

The effect of core–valence intra-atomic quadrupolar interaction in resonant x-ray scattering at the Dy  $M_{4,5}$  edges in  $DyB_2C_2$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2010 J. Phys.: Condens. Matter 22 016001

(<http://iopscience.iop.org/0953-8984/22/1/016001>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 30/05/2010 at 06:29

Please note that [terms and conditions apply](#).

# The effect of core–valence intra-atomic quadrupolar interaction in resonant x-ray scattering at the Dy $M_{4,5}$ edges in $DyB_2C_2$

Javier Fernández-Rodríguez<sup>1</sup>, Alessandro Mirone<sup>1</sup> and Urs Staub<sup>2</sup>

<sup>1</sup> European Synchrotron Radiation Facility, BP 220, 38043 Grenoble Cedex, France

<sup>2</sup> 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](http://stacks.iop.org/JPhysCM/22/016001)

## Abstract

The dependences on energy of the resonant soft x-ray Bragg diffraction intensities in  $DyB_2C_2$  for the  $(00\frac{1}{2})$  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  $DyB_2C_2$ . We reproduce all the features appearing in the  $(00\frac{1}{2})$  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].

$DyB_2C_2$  shows the highest antiferroquadrupole (AFQ) transition with  $T_Q = 24.7$  K [13]. The ordering of quadrupoles in  $DyB_2C_2$  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  $(00\frac{1}{2})$  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  $45^\circ$ . 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  $\bar{M}$  quantum numbers for the  $\bar{J} = \frac{3}{2}, \frac{5}{2}$  core holes at the  $M_{4,5}$  edges. The degeneration of the resonant oscillators would be splitted 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]. Significant interaction between core and valence arise in many systems: in the  $M_5$ -edge in Ho at the magnetic  $(0, 0, \tau)$  reflection [26]. Within the rare-earth diborocarbides, in  $TbB_2C_2$  the same quadrupolar interaction as in  $DyB_2C_2$  affects the energy profiles at the  $M_{4,5}$ -edges [27], also it might appear in  $HoB_2C_2$  [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  $4f^9 \rightarrow 3d^9 4f^{10}$  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

$$\langle g | \mathbf{e}' \mathbf{D} \left| \frac{1}{E_0 - H_c + \hbar\omega + i\Gamma} \right| \mathbf{e} \mathbf{D} | g \rangle, \quad (1)$$

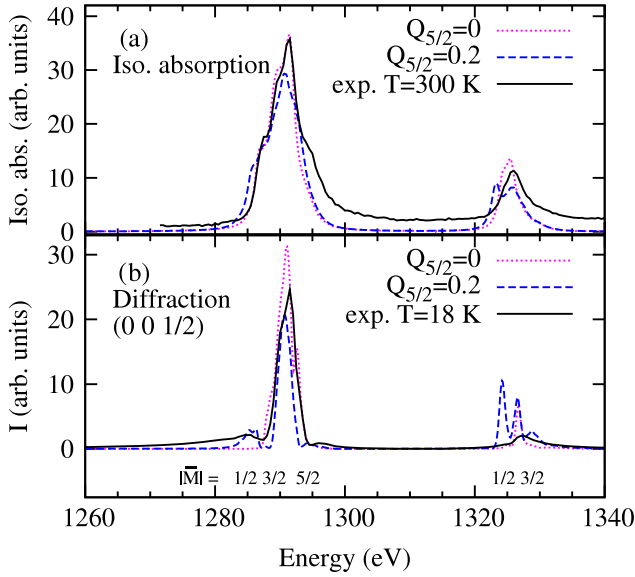
where  $E_0$  is the energy of the initial state  $|g\rangle$ ,  $H_c$  is the Hamiltonian of the excited state,  $\mathbf{e}$  and  $\mathbf{e}'$  are the vectors representing the polarizations of the primary and secondary beams of x-rays,  $\mathbf{D}$  is the dipole operator,  $\hbar\omega$  is the 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,

$$H = H_{\text{atomic}} + H_{\text{CF}}. \quad (2)$$

Cowan's atomic multiplet program provides *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 intra-atomic 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,

$$H_{\text{CF}} = \sum_b V_{\sigma,b} f_{z^3}^+ f_{z^3} \quad (3)$$

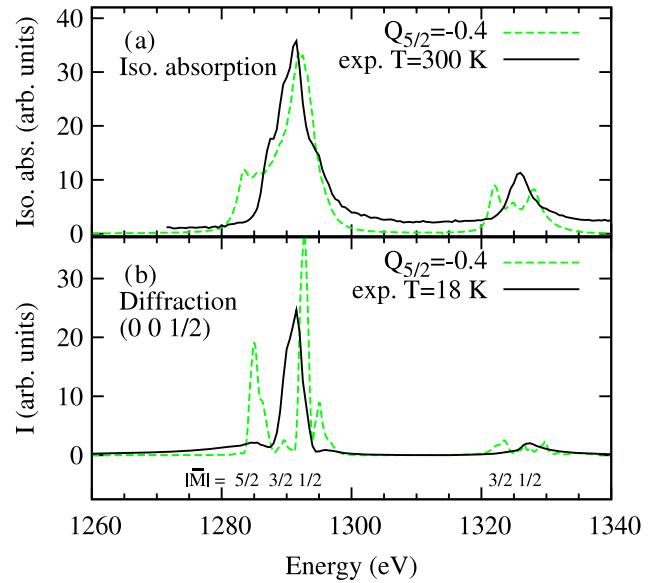
where  $V_{\sigma}$  is the energy displacement in the Dy  $f_{z^3}$  orbital produced by a ligand ion along the  $z$  axis and  $f_{z^3}^{\dagger}/f_{z^3}$  denote creation/destruction operators in the f shell of the Dy ion being the local  $\tilde{z}$  axis orientated along the bond direction of each of the neighbouring atoms. This term is summed over the bonding atoms (we consider eight nearest neighbours). The parameter  $V_{\sigma}$  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  $P4/mbm$  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 quadrupole moment and the average of the f electron electric field gradient experienced by the 3d electrons, which in terms of the quantum numbers of the total core-hole angular momentum  $\bar{J}, \bar{M}$  would be written as  $\epsilon(\bar{J}, \bar{M}) = [3\bar{M}^2 - \bar{J}(\bar{J} + 1)]Q_{\bar{J}} = \frac{7}{3}Q_{\bar{J}=\frac{3}{2}}$ . This is analogous to the term that is used to model the electrostatic interaction between the nuclear and electronic charge distributions in Mossbauer spectroscopy.



**Figure 1.** Experimentally measured isotropic absorption (at room temperature) and resonant x-ray diffraction spectra at the  $(00\frac{1}{2})$  space group forbidden reflection and absorption spectra taken in the AFQ phase ( $T = 18$  K) [21] together with the calculated spectra, corresponding to the parameter  $V_\sigma = 0.1$  eV. Calculated spectra is shown for the cases in which the core-hole interaction is absent ( $Q_{5/2} = 0$ ) and included ( $Q_{5/2} = 0.2$  eV). The positioning in energy of the different core states  $|JM\rangle$  is also shown.

### 3. Modelling of experimental spectra

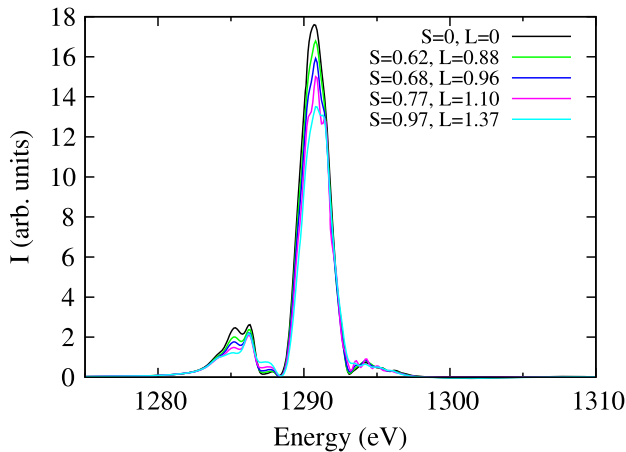
We have calculated the isotropic x-ray absorption and the resonant diffraction energy profile for different values of the parameters  $V_\sigma$  and  $Q_J$  keeping the ratio  $Q_{3/2}/Q_{5/2} = \frac{7}{3}$ . By comparing with the experimental x-ray spectra measured in the AFQ phase ( $T = 18$  K) [21] we find that the best agreement at the  $M_5$ -edge corresponds to the parameter  $Q_{5/2} = 0.2$  eV and  $V_\sigma = 0.1$  eV. For this value of the parameter  $V_\sigma$ , 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  $M_J = -\frac{13}{2}, -\frac{9}{2}, -\frac{5}{2}$ . The weight of the states with other values of  $M_J$  is neglectable. The experimentally measured and calculated isotropic absorption and resonant x-ray diffraction energy profile at the reflection  $(00\frac{1}{2})$  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  $T_Q$ ), 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  $\bar{M}$  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



**Figure 2.** Experimentally measured isotropic absorption (at room temperature) and resonant x-ray diffraction spectra at the  $(00\frac{1}{2})$  space group forbidden reflection and absorption spectra taken in the AFQ phase ( $T = 18$  K) [21] together with the calculated spectra, corresponding to the parameter  $V_\sigma = 0.1$  eV and the value  $Q_{5/2} = -0.4$  eV that was used in [21]. The positioning in energy of the different core states  $|JM\rangle$  is also shown.

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 constraints 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  $\mathbf{S} \cdot \mathbf{H}$  term in the Hamiltonian, being  $\mathbf{S}$  the spin momentum, and  $\mathbf{H}$  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  $Dy M_5$  edge for different values of the spin ( $S_z$ ) and orbital ( $L_z$ ) polarization, where  $\tilde{z}$  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



**Figure 3.** Evolution of the calculated resonant x-ray diffraction spectra in the vicinity of the Dy  $M_5$  edge at the  $(00\frac{1}{2})$  space group forbidden reflection when the magnetic moment is polarized in the  $ab$  plane forming  $23^\circ$  with respect to the  $a$  axis spectra are shown for different values of the polarization of the orbital angular momentum  $L_z$  and the spin angular momentum  $S_z$ . We normalize all the curves to have the same intensity at energies lower than 1282 eV.

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 Bragg diffraction energy profile at the Dy  $M_4$  and  $M_5$  edges in the antiferroquadrupolar phase of  $\text{DyB}_2\text{C}_2$  in terms of a dipolar transition ( $4f^9 \rightarrow 3d^9 4f^{10}$ ). 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 reflect a new interaction usually neglected in the interpretation of resonant soft x-ray data.

#### Acknowledgments

We thank R Caciuffo, 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** 807
- [2] Kuramoto Y, Kusunose H and Kiss A 2009 *J. Phys. Soc. Japan* **78** 072001
- [3] Lovesey S W, Fernández Rodríguez J, Blanco J A and Brown P J 2004 *Phys. Rev. B* **70** 172414
- [4] Fernández-Rodríguez J, Blanco J A, Brown P J, Katsumata K, Kikkawa A, Iga F and Michimura S 2005 *Phys. Rev. B* **72** 052407
- [5] McMorro D F, McEwen K A, Steigenberger U, Rønnow H M and Yakhov F 2001 *Phys. Rev. Lett.* **87** 057201
- [6] Walker H C, McEwen K A, McMorro D F, Wilkins S B, Wastin F, Colineau E and Fort D 2006 *Phys. Rev. Lett.* **97** 137203
- [7] Lovesey S W, Balcar E, Knight K S and Fernández-Rodríguez J 2005 *Phys. Rep.* **411** 233
- [8] Lovesey S W, Fernández-Rodríguez 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] Fernández-Rodríguez J, Lovesey S W and Blanco J A 2008 *Phys. Rev. B* **77** 094441
- [11] Lovesey S W, Fernández-Rodríguez 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 Tonnerre 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, Purton 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 Tonnerre 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, Dhessi 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, Yamauchi H and Yamaguchi Y 1999 *J. Phys. Soc. Japan* **68** 2287
- [38] Adachi H *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 Gschneidner Jr, L Eyring and M B Maple (Amsterdam: North-Holland) p 491