High-order Dy multipole motifs observed in DyB₂C₂ with resonant soft x-ray Bragg diffraction

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Abstract
Resonant soft x-ray Bragg diffraction at the Dy M₄,₅ edges has been exploited to study Dy multipole motifs in DyB₂C₂. Our results are explained by introducing the intra-atomic quadrupolar interaction between the core 3d and valence 4f shell. This allows us to determine for the first time higher-order multipole moments of dysprosium 4f electrons and to draw their precise charge density. The Dy hexadecapole and hexacontatetrapole moment have been estimated at −20% and +30% of the quadrupolar moment, respectively. No evidence for the lock-in of the orbitals at T₅₈ has been observed, in contrast to earlier suggestions. The multipolar interaction and the structural transition cooperate along c but they compete in the basal plane, explaining the canted structure along [110].

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Resonant x-ray Bragg scattering (RXS) has recently become a powerful tool in modern solid state physics to investigate magnetic, orbital and charge order phenomena associated with electronic degrees of freedom. Especially in transition metal oxides, and, possibly, actinide compounds, various phenomena can occur simultaneously, and it is not easy to identify the exact role and interplay of the various order parameters. However, in rare earth based compounds, orbital and magnetic order occur more autonomously from the lattice as the 4f electrons are shielded by the outer 5d electrons. Electronic orbital motifs are usually labelled antiferroquadrupolar (AFQ) or ferroquadrupolar (FQ), but higher-order multipoles are not established by observations. Argon atoms in an excited state with ℓ = 3 show a significant presence of the higher-order multipole moments as concluded from electron scattering [1], but in the solid state multipoles beyond rank 4 have never been detected. Yet the alignment of
higher multipoles to the surrounding charge in the lattice is likely. For 4f electrons ($l = 3$) multipoles up to rank 6 are present, and this results in a undulated and aspheric charge density. Which multipoles dominate these orbital order transitions remains a rather controversial topic, as exemplified in CeB$_6$ [2], NpO$_2$ [3] and URu$_2$Si$_2$ [4]. Using soft x-ray resonant Bragg scattering (SXRS), we have obtained the first direct evidence of high-order Dy multipole moment motifs in DyB$_2$C$_2$.

DyB$_2$C$_2$ has attracted much attention lately as its high AFQ ordering temperature $T_Q = 24.7$ K allows one to study this phenomenon conveniently. At room temperature, DyB$_2$C$_2$ crystallizes in the tetragonal $P4/mnbm$ structure and undergoes a structural transition with small alternating shifts of pairs of B and C atoms along c at $T_Q$ [5] which reduces the symmetry to $P4_2/mnm$ [6]. Below $T_N = 15.3$ K, antiferromagnetic order (AFM) is observed with complex moment orientations due to the underlying orbital interaction [7]. RXS at the Dy L$_3$ edge has been used to elucidate Dy dipole and quadrupole motifs [6, 8]. A dipole transition (E1) occurs between Dy 2p and 5d shells and a quadrupole transition (E2) between Dy 2p and 4f shells. The first and dominant process probes the quadrupolar order of the 5d states and the latter transition probes the quadrupolar order of the 4f states. The quadrupolar origin of the reflection has been confirmed by azimuthal scans (rotation around the Bragg wavevector).

Ground state wavefunctions of the Dy 4f shell have been proposed based on the observed absence of E2 intensity at the (00 2) charge forbidden reflection which implied cancellation of quadrupole (rank 2) and hexadecapole (rank 4) contributions [9]. These wavefunctions are consistent with a recent inelastic neutron scattering study in which the orbital fluctuation timescale has been determined [10]. An alternative explanation for the RXS data suggests that the hexadecapole moment is zero and that the overlap between the E1 and E2 resonances cancels the E2 intensity [11]. However, the mixing parameter of E1 and E2 processes is fixed at unity in the analysis but this is not a priori justified. SXRS at the Dy M$_{4,5}$ edges accesses the 4f shell directly with the E1 transition, without the complication of overlapping E1 and E2 resonances. Our results show that the Coulomb (intra-atomic quadrupole) interaction between the 3d and 4f shells is significant. The ordered quadrupole moment of the 4f shell in the intermediate state reshapes the observed 3d$_{3/2}$ and 3d$_{1/2}$ core hole charge density and leads to a core hole splitting. It is shown that this phenomenon causes interference between different pathways of the scattering amplitude, allowing the extraction of high-order multipole moments of the 4f shell that have rank 4 and rank 6 (hexacontatetrapole).

2. Experimental details

A DyB$_2$C$_2$ single crystal was grown by the Czochralski method using an arc-furnace with four electrodes and cut with (001) perpendicular to the sample surface. Subsequently, it was polished and aligned with 26°, 56° or 86° azimuthal angle. Zero degree azimuth corresponds to alignment of the b axis in the scattering plane. The orbital ordering (00 2) reflection was recorded at the Dy M$_{4,5}$ edges of DyB$_2$C$_2$ at the RESOXS end-station of the SIM beam-line at the Swiss Light Source. The Dy M$_{4,5}$ absorption edges were characterized with fluorescence yield (FY) and electron yield (EY) at RESOXS and the BL25SU beam line at SPring-8, respectively.

3. Results

3.1. Resonant x-ray diffraction

The recorded energy profile of the charge-forbidden (00 2) reflection of DyB$_2$C$_2$ is shown in figure 1(b), together with x-ray absorption (XAS) data (EY) (figure 1(a)). We note that the
diffracted intensity was recorded with a photodiode and the read-out noise results in errors smaller than the point size of the plots in this paper. Multiple features are observed with much larger energy spread than the multiplet structure of the XAS data, in contrast with the single oscillator recorded at the Dy L$_3$ edge [9]. A similar energy profile has been reported for the M$_5$ edge of Ho at the magnetic (0, 0, $\tau$) reflection but the central sharp feature (solid symbol in figure 1) is absent [12]. The authors argue that the large photo-absorption causes this ‘gap’ at the M$_5$ edge because strong absorption is inherent to soft x-ray scattering. To characterize the width of the scattering $\theta/2\theta$-scans were recorded for the (004) reflection at each energy. Subsequently, the integrated intensity was corrected for absorption, and the corrected curve is shown in the figure 1(c). Absorption effects hugely reduce the intensity of the central feature but cannot account for the multiple features in the energy dependent intensity. The different character of those structures becomes even more apparent from the temperature dependence of the scattered intensity. The AFM transition is witnessed at 15 K as a gradual increase in intensity at 1282 eV; however, this increase is absent at 1291 eV (see inset of figure 1). This cannot be caused by absorption effects on a single oscillator resonance. It appears that the scattered intensity at 1291 eV is sensitive to the orbital order only and its gradual increase below $T_N$ shows that there is no lock-in of the orbitals as proposed from neutron diffraction and symmetry analysis [13]. We will return to this point in the discussion.

The structure in the energy profile is similar for $\sigma$ and $\pi$ polarization of the incident x-rays and independent of the sample temperature in the AFQ phase. Azimuthal angles of 56° and 86° give the same spectral shape but show different overall intensity, as expected from the

![Figure 1](image-url)

**Figure 1.** (a) Absorption of DyB$_2$C$_2$ recorded in electron yield, (b) diffraction intensity of orbital ordering (004) reflection in DyB$_2$C$_2$ taken with incident $\sigma$ and $\pi$ polarization at $T = 18$ K and (c) diffracted intensity of (b) corrected for absorption effects. The inset shows the intensity as a function of temperature for $E = 1282$ and 1291 eV normalized to 1 at $T_N$ for easy comparison.
azimuthal angle dependence of a quadrupole. This illustrates that one atomic tensor is active in the scattering process.

We propose that this particular shape of the energy dependence of the (00\(\frac{1}{2}\)) reflection is caused by the splitting of the 3d core states which results in multiple interfering resonators and consequently adds structure to the energy profile. Previously a core hole splitting caused by the intra-atomic magnetic interaction between 5f and 3d was used to describe the unusual double Lorentzian energy profile at the M\(\frac{3}{2}\) resonance in NpO\(_2\) [14]. There is no ordered magnetism in the AFQ phase and we introduce the intra-atomic quadrupolar interaction to partially lift the core hole degeneracy. The energy splitting is determined by the strength of the intra-atomic interaction and we show that the relative amplitudes are determined by the 4f wavefunction.

The scattered photon intensity \(d\sigma/d\Omega\) is proportional to the squared modulus of the amplitude \(f\) [15]

\[
f = \sum_{K,Q} (2K + 1)^{\frac{3}{2}} X_{Q}^{K} \sum_{q} D_{Qq}^{K}(\alpha, \beta, \gamma) F_{q}^{K},
\]

which is described as a product of spherical tensors with rank \(K\). \(F_{q}^{K}\) with \(-K \leq q \leq K\) describes the electronic response of the sample. \(X_{Q}^{K}\) with \(-K \leq Q \leq K\) describes the geometry of the experimental set-up and polarization direction of the incident and reflected x-rays. Lastly, \(D_{Qq}^{K}(\alpha, \beta, \gamma)\) rotates \(F_{q}^{K}\) onto the coordinates of the experimental reference frame used for \(X_{Q}^{K}\) with Euler angles \(\alpha, \beta, \gamma\). The Dy site symmetry of \(2/m\) gives \(q = \pm 2\) and \(K = 2\) due to the absence of charge (\(K = 0\)) and time-odd (magnetic) (\(K = 1\)) order at (00\(\frac{1}{2}\)) in the AFQ phase.

\(F_{q}^{K}\) describes the atomic resonant process which is commonly represented by a harmonic oscillator. In our particular case we extend the existing theory so that \(F_{q}^{K}\) is a sum of several oscillators at the E1 resonance created by the splitting of the core state. The amplitude \(A_{q}^{K}(\bar{J}, \bar{M})\) of each oscillator is labelled by the total angular momentum \(\bar{J} = \frac{1}{2}, \frac{3}{2}\) and magnetic quantum number \(\bar{M}\) of the core hole.

\[
F_{q}^{K} \propto \sum_{J,M} \frac{r_{J} A_{q}^{K}(\bar{J}, \bar{M})}{E - \Delta_{J} - \epsilon(\bar{J}, \bar{M}) + i\Gamma_{J,\bar{M}}},
\]

Here, \(E\) is the photon energy, \(\Delta_{J}\) is the difference in energy between the degenerate 3d\(_{J}\) shell and the 4f empty states and \(\Gamma_{J,\bar{M}}\) the lifetime of the intermediate state. \(\epsilon(\bar{J}, \bar{M}) = [3\bar{M}^2 - \bar{J}(\bar{J} + 1)]Q_{J}\) is the energy shift of the 3d core levels due to the intra-atomic quadrupole interaction \(Q_{J}\), similar to that in Mössbauer spectroscopy. \(Q_{J}\) is a product of the 3d quadrupole moment and the e-electron electric field gradient experienced by the 3d electrons with \(Q_{\pm 1/2}/Q_{\pm 3/2} = 7/3\).

There are three resonant oscillators at the M\(_{5}\) edge (\(\bar{M} = \pm \frac{1}{2}, \pm \frac{3}{2}\)) and two at the M\(_{3}\) edge (\(\bar{M} = \pm \frac{1}{2}, \pm \frac{3}{2}\)). The amplitudes interfere and the branching ratio between the two edges is defined as a real mixing parameter \(r_{J}\). \(A_{q}^{K}(\bar{J}, \bar{M})\) is constructed from the structure factor of...
the chemical unit cell $\Psi_q^*$:

$$A^K_q(\vec{J}, \vec{M}) = (-1)^{J-M} \sum_r (2r + 1) \left( \begin{array}{c} \vec{J} \\ -\vec{M} \end{array} \right) \sum_x \left( \begin{array}{ccc} K & r & x \\ -q & 0 & q \end{array} \right) R^K(r, x) \Psi_q^*,$$

(3)

where $R^K(r, x)$ are reduced matrix elements, $r = 0, 1, \ldots, 2J$, $x = |K - r|, \ldots, |K + r|$ and $q + x$ and $r + x$ are both even integers. The relevant reduced matrix elements $R^K(r, x)$ are listed in Table 1.

The Dy site symmetry, $2/m$, dictates further that $A^2_2 = -A^2_{-2}$ and

$$\Psi_q^* = \sum_d e^{i\tau_d (T^x_d)} |\psi_0\rangle = 2\{\langle T^x_q \rangle - \langle T^{-x}_q \rangle\}$$

(4)

$$\langle T^x_q \rangle = \langle \psi_0 | T^x_q | \psi_0 \rangle.$$  

(5)

$T^x_q$ is the atomic spherical tensor of the Dy 4f shell and $|\psi_0\rangle$ its ground state wavefunction. It follows that $A^K_q(\vec{J}, \vec{M})$ contains the hexadecapole moment $\langle T^4_q \rangle$ and hexacontatetrapole moment $\langle T^6_q \rangle$ in addition to the quadrupole moment $\langle T^2_q \rangle$. In the case $\epsilon(\vec{J}, \vec{M}) = 0$ the terms proportional to $\langle T^2_q \rangle$ and $\langle T^4_q \rangle$ cancel and $A^K_q(\vec{J})$ is proportional to $\langle T^2_q \rangle$ as usual. This allows one to measure the ordered hexacontatetrapole moment of an electronic shell in solid state physics. The azimuthal angle dependence follows from $D^K_{\alpha\beta\gamma}(\alpha, \beta, \gamma)$ (equation (1)) and is independent of the relative oscillator strengths, resulting in a spectral shape that is independent of the azimuthal angle.

Let us here summarize the consequences of this analysis of the scattering. The overall intensity is represented by scattering from the quadrupole $\langle T^2_q \rangle$ of the 4f shell and reflects the same azimuthal angle dependence as the quantity observed in the dipole transition at the $L_1$ edge [9]. The dependence on the higher 4f multipoles arises from the splitting of the core hole states, which results in the $\vec{M}$ dependence of the amplitudes of the different harmonic oscillators (equation (2)). Correspondingly, these amplitudes are influenced by higher 4f multipoles as shown in equation (3). Therefore, the core hole splitting allows one, for the first time, to measure the ordered hexacontatetrapole moment of an electronic shell in solid state physics. Note that this is not in contradiction with the fact that the integrated intensity of a dipole (E1) transition is sensitive to tensors up to rank 2 (quadrupole), while a quadrupole (E2) transition is sensitive to tensors up to rank 4 (hexadecapole).

4. Discussion

Figure 2 shows the measured energy dependence compared to the above theory. The absorption correction is implemented in the theoretical description for easier visual comparison of the
quadrupoles in the $xy$ plane are additional time odd terms due to the magnetic order below $T_N$ observed at 1282 and 1291 eV supports our analysis since the resonant cross section contains contrast, the 90\degree arrangement of the orbitals along [110]. The Dy 4f charge density obtained from the best fit is illustrated in figure 3. It supports a 90\degree zig-zag alignment along $c$ as demonstrated by its protrusions at top and bottom. In the basal plane a 90\degree zig-zag alignment along [110] is preferred so that the concave part points toward the convex part of its nearest neighbour. Yet, the absence of lock-in of the orbitals confirm that the orbital motif in the AFQ phase is similar to that in the combined AFQ and AFM phase. Therefore the Dy charge densities are canted away from [110] as determined by neutron diffraction [7]. Canted charge densities in the AFQ phase are in agreement with RXS studies [5, 6]. In contrast, Zaharko et al [13] argue that a 90\degree arrangement of neighbouring quadrupoles in the $xy$ plane is most likely because the AFM interaction is not strong enough above $T_N$ to oppose the arrangement favoured by the AFQ interaction. However, such a canted AFQ structure logically emerges when the pairwise movement of B and C ions is in competition with the multipolar interaction and promotes parallel alignment of the orbitals along [110].

In contrast, the 90\degree zig-zag alignment along $c$ is supported by both mechanisms. This is consistent with the multipolar interaction and promotes parallel alignment of the orbitals along [110].

Note that the reduced matrix elements are contained in equation (3) while in [9] they are included in $\langle T_2^r \rangle$.

Figure 2. Observed energy profile (crosses) compared to fits of the theory including absorption correction with (a) wavefunction taken from [9] (grey (red)), (b) $\langle T_2^r \rangle$ set to zero (dotted grey (blue)), and (c) $\langle T_2^r \rangle$ as free parameter (black). $\langle T_2^r \rangle$ is normalized to 1, $\langle T_2^r \rangle = -0.2$, $\langle T_2^r \rangle = +0.3$, $\Gamma_{\pm \pm}^\| = 0.8$ eV, $\Gamma_{\mp \pm}^\| = 2.7$ eV, $\Gamma_{\pm \mp}^\| = 5.3$ eV, $\Gamma_{\pm \pm}^{\perp} = 1.9$ eV and $\Gamma_{\pm \mp}^{\perp} = 5.4$ eV, $r_y = 0.22$ and $Q_x = -0.41$ eV. The temperature dependence observed at 1282 and 1291 eV supports our analysis since the resonant cross section contains additional time odd terms due to the magnetic order below $T_N$. These terms may add at $\epsilon(\hat{\tau}_x, \pm \hat{\tau}_y)$ while they cancel at $\epsilon(\hat{\tau}_y, \pm \hat{\tau}_x)$. In addition our analysis predicts a spectral shape independent of azimuthal angle, consistent with our observation.

8 Note that the reduced matrix elements are contained in equation (3) while in [9] they are included in $\langle T_2^r \rangle$.

9 See figure 4b of [13] for specific movement of B and C.
Figure 3. Dy charge density and multipole motif in the AFQ phase of DyB$_2$C$_2$. The basal plane is indicated in grey. Note the $90^\circ$ zig-zag alignment of the Dy orbitals along $c$ and the canted zig-zag alignment along [110]. A spherical charge density has been subtracted to emphasize the asphericity.

with a recent study of (Dy, Y)$_2$B$_2$C$_2$ where quasi-one-dimensional AFQ along the $c$ axis has been reported [17].

We should add that our analysis in terms of core–valence interaction is consistent with the multiplet structure interpretation. In the M$_5$ and M$_4$ absorption the multiplet structure is $\sim$10 eV and $\sim$5 eV wide, respectively, which is mainly due to the strong 3d–4f and 4f–4f Coulomb and exchange interactions [16]. The 3d$^{5/2}$4f$^{10}$ and 3d$^{3/2}$4f$^{10}$ final state multiplets contain 6006 and 4004 levels with an average lifetime width of 0.27 and 0.55 eV, respectively. The strong electron correlation leads to non-diagonal matrix elements in the quantum numbers $\vec{L}$ $\vec{S}$ $\vec{J}$ of the core hole. The levels of the same $\vec{M}$ connected by these non-diagonal elements excite partly coherently. This makes it difficult to separate the core hole states. In the free ion we do not expect an energy shift for distributions of different $|\vec{M}|$. This was confirmed for the x-ray absorption spectrum with Cowan’s atomic Hartree–Fock code, where we found roughly an equally broad multiplet when switching off the quadrupole component of the orbital contribution of the core–valence interaction. This suggests that any energy shifts in the $|\vec{M}|$ distributions will be due to multipolar ordering of the 4f states.

In this theoretical framework the core hole state is uncoupled from the 4f$^{n+1}$ state and the effect of the 4f multiplet structure is indirectly taken into account by the effective widths of the $\vec{M}$ distributions, which exceed the intrinsic life time width and describe the data surprisingly well. Our work merely demonstrates that including the intra-atomic interaction is a viable approach and accounts for the multiple spectral features and their broad distribution in energy. We note that the empty states of the 4f shell selected by the resonant diffraction process, and their corresponding relative transition intensities, are not necessarily the same as for the absorption process. Resonant diffraction is sensitive to the difference between electronic states while absorption spectroscopy is sensitive to its average. For example, the magnetic moment of an antiferromagnet is not visible at the absorption edge, but resonant diffraction may yield large intensities proportional to the magnetic moment [18].

5. Conclusion

In conclusion, the Dy 4f hexadecapole and hexaccontatetrapole moments in DyB$_2$C$_2$ have been measured with SXRS and their magnitudes are determined at $-20\%$ and $+30\%$ of the
quadrupole moment, respectively. The orbital order remains unaffected by magnetic order below $T_N$ and no lock-in of the orbitals takes place, in contrast to CeB$_6$. The structural transition and multipolar interactions cooperate along the $c$ axis while they compete along [110]. These findings amply demonstrate a new extension of the resonant x-ray Bragg diffraction method for the observation of high-order electronic multipole motifs. Of particular interest are materials in which higher-order multipoles are believed to be of importance, such as CeB$_6$, URu$_2$Si$_2$, as well as the RB$_2$C$_2$ and skutterudite families.

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References

[1] Al-Khateeb H M, Birdsey B G and Gay T J 2000 Phys. Rev. Lett. 85 4040
[2] Plakhty V P, Regnault L P, Goltsiev A V, Gavrilov S V, Yakhou F, Floquet J, Vettier C and Kunii S 2005 Phys. Rev. B 71 100407
[3] Kubo K and Hotta T 2005 Phys. Rev. B 71 140404(R)
[4] Kiss A and Fazekas P 2005 Phys. Rev. B 71 054415
[5] Adachi H, Kawata H, Mizumaki M, Akao T, Sato M, Ikeda N, Yanaka Y and Miwa H 2002 Phys. Rev. Lett. 89 206401
[6] Tanaka Y, Inami T, Nakamura T, Yamauchi H, Onodera H, Ohoyama K and Yamaguchi Y 1999 J. Phys.: Condens. Matter 11 L305
[7] Yamauchi H, Onodera H, Ohoyama K, Onimaru T, Kosaka M, Ohashi M and Yamaguchi Y 1999 J. Phys. Soc. Japan 68 2057
[8] Hirota K, Oumi N, Matsumura T, Nakao H, Wakabayashi Y, Murakami Y and Endoh Y 2000 Phys. Rev. Lett. 84 2706
[9] Tanaka Y, Inami T, Lovesey S W, Knight K S, Yakhou F, Mannix D, Kokubun J, Kanazawa M, Ishida K, Nanao S, Nakamura T, Yamauchi H, Onodera H, Ohoyama K and Yamaguchi Y 2004 Phys. Rev. B 69 024417
[10] Staub U, Mulders A M, Zaharko O, Janssen S, Nakamura T and Lovesey S W 2005 Phys. Rev. Lett. 94 036408
[11] Matsumura T, Okuyama D, Oumi N, Hirota K, Nakao H, Murakami Y and Wakabayashi Y 2005 Phys. Rev. B 71 012405
[12] Spencer P D, Wilkins S B, Hatton P D, Brown S D, Hase T P A, Purton J A and Fort D 2005 J. Phys.: Condens. Matter 17 1725
[13] Zaharko O, Sikora W, Bialas F, Staub U and Nakamura T 2004 Phys. Rev. B 69 224417
[14] Lovesey S W, Balcar E, Detelev C, van der Laan G, Sivia D S and Staub U 2003 J. Phys.: Condens. Matter 15 4511
[15] Lovesey S W, Balcar E, Knight K S and Fernández-Rodríguez J 2005 Phys. Rep. 411 233
[16] Thole B T, van der Laan G, Fuggle J C, Sawatzky G A, Kannan T C and Esteve J M 1985 Phys. Rev. B 32 5107
[17] Indoh K, Tobo A, Ohoyama K and Onodera H 2004 J. Phys. Soc. Japan 73 1354
[18] Lovesey S W and Collins S P 1996 X-ray Scattering and Absorption by Magnetic Materials (Oxford: Clarendon)