0. (For $SO_3 \supset SO_2$, the branching is given by $\mu \rightarrow m = \{-\mu, \ldots, \mu\}$, with $m = 0$ the totally symmetric representation.) The amplitude for resonant magnetic scattering in the form derived by Hannon and co-workers (Hannon et al., 1988)[3] for electric dipole transitions reads

$$f^{E1}(\omega) = \frac{3}{2}\lambda \left\{ -\frac{1}{\sqrt{3}}\mathbf{e}_f^* \cdot \mathbf{e}_i F_0^{(0)}(\omega)_{E1} - i\frac{1}{\sqrt{2}}(\mathbf{e}_f^* \times \mathbf{e}_i) \cdot \mathbf{z} F_0^{(1)}(\omega)_{E1} + \frac{1}{\sqrt{30}}[3(\mathbf{e}_i \cdot \mathbf{z})(\mathbf{e}_f^* \cdot \mathbf{z}) - \mathbf{e}_i \cdot \mathbf{e}_f^*] F_0^{(2)}(\omega)_{E1} \right\} . \tag{5}$$

In Eq. (1), any basis can be chosen to perform the coupling to the totally symmetric amplitude:

$$f^{EL} = 4\pi\lambda \sum_{\mu m} (-)^{\mu - m}[\mu]^{-1/2} T_m^\mu \langle F_{-m}^{(\mu)} \rangle$$

$$= 4\pi\lambda \sum_{\mu\gamma} \begin{bmatrix} \mu \\ \gamma \end{bmatrix} [\mu]^{-1/2} T_\gamma^{(\mu)} \langle F_{\gamma}^{(\mu)*} \rangle , \tag{6}$$

with $[\mu] = 2\mu + 1$. Here m and γ label the SO_2 (cylindrical) and an arbitrary point-group basis, respectively; $\binom{\mu}{\gamma}$ denotes a $2j$ symbol [a tabulated phase factor (Butler, 1981)]. The ground-state expectation value $\langle F_\gamma^{(\mu)} \rangle$ is nonzero only for totally symmetric γ, in which case

$$f^{EL} = 4\pi\lambda \sum_\mu \begin{bmatrix} \mu \\ A_1 \end{bmatrix} [\mu]^{-1/2} T_{A_1}^{(\mu)} \langle F_{A_1}^{(\mu)} \rangle . \tag{7}$$

(A $\sum_{A_1}$ must be included when μ branches to A_1 more than once.)

Equation (6) expresses a property of the rotation group and of its subgroups: any point-group basis will serve for writing out the scalar product. Given the local symmetry of the system, it is natural to express the amplitude through the irreducible representations of the corresponding point group, thus introducing point-group coordinates. In this way, the observable spectra of a 2^L-pole electric transition are readily determined by the totally symmetric components of the allowed irreducible tensors, as in Eq. (7). This procedure affords much simplification over Cartesian tensor formulations[4] when dealing with complex problems (see Sec. III).

B. The angular dependence

The analysis of crystal symmetry effects on f^{EL} proceeds equivalently either by keeping the angular dependence fixed and applying the space-group operations to $F_{A_1}^{(\mu)}$, or by keeping the ion fixed and transforming $T_{A_1}^{(\mu)}$, as in the present work.

Consider the diffracted amplitude generated by the whole crystal: $\sum_s e^{i\mathbf{q} \cdot \mathbf{R}_s} f_s^{EL}$, with $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$ the scatter-

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[3]The SO_2 symmetry of an ion is determined by the presence of a local preferred direction, along which a spin is aligned by the exchange interaction with neighboring sites. The orbit is aligned along the same direction by the spin-orbit interaction; this effect (or a spin-orbit split core hole) is crucial for the observation of magnetic effects in the $\mathbf{p} \cdot \mathbf{A}$ coupling.

[4]A complete analysis of anomalous diffraction using a decomposition of Cartesian tensors in their symmetric and antisymmetric parts has been given by Blume (1993).

ing wave vector and s running over all lattice sites. Deriving glide-plane and screw-axis extinction rules results conveniently by expanding the angular dependence in spherical tensors: $T_{A_1}^{(\mu)} = \sum_m t_m T_m^{(\mu)}$, as described by Butler (1981, Chap. 14) and below. The components $T_m^{(\mu)}$ of the angular dependence transform under space rotations like spherical harmonics, with φ dependence: $e^{im\varphi}$. An extra factor, $(-1)^\mu$, is brought in by parity upon reflections and inversions. [The tensors $T^{(\mu)}$ have positive parity, whereas the spherical harmonics $Y^{(\mu)}$ have parity $(-1)^\mu$.] Bragg reflections are observable when any operation of the space group leaves invariant the product of the Bragg factor and of the angular dependence. The roles of screw axes and glide planes will now be discussed in detail. Standard extinction rules hold for $\mu = 0$.

n_j-fold screw axis. When $\mathbf{q}$ ($\equiv \hat{\mathbf{z}}$ axis) lies along an n_j-screw axis parallel to $\mathbf{c}$ (i.e., with rotation $2\pi/n$ and translation $j\mathbf{c}/n$), the $e^{im\varphi}$ factors of harmonics change into $e^{im(\varphi + 2\pi/n)}$ and the Bragg factor $e^{i\mathbf{q}\cdot\mathbf{R}}$ changes into $e^{i\mathbf{q}\cdot(\mathbf{R}+j\mathbf{c}/n)}$, yielding together a factor $e^{i(2\pi m/n + \mathbf{q}\cdot\mathbf{c}j/n)}$. As this global factor must reduce to unity, the reflection is allowed only when $\mathbf{q}\cdot\mathbf{c}/2\pi = (nk-m)/j$, with k an integer. When $2m$ is not a multiple of n, only one of the $e^{\pm im\varphi}$ factors survives: the intensity is then φ independent.

Glide planes. Consider a $\hat{\mathbf{z}}$ axis along $\mathbf{q}$ and parallel to a glide plane at an angle α with the $\hat{\mathbf{x}}$ axis. Reflection in the plane changes φ into $-2\alpha - \varphi$; it is then sufficient to discuss the cases $\alpha = 0$ and $\pi/2$, without loss of generality. The functions $e_{m,\varphi}^{(\pm)} = e^{im\varphi} \pm e^{-im\varphi}$ change by a factor ± 1 under reflection. At $\alpha = 0$, $e_{m,\varphi}^{(+)}$ does not change, and, for the translation, the Bragg factor has to equal $(-1)^\mu$ to allow for this φ dependence; $e_{m,\varphi}^{(-)}$ changes instead into $-e_{m,\varphi}^{(-)}$, requiring a Bragg factor $(-1)^{\mu+1}$. Similarly, when $\alpha = \pi/2$, the factor $e_{m,\varphi}^{(+)}$ changes sign, whereas $e_{m,\varphi}^{(-)}$

remains the same, requiring Bragg factors $(-1)^{\mu+1}$ and $(-1)^\mu$, respectively.

These rules determine the transformation of the angular dependence $T_m^{(\mu)}$ for arbitrary scattering geometry vectors $\{\mathbf{e}_i, \hat{\mathbf{k}}_i, \mathbf{e}_f, \hat{\mathbf{k}}_f\}$. A few special settings yield the following:

(i) For $\mathbf{e}_f^* = \mathbf{e}_i$ (e.g., $\sigma \to \sigma$), $T_m^\mu = 0$ when μ is odd.

(ii) $\pi \to \pi$ vanishes when $L + L' + \mu + m$ is odd (z axis along $\mathbf{q}$). So, when $L = L'$ and $m = 0$, $\pi \to \pi$ vanishes for odd μ (magnetization along $\mathbf{q}$).

(iii) $\sigma \leftrightarrow \pi$ vanishes when m is even (z axis perpendicular to the scattering plane); this applies to magnetization (μ odd) or a crystal field (μ even) "oriented" perpendicularly to the scattering plane.

(iv) When the xz plane coincides with the scattering plane, $\sigma \to \pi$ vanishes for the combination $T_m^{(\mu)} + (-1)^m T_{-m}^{(\mu)}$; $\sigma \to \sigma$ and $\pi \to \pi$ vanish for $T_m^{(\mu)} - (-1)^m T_{-m}^{(\mu)}$. This rule is important when the scattering plane is a mirror or a glide plane. (The $\hat{\mathbf{z}}$ axis has to be specified whenever a rule contains m.)

C. Sum rules

As mentioned in the Introduction, (approximate) sum rules for the frequency-dependent transition operator have provided valuable insight into the nature of x-ray absorption and resonant scattering. The sum rules express the total contribution of all the $c \to l$ electric 2^L-pole transitions of a given $j_\pm = c \pm \frac{1}{2}$ absorption edge to the operator $F_m^{(\mu)}(\omega)_{EL}$, as a linear combination of one-electron spin and orbital coupled-tensor operators, as defined by Judd (1967). Particularly simple expressions result when the energy spread of the $j_\pm$ manifold can be neglected[5]:

$$F_m^{(\mu)}(\omega)_{EL} = R(c,j_\pm;L;l;\omega) \left[\frac{2L+1}{2z+1} \right]^{1/2} \left[-\frac{j_\pm + \frac{1}{2}}{2c+1} a_\mu W_m^{(0,\mu)} \pm \sum_{l=|\mu-1|,\neq\mu}^{\mu+1} b_{\mu l} W_m^{(1,l)\mu} \right], \tag{9}$$

where

$$R(c,j_\pm;L;l;\omega) = \frac{K(cLl)|\langle R_{nl}(r)|r^L|R_{n_c c_{j\pm}}\rangle|^2}{[\bar{E}_I - E_g - \hbar\omega - i\Gamma/2]}, \tag{10}$$

with a_μ, $b_{\mu l}$, and $K(cLl)$ constant factors. [Full details of the derivation are provided by Carra, König, et al. (1993), Carra, Thole, et al. (1993), and Luo et al. (1993).]

The coupled tensors $W^{(\epsilon v)\mu}$ describe the multipole moments of the charge and magnetic distribution of the valence l

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[5]This "fast-collision approximation" amounts to an $n = 0$ truncation in the expansion for the resonant denominator

$$\left[E_I - E_g - \hbar\omega - i\frac{\Gamma}{2} \right]^{-1} = \left[\bar{E}_I - E_g - \hbar\omega - i\frac{\Gamma}{2} \right]^{-1} \sum_{n=0}^{\infty} \left[\frac{\bar{E}_I - E_I}{\bar{E}_I - E_g - \hbar\omega - i\Gamma/2} \right]^n \tag{8}$$

and holds when $\text{Max}(|E_I - E_g - \hbar\omega|, \Gamma) \gg \sqrt{\overline{(E_I - \bar{E}_I)^2}}$, with $\bar{E}_I$ the central energy of the transition.

electrons (making the sum rules *shell-selective*) and can be expressed in terms of elementary operators; for example,

$$W^{(00)} = [2(2l+1)]^{-1/2} n_h \quad \text{(number of holes)},$$

$$W^{(11)0} = [l(l+1)(2l+1)/2]^{-1/2} \sum_i \mathbf{s}_i \cdot \mathbf{l}_i \quad \text{(spin-orbit)},$$

$$W^{(01)} = -[2l(l+1)(2l+1)/3]^{-1/2} \mathbf{L} \quad \text{(orbital)},$$

$$W^{(10)} = -[(2l+1)/2]^{-1/2} \mathbf{S} \quad \text{(spin)},$$

$$W^{(12)1} = -\left[\frac{l(l+1)(2l+1)}{(2l-1)(2l+3)}\right]^{-1/2} \sum_i [\mathbf{s}_i - 3\hat{\mathbf{r}}_i(\hat{\mathbf{r}}_i \cdot \mathbf{s}_i)] \quad \text{(magnetic dipole)}.$$

(11)

For x-ray absorption and dichroism, Eqs. (9)–(11) serve to interpret the observed spectra directly. In the important case of magnetic circular dichroism, they indicate the possibility of an element-specific determination of the orbital and spin contributions to the magnetic moment. This prediction was recently verified experimentally (Chen *et al.*, 1994).

In the case of resonant x-ray scattering, the sum rules yield an effective scattering amplitude from which a dynamic structure factor, $S(\mathbf{q}, \omega)$, can be readily written out in terms of two-particle correlation functions; the allowed operators are selected by the x ray's polarization and point-group symmetry.

III. AN APPLICATION: THE IRON *K* EDGE IN HEMATITE

The method outlined previously affords a detailed, quantitative discussion here of the x-ray quadrupolar
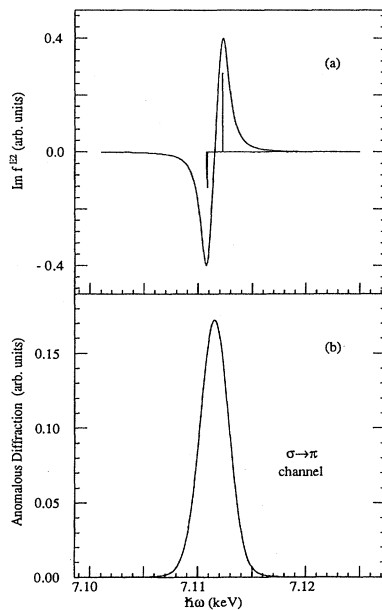

FIG. 2. Calculated quadrupolar anomalous diffraction at the K edge of Fe^{3+} in an octahedral crystal field with $10Dq = 1.45$ eV: (a) imaginary part of the amplitude; (b) cross section. The spectra are in the $\sigma \rightarrow \pi$ polarization channel. (There is no signal in $\sigma \rightarrow \sigma$.)

anomalous diffraction experiment performed by Finkelstein and co-workers (Finkelstein *et al.*, 1992).

The hematite crystal ($R\bar{3}c$) has a rhombohedral primitive cell with two molecules. In the following discussion we use the hexagonal setting, where the crystal displays a threefold symmetry about the c axis and glide planes parallel to this axis. The iron atoms are positioned along the c axis, with an approximately octahedral oxygen environment. Layers of octahedra separated by $c/6$ are equivalent by glide-plane operations. Finkelstein and co-workers measured the (0003) reflection, where the diffraction planes are separated by $c/3$. In αFe_2O_3 the xz plane serves as a mirror plane of the octahedron. The yz plane then is a glide plane with a shift of $c/6$ along $\hat{z}$. For this shift, the Bragg factor with $q = 6\pi/c$ is -1.

For $E1$ transitions in O_h symmetry, the resonant form factor f^{E1} is a product of two scalars (only $\mu = 0$ branches to A_1); thus the (0003) reflection is forbidden as a consequence of the glide-plane symmetry. $E2$ transitions involve instead two contributions: $\mu = 0$ and $\mu = 4$ (as from Fig. 1). Again, the scalar $\mu = 0$ term is forbidden; thus we need only work out the totally symmetric part of the $\mu = 4$ term, as given by Eq. (6). In switching to spherical harmonics, it is convenient to choose the $\hat{z}$ axis along a threefold axis of the octahedron, with basis functions pertaining to the group chain $O_3 \supset O_h \supset C_{3h}$.[6] The angular dependence reads

$$T^4_{A_1(O_h)} = -\frac{\sqrt{10}}{3\sqrt{3}}\left[T^4_3 + \frac{\sqrt{70}}{10}T^4_0 - T^4_{-3}\right], \quad (12)$$

with

$$T^4_{\pm 3} = \frac{5}{6}[Y^1_{\pm 1}(\mathbf{e}_i)Y^1_{\pm 1}(\hat{\mathbf{k}}_i)Y^1_{\pm 1}(\mathbf{e}_f)Y^1_0(\hat{\mathbf{k}}_f) + \text{cyc. perm.}]$$

(13)

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[6]The expansion in spherical harmonics is performed according to Butler's tables (Butler, 1981). Retaining the chain $O_3 \supset O_h \supset C_{3h}$ amounts to having the z axis along a threefold axis of the octahedron, a suitable choice in our case. The chain $O_3 \supset O_h \supset D_{4h} \supset C_{4h}$, for example, would lead to an expansion in spherical harmonics with the z axis along a fourfold axis; the rotations of these functions about a threefold axis would be rather tedious to discuss.

and

$$T_0^4 = \frac{5}{6\sqrt{70}} [\hat{\mathbf{k}}_i \cdot \hat{\mathbf{k}}_f \mathbf{e}_i \cdot \mathbf{e}_f + \hat{\mathbf{k}}_i \cdot \mathbf{e}_f \mathbf{e}_i \cdot \hat{\mathbf{k}}_f$$

$$-5(\hat{\mathbf{k}}_i \cdot \hat{\mathbf{k}}_f \mathbf{e}_i \cdot \mathbf{z}\mathbf{e}_f \cdot \mathbf{z} + \mathbf{e}_i \cdot \mathbf{k}_f \hat{\mathbf{k}}_i \cdot \hat{\mathbf{z}}\mathbf{e}_f \cdot \mathbf{z}$$

$$+ \hat{\mathbf{e}}_i \cdot \hat{\mathbf{e}}_f \mathbf{k}_i \cdot \mathbf{z}\mathbf{k}_f \cdot \mathbf{z} + \hat{\mathbf{e}}_f \cdot \hat{\mathbf{k}}_i \mathbf{e}_i \cdot \mathbf{z}\mathbf{k}_f \cdot \mathbf{z})$$

$$+ 35\hat{\mathbf{k}}_i \cdot \mathbf{z}\hat{\mathbf{k}}_f \cdot \mathbf{z}\mathbf{e}_i \cdot \mathbf{z}\mathbf{e}_f \cdot \mathbf{z}] . \tag{14}$$

In the angular dependence [Eqs. (12)–(14)], T_0^4 does not depend on φ; thus it is invariant upon reflection in the glide plane, and its contribution to the reflection is forbidden. The term $-T_3^4 + T_{-3}^4$ contains the factor $e^{3i\varphi} + e^{-3i\varphi}$, which changes sign upon reflection in the yz plane ($\alpha = \pi/2$). These terms control the quadrupolar anomalous diffraction in hematite. In our derivation, φ is

an abstract angle used to study the transformation properties of $T_m^{(\mu)}$. This angle is strongly connected to the azimuthal angle ψ between the scattering plane and the xz plane of the crystal, as can be seen by writing $\mathbf{e}$ and $\hat{\mathbf{k}}$ in polar coordinates (θ, φ). In the $\sigma \rightarrow \pi$ channel one has $\varphi_{\mathbf{k}_i} = \varphi_{\mathbf{k}_f} = \psi$, $\varphi_{\mathbf{e}_i} = \psi - \pi/2$, $\varphi_{\mathbf{e}_f} = \psi + \pi$. The components $T_{\pm m}^{(\mu)}$ contain the factor $e^{\pm i(m\psi + \alpha)}$, with α a shift angle to be determined; thus the ψ dependence of the $T_{\pm 3}^4$ terms is $\cos(3\psi + \alpha)$. To determine α, Eq. (13) may be written out completely; however, its value can be inferred from extinction rule (iv), Sec. II.B, stating that the $\sigma \rightarrow \pi$ channel vanishes when $\psi = 0$, which implies $\alpha = \pm \pi/2$ or $f^{E2} \sim \sin 3\psi$, as observed experimentally (see Fig. 2 in Finklestein, 1992).

For the transition operator, we obtain

$$\langle \psi_g | F_{A_1(O_h)}^{(4)}(\omega)_{E2} | \psi_g \rangle = \frac{\sqrt{10}}{3\sqrt{3}} \sum_I \frac{1}{\lambda_{Ig}} \left[\frac{\frac{1}{2}|\langle I \| J_{E(O_h)}^2 \| \psi_g \rangle|^2 - \frac{1}{3}|\langle I \| J_{T_2(O_h)}^2 \| \psi_g \rangle|^2}{E_I - E_g - \hbar\omega - i\Gamma/2} \right], \tag{15}$$

where the double vertical bars denote a reduced matrix element.[7] In terms of spherical harmonics, we have

$$\|J_{E(O_h)}^2\|^2 = \frac{1}{3}(\|J_{-2}^2 - \sqrt{2}J_1^2\|^2 + \|J_2^2 + \sqrt{2}J_{-1}^2\|^2)$$

and

$$\|J_{T_2(O_h)}^2\|^2 = \frac{1}{3}(\|J_1^2 + \sqrt{2}J_{-2}^2\|^2\|J_{-1}^2 - \sqrt{2}J_2^2\|^2) + \|J_0^2\|^2 ;$$

here $\| \cdots \|^2$ is shorthand for the squared modulus of the reduced matrix element.

$$\langle \gamma JM | Q_q^k | \gamma' J'M' \rangle = (-1)^{J-M} \begin{bmatrix} J & k & J' \\ -M & q & M' \end{bmatrix} \langle \gamma J \| Q^k \| \gamma' J' \rangle .$$

The calculation of the atomic quadrupolar spectra [Eq. (10)] has been performed with Cowan-Butler's atomic programs (full multiplet structure in a crystal field; see Cowan, 1968 and Butler, 1981). Transitions from the ground state of the $3d^5$ configuration (a >99% pure $^6A_1$) of the Fe^{3+} ion in octahedral symmetry to the full multiplet of $1s^1 3d^6$ have been calculated, assuming the crystal-field splitting $10Dq = 1.45$ eV (Kuiper et al., 1993). The effect of the core-hole width has been taken into account by convoluting the spectra with a $\Gamma = 1.5$ eV (full width at half maximum) Lorentzian.

The imaginary part of the scattering amplitude is depicted in Fig. 2(a). The vertical bars denote the multiplet structure: there are two groups of lines, corresponding to E and T_2 transitions, in order of increasing energy.

From the sum-rule analysis (Sec. II.C), the integral of the curve is known to be proportional to the ground-state expectation value of a fourth-rank tensor, $W^{(0,4)}$, which describes the hexadecapolar moment of the $3d$-electron distribution. The hexadecapolar moment vanishes for a pure d^5, $^6A_1$ state. From Fig. 2(a) we indeed find that,

due to an almost complete cancellation, the total integral of the curve is about one-thousandth of the integral over one of the peaks (E or T_2). This very small value implies that the fast-collision approximation breaks down in this case, as Γ and $10Dq$ are nearly equal at the iron K edge in hematite. Consequently, an appropriate description of the experiment requires that higher-order terms be retained in Eq. (8). However, such an analysis is beyond the scope of the present work.

The calculated scattering cross section, convoluted with a $\sigma = 1$ eV Gaussian function to simulate experimental resolution, is shown in Fig. 2(b). The spectrum consists of a single peak (no structure). This should be compared with the data (see Fig. 1 in Finkelstein, 1992), where a main peak and two shoulders appear. It is not clear whether these additional features are merely experimental artifact; they could reflect a lower-symmetry crystalline environment or hybridization of the Fe ion, effects not considered in our calculation. To account for the main features of the experiment, a d^5 ground state in octahedral symmetry suffices. (In the actual C_3 symmetry of the Fe atoms, $E1$ transitions are still forbidden by the glide plane; other $E2$ contributions with the same ψ dependence could appear.)

Note added in proof. After submitting this work for publication we learned that part of the results discussed in Sec. III were independently derived by Michael Hamrick [Finkelstein, K. D., M. Hamrick, and Q. Shen, 1994, "Resonant x-ray diffraction and polarisation analysis at the iron K edge," in *Resonant Anomalous X-Ray Scattering*, edited by G. Materlik, C. J. Sparks, and K. Fischer (Elsevier, Amsterdam), p. 91, and Doctoral thesis, Rice University, 1994].

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[7] The reduced matrix element is defined by (Wigner-Eckhart)

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