The effect of core–valence intra-atomic quadrupolar interaction in resonant x-ray scattering at the Dy M_{4,5} edges in DyB_{2}C_{2}

Javier Fernández-Rodríguez¹, Alessandro Mirone¹ and Urs Staub²

¹ European Synchrotron Radiation Facility, BP 220, 38043 Grenoble Cedex, France
² Swiss Light Source, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

Received 21 June 2009, in final form 4 November 2009
Published 2 December 2009
Online at stacks.iop.org/JPhysCM/22/016001

Abstract
The dependences on energy of the resonant soft x-ray Bragg diffraction intensities in DyB_{2}C_{2} for the (00\bar{4}) reflection at the Dy M_{4,5} edges have been calculated with an atomic multiplet Hamiltonian including the effect of the crystal field and introducing an intra-atomic quadrupolar interaction between the 3d core and 4f valence shell. These calculations are compared with experimental results (Mulders et al 2006 J. Phys.: Condens. Matter 18 11195) for the antiferroquadrupolar and antiferromagnetic phases of DyB_{2}C_{2}. We reproduce all the features appearing in the (00\bar{4}) reflection energy profile in the antiferroquadrupolar ordered phase, and we reproduce the behaviour of the resonant x-ray scattering intensity at different energies in the vicinity of the Dy M_{5} edge when the temperature is lowered within the antiferromagnetic phase. These calculations show that a detailed description of the energy dependences of resonant x-ray scattering signals at the M edges in 4f and 5f systems with multipolar ordering may require the inclusion of an aspherical intra-atomic Coulomb interaction.

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

1. Introduction
The charge, orbital, and spin degrees of freedom of the few electrons in the valence states of a material play an important role in its electronic properties. Phase transitions in materials often result from cooperative effects involving moments of the electronic distributions of the constituents atoms. In this way, the paramagnetic–antiferromagnetic transition, for example, arise from exchange interactions between the magnetic moments. The potential importance of multipolar interaction in f electron systems has long been recognized and in the particular case for which the angular momentum is zero, phase transitions may be driven by higher order multipolar moments [1, 2]. In 4f or 5f ions high order multipolar interactions may eventually manifest themselves in other subtle effects, such as lifting the degeneracy between single or multi-k structure. Often, the interactions between the 4f shells drive orderings in which their electronic density no longer respect the initial symmetries. The primary order parameter may not be of magnetic nature, but of orbital one (quadrupoles). Resonant x-ray scattering (RXS), enhanced by the brightness, tunability, and a high degree of polarization available at x-ray synchrotron sources, is an effective technique to measure these microscopic variables. In RXS, by studying intensities at space-group-forbidden reflections, dipolar and quadrupolar order parameters can be studied [3–7]. Only recently has it become possible to access such ordering phenomena by means of resonant x-ray diffraction. Higher multipolar orderings can be studied by resonant x-ray diffraction: octupoles [8], hexadecapoles [9, 10], anapoles [11]. Also non-resonant x-ray diffraction can give information on higher order multipolar orderings [12].

DyB_{2}C_{2} shows the highest antiferroquadrupole (AFQ) transition with T_{Q} = 24.7 K [13]. The ordering of quadrupoles in DyB_{2}C_{2} has been studied intensively with resonant x-ray scattering [14, 15, 9, 16] and neutron diffraction in magnetic fields [17, 18]. At the AFQ ordering temperature T_{Q} the space group symmetry of the material is reduced from P4/mbm to P4_{2}/mnm [19] with a doubling of the unit cell along the c-axis. Below T_{N} = 15.3 K magnetic order appears, which has been observed in neutron diffraction [17, 18]. Inelastic neutron scattering has been used to study the magnetic dipolar and orbital fluctuations in this compound [20]. Mulders et al [21] report isotropic absorption measurements and soft x-
ray resonant diffraction at the (00\(\overline{4}\)) space group forbidden reflection at the Dy M_{4,5} edges in the antiferroquadrupolar ordered (AFQ) and antiferromagnetic phase (AFM). A possible charge scattering contribution is ruled out, as then the \(\sigma\) and \(\pi\) incident spectra would differ by orders of magnitude and would have a completely different shape in energy as the Bragg angle is close to 45°. In order to justify the shape of the resonant diffraction energy profile, Mulders et al [21] use an analytical model for describing resonant x-ray scattering in terms of single oscillators for each of the \(M\) quantum numbers for the \(J = \frac{1}{2}, \frac{3}{2}\) core holes at the M_{4,5} edges. The degeneration of the resonant oscillators would be split due to a Coulomb intra-atomic quadrupolar interaction, which would be produced by the ordered quadrupolar moment in the 4f shell. This model was introduced to describe the uncommon energy line shape and temperature dependence of different features. The weakness of the fitting of the data in [21] is, that the multiplet structure caused by the interaction of the core state with the 4f multiplets are not taken into account, which is not necessarily, with its several eV splitting, negligible in such a case.

In some cases, it is possible to calculate analytically the attenuation and resonant scattering of x-rays in terms of an idealized scattering length by making the fast-collision approximation. If the different positioning in energy of the states of the core–hole is neglected, the scattering length can be expressed in terms of different multipolar moments of the ground state of the resonant ion and the influence of the intermediate states is eliminated [7, 22, 23]. Calculations that go beyond the fast-collision approximation, and include explicitly the quantum numbers of the intermediate state have been done [24, 25]. Significative interaction between core and valence arise in many systems: in the M_{3}-edge in Ho at the magnetic (0, 0, \(\tau\)) reflection [26]. Within the rare-earth diborocarbides, in TbB_{2}C_{2} the same quadrupolar interaction as in DyB_{2}C_{2} affects the energy profiles at the M_{4,5}-edges [27], also it might appear in HoB_{2}C_{2} [28], although resonant x-ray scattering measurements in this system have not yet been made. Interaction between the valence octupole moment and the core hole was used as a necessity to explain the NpO_{2} [29] data taken at the Np M_{4}-edge. In this paper we explore the effect of such dependence of the core–hole interaction, going beyond the analysis done in [21] by using a full atomic multiplet Hamiltonian including the effect of the crystal field.

2. A model Hamiltonian

We calculate the resonant x-ray scattering factor for the dipolar transition 4P \(\rightarrow\) 3d^{4}4f^{10} by making use of the program Hilbert ++ [30, 31]. The program starts from a model Hamiltonian accounting for multiplets and hybridization, written in terms of creation and destruction operators, and applies Lanczos tridiagonalization to the Hilbert space spanned by the electronic degrees of freedom of the absorber ion and its nearest neighbours to find the ground state \(|g\rangle\). The resonant x-ray scattering tensor is calculated as

\[
\langle g| e^\dagger D | \frac{1}{E_0 - H_e + \hbar \omega + i\Gamma} eD | g \rangle,
\]

where \(E_0\) is the energy of the initial state \(|g\rangle\), \(H_e\) is the Hamiltonian of the excited state, \(e\) and \(e^\dagger\) are the vectors representing the polarizations of the primary and secondary beams of x-rays, \(D\) is the dipole operator, \(\hbar \omega\) is the photon energy and \(\Gamma\) is the broadening due to the core–hole lifetime. We use a model Hamiltonian that includes the atomic multiplets and the crystal field interaction with the neighbouring ions,

\[
H = H_{\text{atomic}} + H_{\text{CF}}.
\]

Cowan’s atomic multiplet program provides \textit{ab initio} Hartree–Fock (HF) values of the radial Coulomb Slater integrals and the spin–orbit interactions for an isolated ion. In order to take into account the screening effects present in the real system with respect to the HF limit we scale down the theoretical values for the single configuration Slater integrals \(F^K\) and \(G^K\) to 75% of their HF values as it is customarily done [30, 32] to include the effect of the perturbations coming from intratomic configuration interaction. Appropriate scale factors range from 0.7 or 0.8 for neutral atoms to about 0.9 or 0.95 for highly ionized atoms [33]. To model the interaction with the neighbouring ions, we construct a crystal field term based in the local structure simulating the effect of hybridization with the carbon first neighbour ions,

\[
H_{\text{CF}} = \sum_y V_y h f_{y3}^+ f_{y3}^\dagger,
\]

where \(V_y\) is the displacement in the Dy \(f_{y3}\) orbital produced by a ligand ion along the \(z\) axis and \(f_{y3}^+ / f_{y3}^\dagger\) denote creation/destruction operators in the \(f\) shell of the Dy ion being the local \(z\) axis orientated along the bond direction of each of the neighbouring atoms. This term is summed over the bonding atoms (we consider eight nearest neighbours). The parameter \(V_y\) is rescaled according to the bond length. We use the available structural information [34, 35] on the environment of first neighbour C ions around a Dy site. Following Adachi et al [36], in the structure of the quadrupolar ordered phase, we add a displacement along the \(c\) axis to the positions of the C ions from its positions in the high temperature \(P4/mmb\) space group. It is important to note that it is very difficult to model the crystal field of the \(4f\) shell correctly using a crystal field Hamiltonian as shown in equation (3). This is caused by badly defined screening effects and effects such as polarization of the 5d states [37], not well included in this description. This might lead to an insufficient description of the anisotropy of the Coulomb interaction with the core state. To improve the description, we introduce a splitting of the core states caused by the intra-atomic quadrupole interaction similarly as done in [21]. The energy shift of the 3d core levels due to the quadrupolar interaction between the 4f and the 3d charge distributions can be written as the product of the 3d electron field gradient experienced by the 3d electrons, which in terms of the quantum numbers of the total core–hole angular momentum \(J, M\) would be written as \(\epsilon(J, M) = [3M^2 - J(J + 1)] Q_j\) with \(Q_{J = \pm 2} = \frac{2}{3}Q_{J = \pm 2}\). This is analogous to the term that is used to model the electrostatic interaction between the nuclear and electronic charge distributions in Mossbauer spectroscopy.

\[\text{J Phys.: Condens. Matter 22 (2010) 016001 J Fernández-Rodríguez et al}\]
3. Modelling of experimental spectra

We have calculated the isotropic x-ray absorption and the resonant diffraction energy profile for different values of the parameters $V_e$ and $Q_J$ keeping the ratio $Q_1/Q_2 = \frac{1}{2}$. By comparing with the experimental x-ray spectra measured in the AFQ phase ($T = 18$ K) [21] we find that the best agreement at the M5-edge corresponds to the parameter $Q_{5/2} = 0.2$ eV and $V_e = 0.1$ eV. For this value of the parameter $V_e$, our crystal field model gives a ground state with total angular momentum $J = \frac{15}{2}$ where the weights of the different states $|JM_J\rangle$ in the ground state manifold are $\langle |JM_J|g|\rangle^2 = 0.91, 0.01, 0.07$ for $M_J = -\frac{15}{2}, -\frac{13}{2}, -\frac{11}{2}$. The weight of the states with other values of $M_J$ is negligible. The experimentally measured and calculated isotropic absorption and resonant x-ray diffraction energy profile at the reflection $(00\bar{1})$ is shown in figure 1. In the calculated spectra we consider a Boltzmann average in order to take into account the effect of the temperature. In figure 1, we also show the shape that the spectra would have without the core–hole interaction, i.e. with $Q_J = 0$. It is also worth noting that the isotropic absorption measurements were made at room temperature (above $T_0$), and in consequence, the experimental measurements are better reproduced by the model calculation with zero core–hole interaction. In figure 2 we show the shape that the spectra would have with the core–hole interaction $Q_{5/2} = -0.4$ eV reported in [21] and calculated with our multiplet model. The change in the sign of $Q_J$ with respect to [21] would mean that the positioning of the harmonic oscillators with different values of $M$ in figure 2 of [21] would be reversed. Using a negative value of $Q_{5/2}$ in our calculation, would lead to a much worse agreement with the diffraction energy profile. We note here that there is not even a reliable set of crystal field parameters available from inelastic neutron scattering in the high temperature phase, where there are only nine independent crystal field parameters in a phenomenological tensor operator approach. Moreover, we note that the approach of Mulders is free of this problem, as there, no a priori assumptions on the 4f wavefunctions are used. They use a fit to the expectation values for the higher multipole moments, which will give some constrains to the ground state wavefunctions of the Dy$^{3+}$. That model, on the other hand, is not taking the multiplet structure caused by the core hole 4f shell interaction into account. A more sophisticated test for the anisotropic 4f core hole interaction would require a detailed knowledge of the 4f wavefunctions, which is not available to date on this system.

In order to calculate the spectra below $T_N = 15.3$ K in the AFM phase, we calculate the resonant x-ray diffraction spectra introducing an additional term $S \cdot H$ term in the Hamiltonian, being $S$ the spin momentum, and $H$ a magnetic field which polarizes the magnetic moment in the $ab$ plane, forming $23^\circ$ with respect to the $a$ axis. The isotropic absorption does not show any appreciable change when polarizing the magnetic moment. Figure 3 shows the diffraction energy profile of the Dy M5 edge for different values of the spin ($S_z$) and orbital ($L_z$) polarization, where $\bar{z}$ is the local anisotropy axis in the $ab$ plane. The Boltzmann average does not change significantly the spectra, but it reduces notably the values of $S_z$ and $L_z$ from the values they would have at $T = 0$ K. All the curves in figure 3 are normalized to have the same intensity at energies lower than 1282 eV. Our calculated spectra shown in figure 3 are consistent with the experimentally determined behaviour.
of the features in the diffraction spectra at $E = 1282$ and $1291$ eV when lowering the temperature, which is shown in figure 1 of [21].

4. Conclusions

By using a model taking into account an atomic multiplet Hamiltonian, crystal field and intra-atomic quadrupolar interaction between the 3d core–hole and the 4f valence shell we have reproduced the different features in the experimental isotropic absorption and resonant x-ray diffraction energy profile at the Dy M$_4$ and M$_5$ edges in the antiferroquadrupolar phase of DyB$_2$C$_2$ in terms of a dipolar transition ($4f^2 \rightarrow 3d^5 4f^{10}$). When in our model we vary the polarization of the magnetic moment of the Dy ion, we observe a variation of the RXS spectra for different energies around the Dy M$_5$-edge that resembles the experimentally observed behaviour of the measured RXS intensities for different energies when the temperature is lowered in the antiferromagnetic phase. The deviation between experiment and calculations most likely come from the limitations of the crystal field description. These calculations show that the inclusion of the quadrupolar (anisotropic Coulomb) interaction between the core and the 4f states might be a useful physical concept relevant for the study of orbitally ordered systems by soft x-rays at the M$_4$,5 edges of rare earths. Such a concept should be tested in detail on other 4f systems, as it would be necessary to test it in detail on other 4f systems, as it would be necessary.

Acknowledgments

We thank R Caciufo, J A Blanco and V Scagnoli for useful discussions. One of us, JFR, is grateful to Gobierno del Principado de Asturias for the financial support from Plan de Ciencia, Tecnología e Innovación PCTI de Asturias 2006–2009.

References

[1] Santini P, Carretta S, Amoretti G, Caciuffo R, Magnani N and Lander G H 2009 Rev. Mod. Phys. 81 S07
[2] Kuramoto Y, Kasunose H and Kiss A 2009 J. Phys. Soc. Japan 78 072001
[3] Lovesey S W, Fernandez Rodriguez J, Blanco J A and Brown P J 2004 Phys. Rev. B 70 172414
[4] Fernandez-Rodriguez J, Blanco J A, Brown P J, Katsumata K, Kikkawa A, Iga F and Michimura S 2005 Phys. Rev. B 72 052407
[5] McMorrow D F, McEwen K A, Steigenberger U, Roosnino H M and Yakhov F 2001 Phys. Rev. Lett. 87 057201
[6] Walker H C, McEwen K A, McMorrow D F, Wilkins S B, Wainst F, Colineau E and Fort D 2006 Phys. Rev. Lett. 97 137203
[7] Lovesey S W, Balcar E, Knight K S and Fernandez-Rodriguez J 2005 Phys. Rep. 411 233
[8] Lovesey S W, Fernandez-Rodriguez J, Blanco J A and Tanaka Y 2007 Phys. Rev. B 75 054401
[9] Tanaka Y et al 2004 Phys. Rev. B 69 024417
[10] Fernandez-Rodriguez J, Lovesey S W and Blanco J A 2008 Phys. Rev. B 77 094441
[11] Lovesey S W, Fernandez-Rodriguez J, Blanco J A, Sivia D S, Knight K S and Paolasini L 2007 Phys. Rev. B 75 014409
[12] Tanaka Y et al 2004 Europhys. Lett. 68 671
[13] Yamauchi H et al 1999 J. Phys. Soc. Japan 68 2057
[14] Tanaka Y et al 1999 J. Phys.: Condens. Matter 11 L505
[15] Hirota K et al 2000 Phys. Rev. Lett. 84 2706
[16] Matsumura T et al 2002 Phys. Rev. B 65 94420
[17] Yamauchi H et al 2003 J. Phys.: Condens. Matter 15 S2137
[18] Zaharko O et al 2004 Phys. Rev. B 69 224417
[19] Lovesey S W and Knight K S 2001 Phys. Rev. B 64 094401
[20] Staub U et al 2004 Phys. Rev. Lett. 68 671
[21] Mulders A M, Staub U, Scagnoli V, Lovesey S W, Balcar E, Nakamura T, Kikkawa A, van der Laan G and Tonnnerre J M 2006 J. Phys.: Condens. Matter 18 11195
[22] Lovesey S W and Balcar E 1996 J. Phys.: Condens. Matter 8 10983
[23] Lovesey S W and Balcar E 1996 J. Phys.: Condens. Matter 8 11009
[24] Lovesey S W and Balcar E 1997 J. Phys.: Condens. Matter 9 4237
[25] Lovesey S W, Balcar E and Tanaka Y 2008 J. Phys.: Condens. Matter 20 272201
[26] Lovesey S W 1995 J. Phys.: Condens. Matter 9 7501
[27] Lovesey S W and Balcar E 1997 J. Phys.: Condens. Matter 9 8679
[28] Spencer P D, Wilkins S B, Hatton P D, Brown S D, Hase T P A, Parton J A and Fort D 2005 J. Phys.: Condens. Matter 17 1725
[29] Mulders A M, Staub U, Scagnoli V, Tanaka Y, Kikkawa A, Katsumata K and Tonnnerre J M 2007 Phys. Rev. B 75 184438
[30] Yanagisawa T, Goto T, Nemoto Y, Watanuki R, Suzuki K, Suzuki O and Kido G 2005 Phys. Rev. B 71 104416
[31] Lovesey S W, Balcar E, Detlefs C, van der Laan G, Sivia D S and Staub U 2003 J. Phys.: Condens. Matter 15 4511
[32] Mirone A, Dhesi S S and van der Laan G 2006 Eur. Phys. J. B 53 23
[33] Mirone A 2009 arXiv:0706.4170 [cond-mat.str-el]
[34] Wilkins S B et al 2005 Phys. Rev. B 71 245102
[35] Cowan R D 1981 The Theory of Atomic Structure and Spectra (Berkeley, CA: University of California Press) p 464 and references therein
[36] Ohoyama K et al 2001 J. Phys. Soc. Japan 70 3291
[37] Onimaru T, Onodera H, Ohoyama K, Yamaguchi Y 1999 J. Phys. Soc. Japan 68 2287
[38] Ohoyama K et al 2002 Phys. Rev. Lett. 89 206401
[39] Staub U and Soderholm L 2000 Handbook of Chemistry and Physics of Rare Earths vol 30 ed K A Gschneider Jr, L Eyring and M B Maple (Amsterdam: North-Holland) p 491