

Resonant Scattering Tensors in Spherical and Cubic Symmetries

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Abstract

The angular and polarization dependence of resonant scattering of X-rays by spherical atoms, and atoms with the symmetry of one of the cubic point groups, is described by formulae derived from an expansion in tensors of order up to four. At this level of approximation, the scattering can be anisotropic for any crystallographic symmetry. The change of scattering amplitude with Bragg angle is different for different polarization states, even for spherical atoms. The polarization dependence of this scattering offers a new method for estimating this θ dependence.

1. Introduction

This paper explores some of the complications in the coherent resonant scattering of X-rays that are found when atomic size is taken into account for non-magnetic atoms in spherical symmetry (where no atomic anisotropy is possible) and in cubic point groups (which exclude dipole anisotropy). An approximation of the atomic scattering factor f for X-rays is f_0 , often defined as a Fourier transform of the electron density. Some more-accurate definitions of this non-resonant part of the scattering factor are discussed by Kissel *et al.* (1995). This factor is quite sensitive to scattering angle because wavelengths are comparable with atomic dimensions. To correct for effects of resonance, one can add the dispersion terms f' and if'' . These terms, which arise mostly from inner-shell electrons, are less sensitive to angle than is f_0 because, for a given wavelength, retardation effects decrease as dimensions decrease. Usually in the analysis of diffraction data, one uses zero-angle values of f' and f'' , which are derived from absorption experiments or else calculated from theory with neglect of atomic size (the dipole approximation) and thus independent of angle. One also generally assumes that the effect of polarization is an independent factor, the same for all atoms, which can be taken into account in the initial reduction of diffraction intensity data. This separation of polarization from the scattering factor in the structure-factor algebra is impossible in the more nearly exact treatment considered here.

2. Optical model

Here a Cartesian basis is used for components of vectors and tensors; \mathbf{k} and \mathbf{k}' are wave vectors with magnitude

$k = 2\pi/\lambda$ for incident and scattered photons; ε and ε' are unit linear polarization vectors of the same photons; s and p indicate respectively that a polarization vector is perpendicular to or parallel with the plane containing \mathbf{k} and \mathbf{k}' .

The algebraic form of a tensor expansion of the resonant scattering can be obtained from an expression from perturbation theory for electric transitions (James, 1982):

$$f' + if'' \simeq \sum_c B_{ca}^* B_{ca}^0 / (E_a - E_c + \hbar\omega - i\Gamma/2), \quad (1)$$

$$B_{ca}^* = \langle a | \varepsilon' \cdot \mathbf{r} [1 - i\mathbf{k}' \cdot \mathbf{r} - (\mathbf{k}' \cdot \mathbf{r})^2/2 + \dots] | c \rangle, \quad (2)$$

$$B_{ca}^0 = \langle c | \varepsilon \cdot \mathbf{r} [1 + i\mathbf{k} \cdot \mathbf{r} - (\mathbf{k} \cdot \mathbf{r})^2/2 - \dots] | a \rangle. \quad (3)$$

When terms are arranged according to the powers of \mathbf{k} and \mathbf{k}' , (1) can be written as a sum of tensor expressions:

$$f' + if'' = f_S + f_T + f_U + f_V + \dots, \quad (4)$$

$$f_S = \sum_{m,n} \varepsilon_m \varepsilon'_n S'_{mn}, \quad (5)$$

$$f_T = \sum_{m,n,o} (\varepsilon_m \varepsilon'_n k'_o - \varepsilon'_m \varepsilon_n k_o) T_{mno}, \quad (6)$$

$$f_U = \sum_{m,n,o,p} \varepsilon_m k_n \varepsilon'_o k'_p U_{mnop}, \quad (7)$$

$$f_V = \sum_{m,n,o,p} (\varepsilon_m k'_n \varepsilon'_o k'_p + \varepsilon'_m k_n \varepsilon_o k_p) V_{mnop}. \quad (8)$$

This expansion is not the same as the electromagnetic multipole expansion in spherical harmonics, but to designate the terms as if it were is convenient and commonplace: S as electric dipole–dipole, T as dipole–quadrupole *etc.* Magnetic transitions add additional tensors that can be antisymmetric for interchange of certain indices (Brouder, 1990; Blume, 1994). A magnetic dipole–electric dipole combination gives

$$f_W = \sum_{m,n,o} (\varepsilon_m \varepsilon'_n k'_o + \varepsilon'_m \varepsilon_n k_o) W_{wno}. \quad (9)$$

Magnetic dipole–magnetic dipole and magnetic dipole–electric quadrupole give two tensors X and Y like (7) and they can be added to U . But the symmetry of their

elements and the polarization geometry are not the same and it is convenient to keep them separate here. Combination of magnetic quadrupole and electric dipole gives

$$f_Z = \sum_{m,n,o,p} (\varepsilon_m k'_n \varepsilon'_o k'_p - \varepsilon'_m k_n \varepsilon_o k_p) Z_{mnop}. \quad (10)$$

Here and in the following equations, these scattering factors include the polarization factor. The tensors S , T etc. are sensitive functions of wavelengths near absorption edges and their elements are complex numbers. In the atomic coordinate system, they do not change with Bragg angle θ nor azimuthal angle ψ . The dependence of scattering on these angles is contained in the product of each tensor with its vectors.

3. Spherical symmetry

For atoms with spherical symmetry, S is diagonal with $S_{11} = S_{22} = S_{33}$. At this level of approximation, the resonant scattering terms f' and f'' can be defined as scalars (independent of θ) that must be multiplied by $\varepsilon \cdot \varepsilon'$, the same polarization factor as for f_0 . Thus, f_S after correction for polarization in the conventional way is independent of θ .

Tensors of odd rank are zero for atoms of spherical symmetry or any other symmetry that includes a center of inversion. Thus, the third-rank tensors T and W are absent. Tensors Y and Z also are zero in spherical symmetry.

Tensors of fourth rank introduce angular dependence and more complicated polarization effects. When the sequence of vectors and their indices corresponds to (7), the 81 elements of U fit the pattern shown in Table 1 with $a = b + 2c$ and $U_{ijkl} = U_{jikl} = U_{jilk} = U_{ijlk}$. The tensor V has the same pattern with the additional condition that $b = c$.

When the terms of f_U and f_V are written out, they can be arranged to give, after dropping terms with factors $(\varepsilon \cdot \mathbf{k})$ or $(\varepsilon' \cdot \mathbf{k}')$:

$$f_U = U_{1212}[(\varepsilon \cdot \varepsilon')(\mathbf{k} \cdot \mathbf{k}') + (\varepsilon \cdot \mathbf{k}')(\varepsilon' \cdot \mathbf{k})], \quad (11)$$

$$f_V = V_{1212}(\varepsilon \cdot \varepsilon')(\mathbf{k} \cdot \mathbf{k} + \mathbf{k}' \cdot \mathbf{k}'). \quad (12)$$

Let $B_1 = k^2 U_{1212}$ and $B_2 = 2k^2 V_{1212}$. For the polarization normal to \mathbf{k} and \mathbf{k}' , (11) becomes

$$f_U(ss) = B_1 \cos(2\theta). \quad (13)$$

For polarization in the plane of \mathbf{k} and \mathbf{k}' and with some trigonometric manipulation, (11) becomes

$$f_U(pp) = B_1 \cos(4\theta). \quad (14)$$

Equation (12) reduces to

$$f_V(ss) = B_2, \quad (15)$$

Table 1. Elements of U_{mnop} in spherical symmetry

op	11	22	33	23	31	12
mn						
11	a	b	b	0	0	0
22	b	a	b	0	0	0
33	b	b	a	0	0	0
23	0	0	0	c	0	0
31	0	0	0	0	c	0
12	0	0	0	0	0	c

$$f_V(pp) = B_2 \cos(2\theta). \quad (16)$$

This angular dependence for f_V is the same as for f_S and f_0 . In all the above cases, the sp and ps terms are zero. These polarization factors for k^2 terms of isotropic atoms were derived by Hönl (1933). They are also valid for some, but not all, of the terms of higher order.

According to L - S coupling rules, the tensor X is zero for inner-shell resonances but it may be observable in heavy elements as a result of relativistic effects (Brouder, 1990). In spherical symmetry, it is zero except for six equal elements X_{ijij} ($i \neq j$) and six others $X_{ijji} = -X_{ijij}$. The scattering is

$$f_X = X_{1212}(\mathbf{k} \times \varepsilon) \cdot (\mathbf{k}' \times \varepsilon') \quad (17)$$

or, more explicitly, with $B_4 = k^2 X_{1212}$,

$$f_X(ss) = B_4 \cos(2\theta), \quad (18)$$

$$f_X(pp) = B_4, \quad (19)$$

$$f_X(sp) = f_X(ps) = 0. \quad (20)$$

Note that the polarization factors in (18) and (19) are just the reverse of those for conventional scattering.

Another way to treat f_U is to divide (11) into two parts according to the M and N functions of Kissel *et al.* (1995):

$$f_{UM} = U_{1212}(\varepsilon \cdot \varepsilon')(\mathbf{k} \cdot \mathbf{k}'), \quad (21)$$

$$f_{UN} = U_{1212}(\varepsilon \cdot \mathbf{k}')(\varepsilon' \cdot \mathbf{k}). \quad (22)$$

For the ss and pp polarization cases, (21) and (22) become

$$f_{UM}(ss) = B_1 \cos(2\theta), \quad (23)$$

$$f_{UM}(pp) = B_1 \cos^2(2\theta), \quad (24)$$

$$f_{UN}(ss) = 0, \quad (25)$$

$$f_{UN}(pp) = -B_1 \sin^2(2\theta). \quad (26)$$

In the approximation including tensors up to the fourth rank, the total atomic scattering factor, including its

polarization factor, is

$$f(ss) = f_0 + S_{11} + B_1 + B_2 + B_4 - 2(B_1 + B_4) \sin^2 \theta, \quad (27)$$

$$f(pp) = f(ss) \cos(2\theta) - (B_1 - B_4) \sin^2(2\theta). \quad (28)$$

4. Cubic symmetry

There are five cubic point groups: $23-T$, $\bar{4}3m-T_d$, $m\bar{3}-T_h$, $432-O$ and $m\bar{3}m-O_h$. For each of these symmetries, the second-rank tensor S is isotropic and independent of θ , as is the case for spherical symmetry. For $m\bar{3}$, 432 and $m\bar{3}m$, the tensor T is zero. For 23 and $43m$, in a basis with axes along twofold axes, T is zero except for six equal elements (Templeton & Templeton, 1994):

$$T_{123} = T_{231} = T_{312} = T_{321} = T_{132} = T_{213}. \quad (29)$$

In this case, and others below, the magnitudes and functional form of the change of scattering with ψ and θ depends on the direction of $\mathbf{h} = (\mathbf{k}' - \mathbf{k})/2\pi$; ψ represents a rotation of the atom around \mathbf{h} and is zero or π when $\mathbf{k}' + \mathbf{k}$ is in the xy plane of the atom. Let $B_3 = kT_{123}$. For $\mathbf{h} = [h00]$:

$$f_T(ss) = 2B_3 \sin(2\psi) \sin \theta, \quad (30)$$

$$f_T(pp) = 2B_3 \sin(2\psi) \sin^3 \theta, \quad (31)$$

$$f_T(sp) = f_T(ps) = 2B_3 \cos(2\psi) \sin^2 \theta. \quad (32)$$

For $\mathbf{h} = [hh0]$:

$$f_T(ss) = f_T(pp) = 0, \quad (33)$$

$$f_T(sp) = f_T(ps) = B_3 \cos \psi \sin(2\theta). \quad (34)$$

For $\mathbf{h} = [hhh]$, f_T is independent of ψ :

$$f_T(ss) = -(2 \times 3^{1/2}/3)B_3 \sin \theta, \quad (35)$$

$$f_T(pp) = (2 \times 3^{1/2}/3)B_3 \sin \theta [\cos^2 \theta + 1], \quad (36)$$

$$f_T(sp) = f_T(ps) = 0. \quad (37)$$

Tensor W is non-zero only for 432 and 23 among the cubic groups. Its elements are zero except for

$$W_{123} = W_{231} = W_{312} = -W_{321} = -W_{132} = -W_{213}. \quad (38)$$

For any atomic orientation,

$$f_W(ss) = f_W(pp) = 0, \quad (39)$$

$$f_W(sp) = -f_W(ps) = 2kW_{123} \cos^2 \theta. \quad (40)$$

This rotation of polarization gives rise to isotropic optical activity in the forward direction.

In all the cubic point groups, and with x, y, z along the cubic axes, the fourth-rank tensors U and V have the same patterns as for spherical symmetry except that they lack the restriction $a = b + 2c$. It is convenient to divide U into ${}^iU + {}^aU$, where iU is an isotropic atom tensor with ${}^iU_{ijkl} = b + 2c$ in place of U_{ijkl} . All the ψ dependence comes from aU , which is zero except for the elements

$${}^aU_{1111} = {}^aU_{2222} = {}^aU_{3333} = a - b - 2c. \quad (41)$$

The tensor V can be divided in the same manner. Let g be the part of f calculated from ${}^aU + {}^aV$, $C_1 = k^2(2{}^aV_{1111} + {}^aU_{1111})$ and $C_2 = k^2(2{}^aV_{1111} - {}^aU_{1111})$. For $\mathbf{h} = [h00]$:

$$g(ss) = \frac{1}{2}C_1 \sin^2(2\psi) \cos^2 \theta, \quad (42)$$

$$g(pp) = \frac{1}{4}[C_2 - C_1(\cos^4 \psi + \sin^4 \psi)] \sin^2(2\theta), \quad (43)$$

$$g(ps) = -g(sp) = \frac{1}{4}C_1 \sin(4\psi) \sin \theta \cos^2 \theta. \quad (44)$$

For $\mathbf{h} = [hh0]$:

$$g(ss) = \frac{3}{8}C_1 \sin^2(2\psi) \cos^2 \theta + \frac{1}{2}C_2 \sin^2 \psi \sin^2 \theta, \quad (45)$$

$$\begin{aligned} g(pp) = & \frac{1}{8}C_1[4 \cos^2 \psi \cos^4 \theta \\ & - (\cos^4 \psi + 2 \sin^4 \psi) \sin^2(2\theta)] \\ & - \frac{1}{8}C_2[4 \cos^2 \psi \sin^4 \theta - \sin^2(2\theta)], \end{aligned} \quad (46)$$

$$\begin{aligned} g(ps) = & -g(sp) \\ = & \frac{1}{4} \sin(2\psi) \sin \theta [C_2 \sin^2 \theta \\ & + C_1 \cos^2 \theta (\cos^2 \psi - 2 \sin^2 \psi)]. \end{aligned} \quad (47)$$

For $\mathbf{h} = [hhh]$:

$$g(ss) = \frac{1}{6}C_1 \cos^2 \theta + \frac{1}{3}C_2 \sin^2 \theta, \quad (48)$$

$$\begin{aligned} g(pp) = & \frac{1}{6}C_1[\cos(2\theta) - \frac{5}{4}\sin^2(2\theta) + 1] \\ & + \frac{1}{6}C_2[\cos(2\theta) + \sin^2(2\theta) - 1], \end{aligned} \quad (49)$$

$$g(sp) = g(ps) = -(2^{1/2}/6)C_1 \cos(3\psi) \cos^3 \theta. \quad (50)$$

The geometry of tensor X is the same in any cubic symmetry as in spherical symmetry and (17) to (20) are valid. Its magnitude may be greater in this lower symmetry if crystal fields or chemical bonds affect the wavefunctions of excited states.

Tensors Y and Z are zero except in point groups 23 and $m\bar{3}$. The elements of Y are zero except

$$Y_{1221} = Y_{2332} = Y_{3113} = -Y_{2112} = -Y_{3223} = -Y_{1331}. \quad (51)$$

Let $C_3 = k^2 Y_{1221}$. For $\mathbf{h} = [h00]$:

$$f_Y(ss) = f_Y(pp) = 0, \quad (52)$$

$$f_Y(sp) = f_Y(ps) = \frac{1}{4} C_3 \sin(2\psi) \sin(2\theta) \cos \theta. \quad (53)$$

For $\mathbf{h} = [hh0]$:

$$f_Y(ss) = -\frac{3}{4} C_3 \sin \psi \sin(2\psi) \sin(2\theta), \quad (54)$$

$$f_Y(pp) = C_3 [\cos \psi - \frac{3}{4} \sin \psi \sin(2\psi)] \sin(2\theta), \quad (55)$$

$$\begin{aligned} f_Y(sp) &= -f_Y(ps) \\ &= \frac{1}{32} C_3 \{ \sin \psi [11 \cos \theta + \cos(3\theta)] \\ &\quad + \sin(3\psi) [15 \cos \theta - 3 \cos(3\theta)] \}. \end{aligned} \quad (56)$$

For $\mathbf{h} = [hhh]$:

$$f_Y(ss) = f_Y(pp) = (6^{1/2}/6) C_3 \cos(3\psi) \sin(2\theta), \quad (57)$$

$$\begin{aligned} f_Y(sp, \psi) &= f_Y(ps, -\psi) \\ &= -(3^{1/2}/24) C_3 [9 \sin \theta + \sin(3\theta)] \\ &\quad + (6^{1/2}/24) C_3 [5 \cos \theta - \cos(3\theta)] \sin(3\psi). \end{aligned} \quad (58)$$

Tensor Z is zero except for the 12 elements

$$Z_{ijj} = Z_{jij} = -Z_{jji} = -Z_{jii} \quad (ij = 12, 23, 31). \quad (59)$$

Let $C_4 = k^2 Z_{1212}$. For $\mathbf{h} = [h00]$, f_Z is given by (52) and (53) with $2C_4$ in place of C_3 . For $\mathbf{h} = [hh0]$:

$$f_Z(ss) = -\frac{1}{4} C_4 [5 \cos \psi + 3 \cos(3\psi)] \sin(2\theta), \quad (60)$$

$$f_Z(pp) = \frac{3}{2} C_4 \sin \psi \sin(2\psi) \sin(2\theta). \quad (61)$$

With $2C_4$ in place of C_3 , (56) gives $f_Z(sp)$ and $-f_Z(ps)$. For $\mathbf{h} = [hhh]$ and with $2C_4$ in place of C_3 , (57) gives $-f_Z(ss)$ and $-f_Z(pp)$, and (58) gives $f_Z(sp, -\psi)$ and $f_Z(ps, \psi)$.

5. Discussion

The dependence of resonant scattering on θ is a small effect that is of little consequence in many experiments, yet it may be significant for the intensities of weak reflections. Its magnitude may be particularly important for the interpretation of experiments based on small differences of intensities recorded with multiple photon energies. A possible example is differential radial distributions for amorphous materials (Raoux, 1994). Even when it is unimportant, one must understand it to have confidence in such experiments. One can see from (27) and (28) that even for spherical atoms the concept of f' and f'' as scalar functions of θ with the traditional polarization factors fails with the first angle-dependent

terms. The best one can do is to define a double-valued θ dependence for two states of linear polarization. Then the structure factor is also double valued except for special cases such as perfectly polarized radiation or polarization-analyzed detection. Fortunately, the ss case is dominant in many experiments with synchrotron radiation and (28) may enter only as a small correction term, if at all. It is also true that the last term in (28) generally is unimportant, except for some weak reflections, even in experiments with unpolarized radiation. But even this simplicity vanishes when atomic anisotropy is significant, as it often is near an absorption edge.

In symmetries lower than those considered here, the above equations for anisotropic scattering become much more complicated. Then f_s can be strongly anisotropic. It can dominate the higher-order terms and make them difficult or impossible to detect. Most of the studies that have been published concerning anisotropic resonant scattering are based on anisotropy of f_s , even in cubic crystals (*e.g.* Dmitrienko, 1984; Templeton & Templeton, 1985; Kirfel *et al.*, 1991; Nagano *et al.*, 1996). The symmetries considered in this paper are those of the atom, not those of the crystal.

Bergstrom *et al.* (1997) have reported theoretical values of the angle dependence of the resonant scattering (in spherical symmetry) in terms of formulae with lookup tables for any element for photon energies above and not too close to the K edges. For energies close to absorption edges, where resonance is most extreme and most sensitive to chemical state, good theoretical values are not available. Existing experimental values (*e.g.* Templeton *et al.*, 1982) are prone to bias from errors that are correlated with θ , such as those associated with absorption, thermal motion, polarization state of the radiation, or details of instrumental geometry. A particular problem for f' is that its definition is based on a partition of the total amplitude into resonant and non-resonant parts. Thus, its variation measured in an experiment is inversely correlated with that assumed for f_0 , which is a sensitive and imperfectly known function of θ . For these reasons, it is interesting that (27) and (28) offer a new way to estimate this θ dependence, which may avoid much of this bias. In a case where B_4 can be neglected (lighter atoms), parameter B_1 , which determines the θ dependence of the resonant scattering in both polarization states, can dominate the residual pp scattering near $\theta = 45^\circ$. Thus B_1 , or an upper limit on its magnitude, can be derived from measurements of the intensity ratio I_{pp}/I_{ss} for a suitable set of crystal reflections near $\theta = 45^\circ$. While this method is not free of technical problems such as accurate measurement of weak intensities and elimination of multiple scattering, it appears to be possible with synchrotron radiation.

The equations giving the dependence on ψ and θ of the anisotropic scattering for cubic point groups illustrate the great variety of complexity that can occur. They may also be helpful for identification of the most favorable

orientations to be used in experiments that seek to measure such effects. For computer calculations, particularly if there is interest in more general orientations or lower symmetry, it is more convenient to program the arithmetic directly from expressions such as (5)–(10). The equations in this paper are explicit only for two states of linear polarization, but if combined with appropriate attention to phase they can be used for any polarization state of the incident radiation.

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