Anisotropy in Borrmann spectroscopy

S.P. Collins^{1,a}, M. Tolkiehn², T. Laurus², and V.E. Dmitrienko³

¹ Diamond Light Source Ltd., Diamond House, Harwell Science and Innovation Campus, Didcot OX11 0DE, UK

² Deutsches Elektronensynchrotron DESY, FS-DO, Notkestraße 85, 22607 Hamburg, Germany

³ A. V. Shubnikov Institute of Crystallography, 119333 Moscow, Russia

Received 19 December 2011 / Received in final form 23 March 2012
Published online 15 June 2012

Abstract. In this paper we introduce Borrmann Spectroscopy as a method for measuring X-ray absorption spectra under conditions of an exotic wave field, namely, a coherent superposition of two plane waves. The essential features of the Borrmann Effect (also known as anomalous transmission) are outlined. We show that the Borrmann Effect can lead to a very strong relative enhancement of quadrupole absorption. After describing some early results in this field, and some general considerations of multiple-wave absorption, we contrast recent results on anisotropy in Borrmann spectroscopy with normal absorption. Despite the qualitative success of a simple model for quadrupole enhancement, temperature dependence and anisotropy, a general theory of the Borrmann Effect is required which includes anisotropic and non-dipolar scattering. We outline some first steps towards such a theory.

1 Introduction and previous work

1.1 The Borrmann effect

The Borrmann Effect, discovered over 70 years ago, is one of the most remarkable manifestations of the dynamical diffraction of X-rays [1,2]. It can be observed as follows: a thick crystal (typically $\mu t > 10$) is placed in the path of a collimated monochromatic X-ray beam, essentially blocking the beam completely. If the crystal orientation is then manipulated so that a strong diffraction condition is excited, there is a dramatic increase in the transmission of the beam (reduction in absorption) for that precise setting. This phenomenon is known as anomalous transmission or the Borrmann Effect.

The physical origin of the Borrmann effect is illustrated in Fig. 1. The beam, which enters the sample face on the right, is a single plane wave of wave-vector $\mathbf{q}$. Initially the X-ray beam undergoes normal absorption. However, as it penetrates further into the crystal an increasing fraction of its energy is transferred to the diffracted beam

^a e-mail: steve.collins@diamond.ac.uk

Fig. 1. The Borrmann Effect and quadrupole enhancement. An X-ray beam enters a thick crystal and is diffracted from the atomic planes, establishing a second wave. After many scattering events two standing wave fields are formed along the direction $\mathbf{k}$, differing in phase by $\pi/2$. One of these standing waves – the α -branch – has nodes at the atomic planes and so the wave field (red and blue indicate positive and negative amplitude) propagates along the crystal planes with anomalously low absorption until reaching the opposite face, where beams of equal intensity along $\mathbf{q}$ and $\mathbf{q}'$ emerge. While the normal dipole absorption is dramatically reduced due to the low field intensity at the atomic planes, the field gradient, which drives quadrupole absorption, remains strong and leads to a large effective quadrupole enhancement of the absorption spectrum.

direction, $\mathbf{q}'$, which at some point becomes more intense than the remaining beam along $\mathbf{q}$. There then follows a *pendellosung* oscillation of the relative intensity between the two waves, which eventually dies away and a steady state is reached whereby the two waves have identical intensity and any information about the initial beam direction is lost. Such a coherent superposition of the two waves has two possible solutions for each of two linear polarization states: the β -branch, where the standing-wave field formed perpendicular to the diffracting crystal planes has the strongest interaction with the lattice, and the α -branch, where the interaction is minimum. For the α -branch with polarization perpendicular to the scattering plane (σ polarization), and a crystal where all the atoms lie on equidistant planes, there are Laue reflections for which every atom is at a wave field node and so absorption is essentially switched off. (We note that this is not the case for π polarization, parallel to the scattering plane, since the electric vector is then rotated upon scattering and there are no conditions for which both components of the polarization cancel simultaneously). From Fig. 1 we see how the combination of diffracted and forward-diffracted beams builds up such a wave field, which travels along the crystal planes from right to left, emerging as two beams of equal intensity.

1.2 Quadrupole enhancement

We have previously shown [3–5] that while the Borrmann effect leads to a dramatic reduction in dipole absorption, which is driven by the electric field strength, quadrupole

Fig. 2. Normal (black) and Borrmann (red) absorption spectra for the Gd L -edges in gadolinium gallium Garnet (GGG). The Gd L_3 -edge spectrum at 10 K is shown in the top-left, with the same spectrum at 300 K in the bottom-left panel. Top right: the Gd L_2 -edge spectrum. Bottom right: A huge quadrupole peak at the Gd L_1 -edge.

absorption, which depends on the field *gradient* is not diminished, and is therefore effectively enhanced by a very large factor (~ 20 or so) relative to dipole absorption. Moreover, while the gradient of a single wave points along its wave-vector $\mathbf{q}$, it is clear from Fig. 1 that in the Borrmann (two wave) case, the gradient is perpendicular to the crystal planes, in the direction $\mathbf{k} = \mathbf{q}' - \mathbf{q}$. We will revisit this important point in §2.2.

Quadrupole enhancement not only permits weak quadrupole spectral features to be resolved above the dominant dipole absorption, but the fact that *only* the quadrupole part is enhanced provides a very useful qualitative fingerprint of these important transitions. From a spectroscopic perspective quadrupole transitions provide direct access, due to their ability to transfer two units of angular momentum, to orbitals that play the most vital roles in the electronic properties of materials, such as $3d$ levels in transition metals and $4f$'s in rare earths.

1.3 Gadolinium gallium garnet

The first measurements to illustrate this effect [3] are reproduced in Fig. 2, which shows the conventional absorption spectrum (black line) for various Gd L -edges, along with the equivalent spectra for the Borrmann case. The latter are characterized by additional sharp peaks in the pre-edge region. For the Gd $L_{2,3}$ -edges, these new peaks are at the precise energies where the resonant inelastic X-ray scattering (RIXS) and deconvolution techniques [6, 7] have shown the presence of a weak pre-edge feature, which was assumed to be a quadrupole transition from a $2p$ core level to empty $4f$ states. Borrmann spectroscopy not only gives a huge signal but an unambiguous assignment of its multipole character, since the technique relies on quadrupole absorption. The Gd L_1 -edge is particularly interesting because the pre-edge quadrupole

peak in the Borrmann case, to the same $5d$ orbitals that are observed in the dipole Gd $L_{2,3}$ -edge spectra, is even stronger than the main edge, and had not been observed previously.

1.4 Temperature dependence

Another intriguing aspect of the data in Fig. 2 is the dependence of the quadrupole enhancement on temperature. The effect is greatly diminished upon heating the crystal to room temperature. In fact, this is slightly misleading as it is believed that the quadrupole absorption varies little with temperature [3–5] whereas the dipole absorption increases dramatically as the sample is heated [8]. Again, a qualitative understanding of this phenomenon can be gleaned from Fig. 1. Dipole absorption becomes very weak when the atoms sit precisely on the nodes of the wave field. However, any small displacement from the ideal planes, caused by defects or thermal motion, will cause the atoms to experience a much larger electric field strength. Such a small displacement will have little effect on the quadrupole absorption, which is at its maximum. This strong temperature dependence in the quadrupole enhancement provides a useful additional method for identifying the multipole character of spectral features. Even for ideal crystals, thermal and zero-point motion limit the size of the quadrupole enhancement and a simple model that considers only absorption by a perfect α -branch standing-wave (i.e. normal absorption during the early stages of wave field formation is neglected) provides a reasonable estimate of the quadrupole enhancement in Borrmann spectroscopy [4].

2 Absorption in a complex wave field

2.1 General case

We now turn our attention, briefly, to a generic description of X-ray absorption by a complex wave field. By this, we mean the wave field of a single photon that is composed of a coherent superposition of waves with different polarization- or wave-vectors. We neglect non-linear processes.

The form of the absorption cross-section for pure multipole processes is well-documented in the literature [9] and leads to sums over products of multipole matrix elements and their Hermitian conjugates. This is conventionally expressed as a coupling between tensors representing the sample and X-ray beam properties, where the tensor components for the sample are either computed via the matrix elements with suitable wavefunctions, or treated phenomenologically after applying any known symmetries. Such a tensor analysis can be carried out in any appropriate basis, with Cartesian [10] and spherical [11, 12] formalisms appearing in the literature with comparable prominence. Here, we will not reproduce these treatments but merely consider how they can be extended to encompass the case of multiple wave fields.

We begin with a generic description of the geometrical aspects of the absorption cross-section (or absorption coefficient) for pure dipole (E1E1) and pure quadrupole (E2E2) processes:

$$\mu = \mathbf{D} \circ \mathbf{X}_D + \mathbf{Q} \circ \mathbf{X}_Q \quad (1)$$

where $\mathbf{D}$ and $\mathbf{Q}$ are tensors that describe the sample dependence of the absorption (sometimes called atomic multipoles) and $\mathbf{X}_{D,Q}$ are tensors that represent the relevant properties of the X-ray beam (*e.g.* polarization vector, $\boldsymbol{\varepsilon}$, and wavevector, $\mathbf{q}$). We do not concern ourselves with the details of how the tensors couple to give the (scalar)

absorption coefficient, as this is dealt with elsewhere [9–12, 14] but simply represent some generic tensor coupling with the symbol, $\circ$. The $\mathbf{X}$ tensors in turn can be written as a generic coupling of the X-ray beam vectors,

$$\begin{aligned}\mathbf{X}_D &= \boldsymbol{\varepsilon} \circ \boldsymbol{\varepsilon}^* \\ \mathbf{X}_Q &= \boldsymbol{\varepsilon} \circ \mathbf{q} \circ \boldsymbol{\varepsilon}^* \circ \mathbf{q}^*\end{aligned}\tag{2}$$

where $*$ indicates a complex conjugate.

We now consider the form of the $\mathbf{X}$ tensors for multiple wave field components. Each matrix element that contributes to the absorption must be replaced with a sum over matrix elements for each wave field, λ , with amplitude A_λ , giving,

$$\mathbf{X}_D = \left\{ \sum_{\lambda} A_{\lambda} \boldsymbol{\varepsilon}_{\lambda} \right\} \circ \left\{ \sum_{\lambda} A_{\lambda}^* \boldsymbol{\varepsilon}_{\lambda}^* \right\}\tag{3}$$

$$\mathbf{X}_Q = \left\{ \sum_{\lambda} A_{\lambda} \boldsymbol{\varepsilon}_{\lambda} \circ \mathbf{q}_{\lambda} \right\} \circ \left\{ \sum_{\lambda} A_{\lambda}^* \boldsymbol{\varepsilon}_{\lambda}^* \circ \mathbf{q}_{\lambda}^* \right\}.\tag{4}$$

For the dipole case, Eq. (3) shows that the detailed treatments in the literature can be extended to the multiple wave field case simply by making the substitution,

$$\boldsymbol{\varepsilon} \rightarrow \sum_{\lambda} A_{\lambda} \boldsymbol{\varepsilon}_{\lambda}.\tag{5}$$

For the quadrupole absorption, we cannot proceed further without knowing the details of the tensor couplings required for the calculations. However, there are two exceptions to this. If the $\mathbf{q}$ vectors of all wave field components are the same, then these factor out and we are left with an expression that is identical to the case of a single wave but with the polarization vector replaced by a weighted sum over the polarization vectors for each field components, as in the dipole case. This case is well-documented [15] and allows, for example, a formalism based on linear polarization states to compute cross-sections for circularly polarized X-ray beams, which can be expressed as pairs of linearly polarized wave field components with orthogonal polarization vectors and orthogonal phases for the wave field amplitudes. The second exception, of which the Borrmann effect is an example, and has wave fields with the same polarization vector but different wave-vectors. In this case, we simply replace the wave vectors in the single wave field expression, with a coherent sum of the wave vectors for each component:

$$\mathbf{q} \rightarrow \sum_{\lambda} A_{\lambda} \mathbf{q}_{\lambda}\tag{6}$$

allowing us again to take advantage of the extensive existing treatments of quadrupole absorption by a single wave field [9–12, 14]. Drawing parallels with the superposition of polarization vectors, this suggests the intriguing possibility (*not* realized in the Borrmann case) of permitting the effective wave vector to become complex, possibly coupling to chiral sample properties.

2.2 Two beam case

We now consider the specific case of absorption by a coherent superposition of two wave fields with the same linear polarization vector, where the second wave field is

a reflection of the first, and the polarization vector is perpendicular to the plane containing the two beams. The relevant parameters for the two beams are:

$$\begin{aligned} A_1 &= 1, \varepsilon_1 = \varepsilon, \mathbf{q}_1 = \mathbf{q} \\ A_2 &= Re^{i\phi}, \varepsilon_2 = \varepsilon, \mathbf{q}_2 = \mathbf{q}' \end{aligned} \quad (7)$$

where R and $e^{i\phi}$ are the amplitude and phase of the reflected wave at the position of the absorbing atom. The effective polarization vector for dipole absorption is then

$$\varepsilon \rightarrow \varepsilon(1 + Re^{i\phi}) \quad (8)$$

and for the quadrupole absorption the effective wave-vector becomes

$$\begin{aligned} \mathbf{q} &\rightarrow \mathbf{q} + Re^{i\phi}\mathbf{q}' \\ &= \frac{1}{2}\mathbf{k}^+(1 + Re^{i\phi}) - \frac{1}{2}\mathbf{k}(1 - Re^{i\phi}) \end{aligned} \quad (9)$$

where

$$\begin{aligned} \mathbf{k} &= \mathbf{q}' - \mathbf{q} \\ \mathbf{k}^+ &= \mathbf{q}' + \mathbf{q}. \end{aligned} \quad (10)$$

For diffraction or reflection, $\mathbf{k}$ is the momentum transfer, $\mathbf{k}^+$ lies parallel to the reflecting planes (Fig. 1), and

$$\begin{aligned} |\mathbf{k}| &= 2q \sin \theta = \frac{4\pi}{\lambda} \sin \theta \\ |\mathbf{k}^+| &= 2q \cos \theta = \frac{4\pi}{\lambda} \cos \theta. \end{aligned} \quad (11)$$

For the Borrmann effect, we are interested in the case where the two wave fields cancel at the absorbing atom, *i.e.* $Re^{i\phi} \simeq -1$. In that case the effective polarization vector (Eq. (8)) becomes vanishingly small, leading to vastly reduced dipole absorption. Turning to the quadrupole absorption, we see that the first term in the effective wave vector (Eq. (9)) vanishes, while the second, which is now directed along $\mathbf{k}$, does not. This is entirely consistent with the wave fields shown in Fig. 1 and leads to a huge quadrupole enhancement.

Finally, we can estimate the effective quadrupole enhancement in the absorption spectrum, defined as the quadrupole/dipole absorption ratio for the two-beam case, divided by the same ratio for the single beam case. If we assume that the resonant tensors $\mathbf{D}$ and $\mathbf{Q}$ are isotropic (scalars) then they cancel in the calculation, leaving a quadrupole enhancement,

$$\chi = \cos^2 \theta + \sin^2 \theta \frac{|1 - Re^{i\phi}|^2}{|1 + Re^{i\phi}|^2} \quad (12)$$

and so we see that a large quadrupole enhancement requires $Re^{i\phi} \simeq -1$ and θ not to be too small. This is indeed the case with the Borrmann effect and may also be achieved using, for example, wave guides. For X-ray mirrors, the reflectivity is always a little below unity, and the scattering angle is small, suggesting that this may not be an appropriate method for observing large quadrupole enhancements. The situation is different for longer wavelengths (*e.g.* optical spectroscopy), but the intrinsic strengths of the quadrupole transitions is low and it is not clear whether the quadrupole enhancement for mirror reflection would render them measurable.

Fig. 3. A cubic unit cell of SrTiO_3 . The central titanium atom is surrounded by an oxygen octahedron.

3 Anisotropy in SrTiO_3

3.1 Background

We now turn our attention to one of the main themes of this paper, and one that highlights some recent experimental results: anisotropy in Borrmann spectroscopy. Anisotropy in quadrupole absorption (and resonant scattering) has been shown in recent years to provide considerable insight into the interaction between electronic orbitals and X-rays, and the properties of the orbitals. Dipole absorption, in the absence of magnetism, has a very simple orientation dependence. It is described by a symmetric second-rank tensor *i.e.* its anisotropy takes the form of an ellipsoid, which is in turn constructed from a scalar plus atomic quadrupoles. (Note that *atomic* multipoles describe the angular dependence of the atomic or sample properties, whereas multipole absorption or scattering describes the angular dependence of the *interaction* between the photon and sample). For highly asymmetric systems the anisotropy can be very strong, but with cubic symmetry the only ellipsoid with the required symmetry is a sphere – the atomic quadrupoles vanish and there is no anisotropy.

Quadrupole absorption, on the other hand, is described by a fourth-rank tensor that couples twice to $\mathbf{q}$ and twice to $\boldsymbol{\varepsilon}$ (see Eq. (2)) leading to a much richer angle dependence. Atomic multipoles up to hexadecapoles can be observed even with cubic symmetry. This not only provides a much more sensitive probe (*i.e.* higher ‘angular resolution’) than dipole absorption, but the resulting anisotropy becomes a unique fingerprint of quadrupole absorption. Borrmann spectroscopy provides an alternative fingerprint, due to its quadrupole enhancement, and although it does not rely on anisotropy, the prospect of combining the two approaches is compelling.

The system under investigation for the present work – SrTiO_3 – has long attracted interest due to the proximity of a ferroelectric phase transition at zero Kelvin (a quantum phase transition). Here, we focus on its cubic phase, whose unit cell has a central titanium atom surrounded by an oxygen octahedron (Fig. 3), serving to remove the Ti 3d electrons and split the empty levels into e_g and t_{2g} orbitals via the octahedral (cubic) crystal field. The X-ray absorption spectrum exhibits four pre-edge peaks, labeled A-D (Fig. 4), where A and B are interpreted as arising from quadrupole transitions to the empty 3d t_{2g} and e_g orbitals [13] while C and D are electric dipole transitions.

Fig. 4. Top left: Ti K -edge absorption (fluorescence) spectra from SrTiO_3 , showing four peaks (A-D) in the pre-edge region, with the experimental geometry illustrated in the insert. (Note that, while this is not a diffraction measurement, we find it convenient to borrow the familiar symbols in order to facilitate later comparison with diffraction-based data). Top right: The measured variation in the pre-edge fluorescence intensity with azimuthal rotation (ψ) about the surface normal for $\theta \sim 10^\circ$. Bottom: A symmetry-based calculation of the variation in the intensity of quadrupole peaks *vs* ψ and θ , for (001) and (101) surface normals.

3.2 Fluorescence spectra

Before discussing the Borrmann data, we consider anisotropy in normal absorption, measured via the variation in fluorescence intensity as a flat crystal is rotated about its surface normal (Fig. 4). The results, from Beamline I16, Diamond Light Source, show a clear and complementary anisotropy for peaks A and B, with a four-fold dependence on the azimuthal angle, ψ – all consistent with the assignment of quadrupole transitions to an empty crystal-field-split $3d$ orbital. There is no anisotropy in peaks C and D, as expected for dipole transitions. ($\psi = 0$ is orientation that brings $\mathbf{n}$ into the same plane as $\mathbf{q}$ and $\mathbf{h}$, with $\mathbf{n}$ having a positive projection along $\mathbf{q}' + \mathbf{q}$).

The shape of the anisotropy (although not its magnitude or sign) can be determined from a symmetry analysis of the resonant absorption tensor [9, 14] as shown in Fig. 4, bottom left. The four-fold pattern is clearly reproduced for small θ , and the calculation predicts that as θ approaches 90° (normal incidence) the azimuthal dependence vanishes and all spectra take the form of the one at $\psi = 0$.

3.3 Borrmann spectra

Cubic SrTiO_3 is a good candidate for the Borrmann effect because the simple structure can accommodate all atoms at the wave field nodes of the (002) reflection, and

Fig. 5. Normalized Borrmann spectra at the Ti K edge in SrTiO_3 (red, blue) compared to the fluorescence spectrum (black), all measured at the XMaS Beamline, ESRF. The red spectrum is for $\mathbf{h} = (002)$, $\mathbf{n} = (100)$, $\psi = 0$, and the blue line corresponds to $\mathbf{h} = (011)$, $\mathbf{n} = (100)$, $\psi = 0$, equivalent to $\mathbf{h} = (101)$, $\mathbf{n} = (100)$, $\psi = 90^\circ$ (Fig. 4). The experimental geometry (Laue-case diffraction) is shown on the right.

all heavy atoms (*i.e.* all but the oxygen atoms) for the (011). Since the assignment of peaks A and B to quadrupole transition is confirmed by the fluorescence spectra, we would expect the Borrmann spectra to show a significant enhancement of their intensity. Peaks C and D show no anisotropy and so the fluorescence data cannot determine directly their multipole nature, since isotropic spectra can be produced by dipole or quadrupole transitions. However, theoretical calculations [16] suggest they are dipolar in origin which, if correct, would give no quadrupole enhancement in the Borrmann spectra.

The pertinent question is, what role does absorption anisotropy play in Borrmann spectroscopy? We have seen that absorption in the Borrmann case is different from, but very closely related to, normal single-wave absorption. Absorption calculations and measurements can be transformed to the Borrmann case simply by replacing $\mathbf{q}$ with $\mathbf{k}$. Indeed, this relationship is implicit in the description of the experimental geometry for fluorescence anisotropy, illustrated in Fig. 4. For the Borrmann case we set $\theta = -90^\circ$ (equivalent to $\theta = +90^\circ$) and the vector $\mathbf{h}$ becomes the scattering vector. As already pointed out, there is no anisotropy for the (001) direction for $\theta = 90^\circ$ and so we expect the Borrmann spectra for any azimuthal angle ψ to reflect the absorption spectrum taken at small θ with $\psi = 0$. From the absorption data, we see that this corresponds to a maximum intensity in peak A and nothing in peak B.

Experimental Borrmann spectra for the (002) reflection are shown in Fig. 5 (red line), compared to the fluorescence data (black line) and show a huge enhancement in peak A, with no significant enhancement in peaks B, C or D, precisely as predicted by our simple model.

While this agreement gives confidence that our physical interpretation is substantially correct, the absence of anisotropy seems slightly disappointing! However, all is not lost. Tensor calculations for the (011) (or (101)) direction (Fig. 4, bottom right) suggest a large anisotropy even at $\theta = 90^\circ$, due to the fact that rotations about this direction should have two-fold, rather than four-fold symmetry, which can be picked out by coupling to the two vectors ($\boldsymbol{\epsilon}$ taken twice) that are free to move during the azimuthal rotation. Laue diffraction measurements with plate-like samples are not ideal for direct measurements of the azimuthal dependence, but a crystal that is suitably cut should provide access to (101) reflection with $\psi = 90^\circ$ (or, equivalently, the (011) reflection with $\psi = 0$), and the calculations suggest that this orientation should enhance only peak B. The resulting data are shown Fig. 5 (blue line), and confirm

this prediction very clearly. (Note that the enhancement of peak B is less than that of peak A, probably due to the additional dipole absorption by oxygen atoms for the (101) reflection).

4 Towards a general theory of the Borrmann effect in crystals with anisotropic scattering

Up to now we have considered a very simple model for the Borrmann Effect, whereby we have neglected the wave field close to the entrance face of the crystal and assumed that the role of dynamical diffraction is merely to establish the standing wave field that leads to quadrupole enhancement. Resonant scattering and its associated anisotropy are not considered. Since absorption and scattering are two manifestations of the same physical processes, such a picture is fundamentally flawed and a detailed quantitative model of the Borrmann effect must therefore include resonant and anisotropic scattering as well as the effects of finite sample thickness. Here we outline some first steps towards such a theory.

For a quantitative description of the Borrmann effect, we should consider and evaluate all possible sources of residual absorption of the standing wave. In keeping with the rest of this paper, we will restrict our consideration to the two-wave approximation because the multiple-wave case plays a significant role only for specific ‘multiple diffraction’ conditions and will mimic an important feature of anisotropy – entanglement of σ and π polarizations caused by magnetic- and/or charge-ordering effects (dipole, quadrupole, etc.).

Since suppression of absorption is strong only for the σ polarization we will consider those solutions of dynamical diffraction equations where the π polarization is a small perturbation, or is absent. The validity of this approximation will be proved by its results: the calculated π -polarization will be shown to be much smaller than the σ -component. We assume throughout that the incident wave is σ -polarized. The following discussion borrows terminology from well-established papers on dynamical diffraction theory [2, 17] and resonant X-ray scattering [10].

The polarization dependence of the structure factors $\hat{F}_H$, that determines the scattering amplitude, can be expressed as a general second-rank tensor which include both symmetric and antisymmetric parts of tensor atomic factors $\hat{f}_j$, where index j numbers atoms in the unit cell:

$$\hat{F}_H = \sum_j \hat{f}_j \exp(i\mathbf{H}\mathbf{r}_j). \quad (13)$$

While the tensor atomic factors $\hat{f}_j$ for dipole-quadrupole, quadrupole-quadrupole, etc. depend also on the wave vectors, those vectors are fixed and well-defined for the pairs of waves involved with a particular Bragg reflection and azimuthal angle.

We will write the dynamical equations using the unit vectors σ and π so that the solution of the Maxwell equations for $\mathbf{E}(\mathbf{r})$ is given by a superposition of direct and diffracted waves, in close analogy with conventional dynamical diffraction theory [2]:

$$\mathbf{E}(\mathbf{r}) = (E_0^\sigma \sigma + E_0^\pi \pi) \exp(i\mathbf{K}_0 \mathbf{r}) + (E_H^\sigma \sigma + E_H^\pi \pi) \exp(i\mathbf{K}_H \mathbf{r}) \quad (14)$$

where the wave vectors of the direct and diffracted waves, $\mathbf{K}_0$ and $\mathbf{K}_H$, are related via the reciprocal lattice vector $\mathbf{H}$:

$$\mathbf{K}_H = \mathbf{K}_0 + \mathbf{H} \quad (15)$$

(In relation to Fig. 1 we equate $\mathbf{K}_0$, $\mathbf{K}_H$ and $\mathbf{H}$ with $\mathbf{q}$, $\mathbf{q}'$ and $\mathbf{k}$, where the new symbols are adopted to preserve standard notation from the literature [2, 17].) We will also adopt dimensionless wave-vectors κ_0 and κ_H defined so that

$$\kappa_0 = c\mathbf{K}_0/\omega \quad (16)$$

$$\kappa_H = c\mathbf{K}_H/\omega. \quad (17)$$

Owing to anisotropy of $\hat{F}_H$, the σ and π polarized waves are mixed and we have a system of four entangled equations which can be written in the most general form as

$$(\kappa_0^2 - 1 + F_{00}^{\sigma\sigma})E_0^\sigma + F_{0\bar{H}}^{\sigma\sigma}E_H^\sigma + F_{00}^{\sigma\pi}E_0^\pi + F_{0\bar{H}}^{\sigma\pi}E_H^\pi = 0 \quad (18)$$

$$F_{H0}^{\sigma\sigma}E_0^\sigma + (\kappa_H^2 - 1 + F_{HH}^{\sigma\sigma})E_H^\sigma + F_{H0}^{\sigma\pi}E_0^\pi + F_{HH}^{\sigma\pi}E_H^\pi = 0 \quad (19)$$

$$F_{00}^{\pi\sigma}E_0^\sigma + F_{0\bar{H}}^{\pi\sigma}E_H^\sigma + (\kappa_0^2 - 1 + F_{00}^{\pi\pi})E_0^\pi + F_{0\bar{H}}^{\pi\pi}E_H^\pi = 0 \quad (20)$$

$$F_{H0}^{\pi\sigma}E_0^\sigma + F_{HH}^{\pi\sigma}E_H^\sigma + F_{H0}^{\pi\pi}E_0^\pi + (\kappa_H^2 - 1 + F_{HH}^{\pi\pi})E_H^\pi = 0 \quad (21)$$

where $F_{00}^{\sigma\sigma} = \sigma\hat{F}_0\sigma$, $F_{00}^{\pi\pi} = \pi\hat{F}_0\pi$, $F_{H0}^{\sigma\pi} = \sigma\hat{F}_H\pi$, etc. If we neglect the terms $\pi\sigma$ and $\sigma\pi$ that mix polarization states, we obtain from Eqs. ((18)–(21)) the conventional systems of dynamical equations [2] for separate σ and π polarizations.

Let us consider our case when σ -component is strong and π -component is a small perturbation. The values of vectors κ_0 and κ_H are determined mainly by the interaction of the strong component, and near the maximum of the Borrmann transmission this strong component has a form of a standing wave with nodes on atoms. In Eqs. ((20), (21)) for the small component, we can put the values of κ_0 and κ_H corresponding to the weakly-absorbed σ standing wave in the centre of the reflection region, where, by symmetry, $\kappa_0^2 = \kappa_H^2$. We assume that the small deviation from unity in these parameters is dominated by the strongest interactions with the lattice. Neglecting the (relatively weak) polarization-mixing terms in Eqs. ((18), (19)), and forming a determinant from these equations that must be satisfied by any non-trivial solution, yields

$$\kappa_0^2 - 1 + F_0 = \kappa_H^2 - 1 + F_0 = F_H \quad (22)$$

where F_0 and F_H are the conventional scalar Fourier harmonics of the structure factor (F_H includes the Debye-Waller factor and we also take into account that in centrosymmetric crystals $F_{\bar{H}} = F_H$). Then we can hold only the Thompson scattering term and ignore anisotropy in $F_{00}^{\pi\pi}$, $F_{HH}^{\pi\pi}$, $F_{H0}^{\pi\pi}$, $F_{0\bar{H}}^{\pi\pi}$ and put approximately $F_{00}^{\pi\pi} = F_{HH}^{\pi\pi} = F_0$ and $F_{H0}^{\pi\pi} = F_{0\bar{H}}^{\pi\pi} = F_H \cos 2\theta_B$. Now we can easily solve Eqs. ((20), (21)) for E_0^π and E_H^π :

$$E_0^\pi = [(\cos 2\theta_B F_{H0}^{\pi\sigma} - F_{00}^{\pi\sigma})E_0^\sigma + (\cos 2\theta_B F_{HH}^{\pi\sigma} - F_{0\bar{H}}^{\pi\sigma})E_H^\sigma] / (F_H \sin^2 2\theta_B) \quad (23)$$

$$E_H^\pi = [(\cos 2\theta_B F_{00}^{\pi\sigma} - F_{H0}^{\pi\sigma})E_0^\sigma + (\cos 2\theta_B F_{0\bar{H}}^{\pi\sigma} - F_{HH}^{\pi\sigma})E_H^\sigma] / (F_H \sin^2 2\theta_B). \quad (24)$$

We see that the π -components are indeed smaller than the σ -components because the absolute value of F_H is larger than the values of anisotropic terms $F^{\pi\sigma}$ or $F^{\sigma\pi}$. We can now substitute Eqs. (23) and (24) into (18) and (19) to obtain the dynamical

equations for σ -components in the usual form but with renormalized coefficients:

$$(\kappa_0^2 - 1 + \tilde{F}_{00})E_0^\sigma + \tilde{F}_{0H}E_H^\sigma = 0 \quad (25)$$

$$\tilde{F}_{H0}E_0^\sigma + (\kappa_H^2 - 1 + \tilde{F}_{HH})E_H^\sigma = 0 \quad (26)$$

where $\tilde{F}_{00} = F_{00}^{\sigma\sigma} + [(\cos 2\theta_B F_{H0}^{\pi\sigma} - F_{00}^{\pi\sigma})F_{00}^{\sigma\pi} + (\cos 2\theta_B F_{00}^{\pi\sigma} - F_{H0}^{\pi\sigma})F_{0H}^{\sigma\pi}]/(F_H \sin^2 2\theta_B)$, $\tilde{F}_{0H} = F_{0H}^{\sigma\sigma} + [(\cos 2\theta_B F_{HH}^{\pi\sigma} - F_{0H}^{\pi\sigma})F_{00}^{\sigma\pi} + (\cos 2\theta_B F_{0H}^{\pi\sigma} - F_{HH}^{\pi\sigma})F_{0H}^{\sigma\pi}]/(F_H \sin^2 2\theta_B)$, etc. For any particular case we can write the solution of Eqs. (25) and (26) from textbooks on dynamical diffraction theory [17] and analyze the contribution of anisotropic terms to new ‘renormalized’ values of κ_0 and κ_H determining the Borrmann absorption. An interesting question for future studies is how important could be this ‘leakage’ from σ - to π -polarized (strongly absorbing!) wave. And of course, we can prove this approximation by solving numerically the initial set of Eqs. ((18)–(21)).

We have thus made the first steps towards extending the dynamical theory of X-ray diffraction towards anisotropic resonant scattering: we have introduced a simple framework for allowing weak polarization mixing, and expect this formalism to allow a more quantitative description of Borrmann spectroscopy in the future.

5 Conclusions and future perspectives

The Borrmann Effect is not only one of the most fascinating manifestations of the dynamical theory of X-ray diffraction, but also provides an extremely simple and elegant vehicle for studies of absorption spectroscopy with exotic wave fields. We have shown how the Borrmann Effect leads to a strong enhancement of quadrupole absorption, and we give a physically-appealing, if highly simplistic, model, that lends feasibility to our interpretation of experimental results. The observation of quadrupole absorption is important in order to gain insight into the ground-state properties of, for example, 3d transition metal and lanthanide compounds. Future progress towards the development of the techniques discussed in this paper are likely to include (a) the development of a general theory of the Borrmann Effect along the lines discussed in the text, (b) application of the techniques to highly anisotropic materials and (c) the potential use of alternative techniques for carrying out spectroscopy with exotic wave fields.

The authors are grateful to the beamline staff at BM-28 (XMaS), ESRF, and I16, Diamond Light Source, for their assistance and support. V.E.D. is grateful to the basic research program of the Presidium of the Russian Academy of Sciences ‘Resonant X-ray Diffraction and Topography in Forbidden Reflections’ and to grant RFBR 11-02-08158 for financial support. We are also grateful to one of the referees of this paper for indicating an important mistake in our initial consideration of the wave fields.

References

1. G. Borrmann, Phys. Z. **42**, 157 (1941)
2. B.W. Batterman, H. Cole, Rev. Mod. Phys. **36**, 681 (1964)
3. R.F. Pettifer, S.P. Collins, D. Laundy, Nature **454**, 196 (2008)
4. S.P. Collins, M. Tolkiehn, R.F. Pettifer, D. Laundy, J. Phys: Conf. Ser. **190**, 012045 (2009)
5. M. Tolkiehn, T. Laurus, S.P. Collins, Phys. Rev. B **84**, 241101 (2011)

6. P.W. Loeffen, R.F. Pettifer, S. Müllender, M.A. van Veenendaal, J. Röhler, D.S. Sivia, *Phys. Rev. B* **54**, 14877 (1996)
7. K. Hämäläinen, D.P. Siddons, J.B. Hastings, L.E. Berman, *Phys. Rev. Lett.* **67**, 2850 (1991)
8. C. Ghezzi, A. Merlini, S. Pace, *Phys. Rev. B* **4**, 1833 (1971)
9. Ch. Brouder, *J. Phys.: Condens. Matter* **2**, 701 (1990)
10. V.E. Dmitrienko, K. Ishida, A. Kirfel, E.N. Ovchinnikova, *Acta Cryst. A* **61**, 481 (2005)
11. S.W. Lovesey, E. Balcar, K.S. Knight, J. Fernández Rodríguez, *Phys. Rep.* **411**, 233 (2005)
12. S.P. Collins, S.W. Lovesey, E. Balcar, *J. Phys. Condens. Matter* **19**, 213201 (2007)
13. T. Yamamoto, T. Mizoguchi, I. Tanaka, *Phys. Rev. B* **71**, 245113 (2005)
14. S.P. Collins, A. Bombardi, *Resonant X-ray Scattering and Absorption in Magnetism and Synchrotron Radiation: New Trends* (Springer, 2010)
15. S.W. Lovesey, *Rep. Prog. Phys.* 245 (1993)
16. R.V. Vedrinskii, V.L. Kraizman, A.A. Novakovich, Ph.V. Demekhin, S.V. Urazhdin, *J. Phys. Condens. Matter* **10**, 9561 (1998)
17. A. Authier, *Dynamical Theory of X-Ray Diffraction* (Oxford University Press, 2001)