Borrmann spectroscopy

S P Collins\textsuperscript{1,2}, M Tolkiehn\textsuperscript{1,3}, R F Pettifer\textsuperscript{2,4} and D Laundy\textsuperscript{5}

\textsuperscript{1} Diamond Light Source Ltd, Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0DE
\textsuperscript{2} Physics Department, University of Warwick, Coventry, CV4 7AL, UK
\textsuperscript{5} STFC Daresbury Laboratory, Warrington, WA4 4AD, UK
E-mail: steve.collins@diamond.ac.uk

Abstract. Under conditions of Anomalous X-ray Transmission (known as the Borrmann Effect), an X-ray standing wave is set up inside a crystal, leading to a strong reduction in electric dipole absorption. We show that electric quadrupole absorption is not similarly diminished and is thus relatively enhanced by a large factor. Absorption measurements, made under thick-crystal Laue (transmission) diffraction conditions in Gd\textsubscript{3}Ga\textsubscript{5}O\textsubscript{12} (GGG) and Y\textsubscript{3}Fe\textsubscript{5}O\textsubscript{12} (YIG), show a range of spectral features that can be assigned unambiguously to electric quadrupole events. This phenomenon, which seems to have been overlooked for decades, opens up new possibilities for studying important electronic states with hard x-ray beams. In this paper, we outline the origin of the effect and a phenomenological description of its temperature dependence, and consider the possibility of measuring the angle dependence of enhanced quadrupole absorption.

1. Background

Most x-ray absorption measurements are interpreted within the electric dipole approximation, whereby only the effects of an oscillating electric field at the absorbing atoms are taken into account. Higher order terms, such as electric quadrupole absorption, are neglected. The latter corresponds the absorption via the interaction of the atom with the electric field gradient, and accounts typically for just a few percent of the total absorption. Similarly, resonant x-ray scattering, which can be though of as the absorption and emission of a photon, is dominated by dipole interactions.

Going beyond the dipole approximation is important in two key respects. First, one finds, close to absorption edge resonances, weak diffraction signals that arise from high order scattering tensors in magnetic, anisotropic, and orbitally-ordered systems. The second important feature of such processes concerns angular momentum selection rules and the symmetry of the unoccupied electronic states probed in the absorption process. For example, dipole transitions at the K-edge of transition metals can probe only the empty p bands, whereas quadrupole absorption, which can change the angular momentum by two units, is sensitive to the 3d band, which is of prime importance to magnetism and other electronic properties. Similarly, quadrupole transitions at rare-earth L\textsubscript{2,3}-edges probe the important 4f states. The conventional approach to observing
these valence states is to utilize very low energy x-ray beams, under high-vacuum conditions, or
to employ photon-hungry inelastic scattering techniques.

Information obtained previously concerning electric quadrupole (E2) contributions to
absorption spectra have relied on the fact that, due to differences in electronic screening, at
least part of the weak E2 contribution can appear slightly below the normal (E1) absorption
edge [1, 2]. The appearance of such peaks below the edge is usually the sole basis for assuming
that they are quadrupolar in character. The few examples of direct verification of the E2
absorption have relied on anisotropy of the states under investigation [3, 4].

The Borrmann effect, first published in 1941 [5] and described theoretically by Batterman and
Cole [6], is one of the most remarkable manifestations of dynamical x-ray diffraction, and has
found a number of important applications in physics [7] and materials science [8]. The idea of
studying quadrupole absorption in the Borrmann effect was first discussed by Wagenfeld in 1966
[9] but the possibility of using this approach to enhance quadrupole features in absorption-edge
spectra has, to our knowledge, been missed until very recently [10]. In essence, the Borrmann
effect occurs under conditions of Laue diffraction, when the crystal is many times thicker than
the absorption length. A single standing wave field forms perpendicular to the crystal planes,
with nodes at the atomic planes and polarization (electric field) parallel to the planes. Because
the wave field is weak at the absorbing sites, one observes anomalous transmission of the x-ray
beam.

As with other diffraction phenomena, the Borrmann Effect is governed by a 1d projection
of the electronic and atomic properties along the momentum transfer \( \mathbf{k} \). The simplest and
most studied scenario for the Borrmann Effect is where the 1d electron density contains mirror
symmetry. Translational symmetry then generates an infinite set of mirrors separated by the
translational period, \( d \), as well as a second set, equidistant from the first (see Figure 1). It
is useful to consider two domains within the crystal. The first describes the region where the
beam enters the sample and the diffracted beam is built up. The net flow of energy alternates
between the incident (forward-diffracted) and diffracted beams with decreasing amplitude [6]
until two waves of identical intensity are established. These two waves then propagate through
the remainder of the crystal, in the second domain where all memory of the original beam is lost
and the wave field is an eigenstate of the crystal, with energy flow parallel to the crystal planes.
The Borrmann effect requires that the crystal is sufficiently thick for the second domain to be
much larger than the first, and therefore to dominate the physics of the x-ray transmission. In
the second domain the wave field adopts the symmetry of the crystal and is therefore symmetric
with respect to the mirror planes. The theory of dynamical diffraction tells us that there are
four possible solutions for the wave field: two with polarization perpendicular to the crystal
planes, which do not produce a large Borrmann Effect [6], and two with polarization parallel to
the planes. The latter form a standing wave perpendicular to the planes (and traveling waves
parallel to them) and, by symmetry, have nodes and antinodes at one or other of the mirror
planes. If one of the mirrors has a much higher density of absorbing atoms than the other then
the solution with nodes at these planes, called the \( \alpha \)-branch, will have reduced absorption and
will lead to anomalous transmission. This is the essence of the Borrmann effect. To understand
how the Borrmann effect produces a relative enhancement of electric quadrupole absorption is
straightforward in this picture: the \( \alpha \)-branch wave has a node at the heavy atoms, meaning that
the electric field intensity that drives dipole absorption is minimised. At the same time, the field
gradient of this wave, which drives quadrupole absorption, is maximised.

Our phenomenological model of the Borrmann effect is based on a number highly simplistic
assumptions, including that the second domain of the crystal is very much larger than the first
and that the scattering processes that govern the first domain can be neglected; similarly, that
there is no significant scattering between the two orthogonal wave fields. If these assumptions are
valid then the energy spectrum of the transmitted beam will reflect that of normal absorption,
albeit with enhanced quadrupole and diminished dipole contributions. The fact that, at least in some cases, the spectra do resemble absorption spectra, suggests that the model has some sound basis. However, a more complete theory of Borrmann spectroscopy must include all scattering processes and their polarization dependence, as well as a description of the effects of atomic displacements and crystal imperfection.

To demonstrate the feasibility of quadrupole enhancement via the Borrmann effect, we consider briefly the quadrupole/dipole (E2/E1) absorption ratios for normal case (away from diffracting conditions) and in the Borrmann effect. Neglecting energy denominators, and other factors which are unimportant for the present discussion, the absorption cross-section can be written,

\[ \sigma = \sum_f |\langle f| p \cdot A|i \rangle|^2 \]  

(1)

where \( p \) is the electron momentum, \( A \) the vector potential of the photon, and the sum runs over all possible final state configurations of the correct energy. One can write the transition operator as a Taylor series, first in terms of \( p \), and then, via appropriate commutation relations [11], in terms of the position operator \( r \),

\[ p \cdot A \propto p \cdot \varepsilon e^{iq \cdot r} = p \cdot \varepsilon + i p \cdot \varepsilon q \cdot r + ... \]

\[ = \frac{m}{i\hbar} [\varepsilon \cdot r, \mathcal{H}] - \frac{m}{2\hbar} [\varepsilon \cdot r q \cdot r, \mathcal{H}] + ... \]

(2)

Here the first two terms correspond to electric dipole (E1) and quadrupole (E2) transitions, and magnetic terms are neglected due to their weakness [11]. For the current discussion we neglect mixed dipole-quadrupole transitions, which average to zero in centro-symmetric crystals. From Equations (1) and (2) we can deduce a simple expression for the E2/E1 ratio,

\[ \frac{\sigma_{E2}}{\sigma_{E1}} = \frac{1}{4} \sum_f |\langle f| \varepsilon \cdot r q \cdot r|i \rangle|^2 = \frac{q^2}{4} \sum_f |\langle f|z i \rangle|^2 \]

(3)

where we adopt a coordinate system in which \( q \) lies along the y-axis and the (linear) polarization is along z.

![Figure 1.](image1.png)

**Figure 1.** The standing wave part of the x-ray wave field in thick-crystal Laue diffraction. The α-branch undergoes ‘anomalous transmission’ since it has nodes where the density of absorbing atoms (filled circles) is highest.

![Figure 2.](image2.png)

**Figure 2.** The Cartesian coordinate system adopted in [12] and employed for most of the present discussions. For the case of absorption, \( \theta = 0 \). Spherical and Cartesian vectors are related in the conventional way.
The reason for revisiting the familiar form of the electric multipole expansion is that the Borrmann case can be treated in a very similar way, by making just two changes. First, the vector potential for a single traveling wave is replaced by that of two waves, one along the incident beam direction, $q$, and the other, of equal amplitude, along the diffracted beam direction, $q'$, where the two waves are phased so as to give zero field at the diffracting planes. The second difference is that we consider absorption by atoms that are displaced from their ideal positions by a small distance $U$. The resulting interaction operator becomes,

$$\mathbf{p} \cdot \mathbf{A} \propto \mathbf{p} \cdot \hat{\varepsilon} \left( e^{i\mathbf{q} \cdot (\mathbf{r} + \mathbf{U})} - e^{i\mathbf{q}' \cdot (\mathbf{r} + \mathbf{U})} \right)$$  

$$= -i\mathbf{p} \cdot \hat{\varepsilon} \left( \mathbf{k} \cdot \mathbf{r} + \mathbf{k} \cdot \mathbf{U} \right) + ...$$

(4)

where $\mathbf{k} = \mathbf{q}' - \mathbf{q}$ is the momentum transfer. Here we see that the first (dipole) term in the normal absorption case has vanished, leaving two terms of the same order. The first of these is the quadrupole term, and the second is the dipolar absorption that arises due to the atomic displacement. The ratio of the (time-averaged) $E_2/E_1$ ratio in the Borrmann case is obtained by factoring out the mean-squared (assumed isotropic) atomic displacement, $\langle U^2 \rangle$, leading to the result,

$$\frac{\sigma_{E2}}{\sigma_{E1}} = \frac{3}{4} \frac{\sum_f |\langle f | \hat{z} \hat{x} | i \rangle|^2}{\sum_f |\langle f | \hat{z} | i \rangle|^2},$$

(5)

and one can obtain an expression for the quadrupole enhancement (relative increase in $E_2/E_1$ ratio) in the Borrmann effect:

$$\eta = \frac{3\lambda^2}{4\pi^2 \langle U^2 \rangle}.$$  

(6)

This simple model highlights several important results. First, $\sigma_{E2}/\sigma_{E1}$ is strongly enhanced if $\langle U^2 \rangle$ is much smaller than $\lambda^2$. This is the basis of Borrmann Spectroscopy. As $\langle U^2 \rangle$ increases, due to thermal motion or crystal defects, one would expect a dramatic reduction in the (relative) quadrupole absorption. Another important result is the quadrupole absorption is now sensitive to a different component of the quadrupole matrix element compared to normal absorption, along directions $k$ and $\varepsilon$ rather than $q$ and $\varepsilon$.

2. Measurements on GGG and YIG

Here, we report experimental studies of the 008 reflection from the cubic garnet crystals $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (GGG) and $\text{Y}_3\text{Fe}_5\text{O}_{12}$ (YIG). The garnet structure is favourable for the Borrmann effect as the heavy atoms are located at equidistant planes, with only moderately absorbing oxygen atoms between. High quality crystals are readily available. The Laue peak widths of these reflections were found to be 0.005° and 0.01°, respectively - still larger than either the theoretical widths or instrument resolution.

Measurements on GGG were carried out on the SRS high-resolution diffraction beamline 16.3 at Daresbury Laboratory, and those on YIG, at beamline I16, Diamond Light Source. The samples, of thickness 0.57 mm and 0.5 mm for GGG and YIG, were attached to the cold-finger of a cryostat and held at 10K or 300K (GGG) and 6K (YIG). An interesting aspect of the Borrmann effect is that two identical beams emerge from the sample: one parallel to $q$, the other to $q'$. Both beams were measured in the present study. After confirming that the resulting spectra were the same in each case, only the diffracted beam was used for quantitative analysis as it gave the best signal/noise ratios. Intensities were obtained by integrating over the narrow Laue peaks. The Borrmann spectra were then compared with the results of conventional absorption data from thin powder samples of the same materials in order to make a direct comparison between the two spectra.
Figure 3. A unit cell of the garnet structure, showing the wave field for the 008 reflection, which moves from right to left, parallel to the atomic planes. Red and blue regions indicate positive and negative field; uncoloured regions have almost zero field. Only oxygen atoms (yellow) experience a significant field intensity. The plane of the heavy atoms have minimum field but maximum field gradient.

Figure 4. The normal (powdered foil) and Borrmann absorption at the Gd L edges in GGG [10]. The top plots show the L3 spectra at temperatures of 10K and 300K; the bottom left plot shows the L2 spectrum. The absorption coefficients are given on absolute scales, with vertical plot ranges chosen to give the same height for the dipolar peak in both cases. Continuous lines represent the normal absorption, with circular symbols indicating Borrmann data. The normal and Borrmann absorption at the Gd L1 edge in GGG are shown bottom right, where the dominant feature of the Borrmann spectrum is the huge quadrupole peak, corresponding to transitions to empty 4d states.

Some of the main findings are shown in Figures 4 & 5. The most spectacular results, which establish this new phenomenon on a firm footing, concern the Gd L-edge spectra in GGG.
Figure 4 shows the normal and Borrmann absorption spectra at the $L_{2,3}$ edges. The normal absorption is dominated by a sharp white-line feature at the absorption edge, corresponding to transitions to holes in the narrow 4d band. The Borrmann spectra are similar, but show an extra peak 7.2 eV below the dipole peak, corresponding to transitions to 4f holes. The position of this feature is consistent with previous observations [2] but can, for the first time, be assigned unambiguously to a quadrupole event.

The dramatic reduction (by a factor of 2.6) in the quadrupole peak amplitude as the sample temperature is increased from 10K to 300K is entirely consistent with Equation 6 if one assumes that the mean-squared displacement is dominated by thermal fluctuations which, in turn, are adequately described by the Debye model with $\Theta = 400$ K. The absolute value of the quadrupole enhancement is estimated to be $\approx 18$ at $T=10K$ and $\approx 6$ at $T=300K$. This is somewhat lower than the value of 40 estimated from Equation 6 for $T=10K$ (again adopting the Debye model for $\langle U^2 \rangle$), although this is to be expected as this estimate assumes a perfect crystal.

The reduction in the E2 intensity (relative to E1) on going to the Gd $L_2$-edge, by a factor of 1.8 was significantly larger than expected. The statistical value of the $L_2/L_3$ branching ratio is 1/2 for both cases, suggesting that the measured branching ratios should be very similar. In the $L-S$ coupling scheme, the branching ratio for Gd takes on exactly the statistical value [13], although detailed atomic multiplet calculations [14] suggest that a slight departure can be caused by spin-orbit coupling. Since there exists surprisingly little experimental data on the branching ratios in the normal absorption it is, as yet, unclear where the physical origin of this anomaly lies. Further detailed studies are required to resolve this question.

The Gd $L_1$ absorption spectra is, remarkably, dominated by quadrupole absorption in the Borrmann case. The sharp pre-edge peak corresponds to E2 transitions to the 4d band, and is the counterpart of the strong white-line resonance seen in the $L_{2,3}$-edge spectra. While this feature has not been observed before, even the normal absorption shows a pre-edge bump at the same energy, suggesting the presence of a weak peak.

Figure 5. The (rescaled) normal and Borrmann absorption at the Fe $K$-edge in YIG with arbitrary scales with the vertical axes chosen to highlight the differences between the two spectra. The main differences between the spectra is a large enhancement of the pre-edge peak from the Borrmann data.

Figure 5 shows that the normal and Borrmann Fe $K$-edge spectra in YIG are very similar except for a strong enhancement of the pre-edge peak, and a slight increase at 15 eV above the edge, in the Borrmann case. The pre-edge peak is understood as a (predominantly) dipole transition to the mixed 3p-d band. An enhancement in the amplitude of this feature in the Borrmann case demonstrates the presence of a sizeable quadrupole component.
3. Angle dependence of quadrupole absorption in the Borrmann case

The angle dependence for normal electric quadrupole absorption is given in terms of spherical tensor components by Brouder [11], and for resonant scattering by Lovesey et al [12]. Here, we follow the method of Lovesey et al to reproduce Brouder’s result for normal absorption, and the equivalent expressions for the Borrmann case. The angle dependence of absorption is equivalent to that of forward scattering with no polarization change. Thus, angle dependence of the normal quadrupole absorption is [12]

$$\sigma_{E^2} = \sum_{KQ} (-1)^K+Q H_{-Q}^K \sigma_{QK}$$

where $$\sigma_{QK}$$ are the spherical tensor components of the absorption cross-section, of rank $$K$$ and projection $$Q$$, and

$$H_{Q}^K = \sum_{nm'} h(m)h'(m')(2m2m'|KQ)$$

with

$$h(q) = \sum_{nm'} \hat{\varepsilon}_n \hat{q}_{nm'} (1n1n'|2m)$$

where $$(lml'm'|LM)$$ are Clebsch-Gordon coupling coefficients and $$\hat{\varepsilon}_n$$, $$\hat{q}_{nm'}$$ are spherical components of the polarization and wave (unit) vectors, respectively.

In the absence of magnetism, only even tensor ranks contribute to the (parity-even) pure quadrupole absorption, and so we consider only $$K = 0, 2, 4$$. Moreover, for spherical tensors we can exploit the symmetry [11]

$$\sigma_{K,-Q} = (-1)^Q \sigma_{QK}$$

and so we need only consider components with positive projection, $$Q$$.

As the general expression for the angular dependence of quadrupole absorption is rather unwieldy, we consider here only rotations by and angle $$\psi$$ about each of the coordinate axes $$x$$, $$y$$ and $$z$$, with the results,

$$\sigma_{x,normal}^{E^2} = \sigma_{00}^{E^2} + \frac{1}{112} \left( 16 \sqrt{105} \Re \sigma_{22}^{E^2} + 4 \sqrt{35} \Re \sigma_{42}^{E^2} + 14 \sqrt{5} \Re \sigma_{44}^{E^2} - 8 \sqrt{70} \sigma_{20}^{E^2} + 3 \sqrt{14} \sigma_{40}^{E^2} \right)$$

$$+ 7 \left( 4 \sqrt{35} \Re \sigma_{22}^{E^2} + 2 \sqrt{5} \Re \sigma_{44}^{E^2} + 5 \sqrt{14} \sigma_{40}^{E^2} \right) \cos(4\psi)$$

$$+ 28 \sqrt{10} \left( \sqrt{7} \Re \sigma_{41}^{E^2} + 3 \Re \sigma_{43}^{E^2} \right) \sin(4\psi)$$

$$\sigma_{y,normal}^{E^2} = \sigma_{00}^{E^2} + \frac{1}{28} \left( \sqrt{70} \sigma_{20}^{E^2} - 3 \sqrt{14} \sigma_{40}^{E^2} + 4 \sqrt{35} \left( \sqrt{3} \Re \sigma_{22}^{E^2} - 2 \Re \sigma_{42}^{E^2} \right) \cos(\psi)^2 \right.$$

$$- \sqrt{14} \left( 3 \sqrt{5} \sigma_{20}^{E^2} + 5 \sigma_{40}^{E^2} \right) \cos(2\psi) - 28 \sqrt{5} \Re \sigma_{42}^{E^2} \sin(2\psi)^2$$

$$- 2 \sqrt{5} \left( 2 \sqrt{21} \Re \sigma_{21}^{E^2} + \sqrt{14} \Re \sigma_{41}^{E^2} + 7 \sqrt{2} \Re \sigma_{43}^{E^2} \right) \sin(2\psi) \right)$$

$$\sigma_{z,normal}^{E^2} = \sigma_{00}^{E^2} - \frac{\sqrt{5} \sigma_{20}^{E^2}}{\sqrt{14}} + 4 \frac{\sigma_{40}^{E^2}}{\sqrt{14}} + \sqrt{\frac{5}{7}} \left( \sqrt{3} \Re \sigma_{22}^{E^2} - 2 \Re \sigma_{42}^{E^2} \right) \cos(2\psi)$$

$$+ \sqrt{\frac{5}{7}} \left( - \left( \sqrt{3} \Re \sigma_{22}^{E^2} + 2 \Re \sigma_{42}^{E^2} \right) \sin(2\psi) \right)$$

where $$\Re$$ and $$\Im$$ represent the real and imaginary parts of the tensor components. As shown in §1, the angle dependence of quadrupole absorption that is enhanced in the Borrmann case is
Therefore, no angle dependence for Borrmann spectroscopy then becomes,

\[ \sigma_{x,Borrmann}^{E^2} = \frac{1}{28} \left( \sqrt{70} \sigma_{20}^{E^2} - 3 \sqrt{14} \sigma_{40}^{E^2} - 4 \sqrt{3} \sigma_{22}^{E^2} - 2 \sigma_{42}^{E^2} \right) \cos(\psi)^2 \]

\[ - \sqrt{14} \left( 3 \sqrt{5} \sigma_{20}^{E^2} + 5 \sigma_{40}^{E^2} \right) \cos(2\psi) - 28 \sqrt{3} \sigma_{44}^{E^2} \sin(\psi)^2 \]

\[ + 2 \left( 2 \sqrt{105} \Im \sigma_{21}^{E^2} + \sqrt{70} \Im \sigma_{41}^{E^2} - 7 \sqrt{10} \Im \sigma_{43}^{E^2} \right) \sin(2\psi) \]  

(14)

\[ \sigma_{y,Borrmann}^{E^2} = \sigma_{00}^{E^2} + \frac{1}{112} \left( -16 \sqrt{105} \Re \sigma_{22}^{E^2} + 4 \sqrt{35} \Re \sigma_{42}^{E^2} + 14 \sqrt{5} \Re \sigma_{44}^{E^2} - 8 \sqrt{70} \sigma_{20}^{E^2} + 3 \sqrt{14} \sigma_{40}^{E^2} \right) \cos(4\psi) \]

\[ + 28 \sqrt{10} \left( - \left( \sqrt{7} \Re \sigma_{41}^{E^2} + \Re \sigma_{42}^{E^2} \right) \sin(4\psi) \right) \]  

(15)

\[ \sigma_{z,Borrmann}^{E^2} = \sigma_{00}^{E^2} - \frac{\sqrt{5} \sigma_{20}^{E^2} + 4 \sigma_{40}^{E^2}}{\sqrt{14}} + \sqrt{\frac{5}{7}} \left( - \left( \sqrt{3} \Re \sigma_{22}^{E^2} + 2 \Re \sigma_{42}^{E^2} \right) \cos(2\psi) + \sqrt{\frac{5}{7}} \left( \sqrt{3} \Im \sigma_{22}^{E^2} - 2 \Im \sigma_{42}^{E^2} \right) \sin(2\psi) \right) \]  

(16)

While the expressions for the normal and Borrmann cases are very similar, the full fourth-rank angle dependence, given by trigonometric functions of 4\psi, is observed only via rotations about the x-axis in the normal case, and the y-axis in the Borrmann case. This is slightly disappointing as only rotations about x in the Borrmann case are convenient and continuous, since it corresponds to a rotation about the scattering vector, k. However, the result is not surprising as sampling of the fourth-rank angle dependence requires both of the relevant vectors to rotate. In the Borrmann case, x is fixed as it is parallel to k. (It is interesting to note that the angle dependence in Borrmann Spectroscopy can be derived from Brouder’s results [11] by making the substitution, \psi \rightarrow \psi + \pi/2).

A more convenient coordinate system for the Borrmann case is one where we rotate about \hat{k} = \hat{z}, since the rotational properties of spherical tensors then take on a simple and more intuitive form. With \hat{\xi} = \hat{y}, we obtain,

\[ \sigma_{z',Borrmann}^{E^2} = \sigma_{00}^{E^2} - \frac{\sqrt{5} \sigma_{20}^{E^2} + 4 \sigma_{40}^{E^2}}{\sqrt{14}} + \sqrt{\frac{5}{7}} \left( - \left( \sqrt{3} \Re \sigma_{22}^{E^2} + 2 \Re \sigma_{42}^{E^2} \right) \cos(2\psi) + \sqrt{\frac{5}{7}} \left( \sqrt{3} \Im \sigma_{22}^{E^2} - 2 \Im \sigma_{42}^{E^2} \right) \sin(2\psi) \right) \]  

(17)

For the present case of cubic symmetry, with the crystal axes taken to be parallel to the Cartesian axes, all tensor components are zero except for the scalar term, \sigma_{00}^{E^2}, and two components of the fourth-rank terms, which are related by \sigma_{44}^{E^2} = \sqrt{5/14} \sigma_{40}^{E^2} [11]. Rotating the sample about the k vector gives the following angle dependences for the normal and Borrmann case:

\[ \sigma_{normal}^{E^2} = \sigma_{00}^{E^2} + \frac{1 - 5 \cos(4\psi)}{\sqrt{14}} \sigma_{40}^{E^2} \]  

(18)

\[ \sigma_{Borrmann}^{E^2} = \sigma_{00}^{E^2} - 2 \sqrt{\frac{5}{7}} \sigma_{40}^{E^2} \]  

(19)

Therefore, no angle dependence is expected for the present (Borrmann) case.
4. Conclusions

In summary, we have:

- Demonstrated an elegant new application of one of the most beautiful phenomena in X-ray physics, namely, the enhancement of quadrupolar absorption in the Borrmann effect;
- Developed a simple model for the magnitude of the enhancement, and its variation with temperature, which is shown to agree well with experimental results;
- Used the technique to study the quadrupole pre-edge features in GGG and YIG;
- Derived expression for the expected angle dependence of Borrmann Spectroscopy.

Further developments in Borrmann spectroscopy will focus on a more complete theory of the Borrmann Effect, and the analysis of other systems of interest, including TiO$_2$. Future measurements should shed light on the ground states of systems that exhibit important electronic phenomena such as charge, orbital and magnetic ordering. Finally, we note that quadrupole enhancement in absorption spectroscopy should not be limited to the Borrmann case. Similar effects are expected in Bragg diffraction, and potentially with waveguides and mirrors, although the latter may require longer wavelengths.

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