Triakontadipole and high-order dysprosium multipoles in the antiferromagnetic phase of DyB$_2$C$_2$

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Received 16 March 2011, in final form 13 May 2011
Published 15 June 2011
Online at stacks.iop.org/JPhysCM/23/266002

Abstract

Resonant soft x-ray Bragg diffraction at the Dy M$_{4,5}$ edges has been used to study Dy multipoles in the combined magnetic and orbitally ordered phase of DyB$_2$C$_2$. The analysis incorporates both the intra-atomic magnetic and quadrupolar interactions between the 3d core and 4f valence shells. Additionally, we introduce to the formalism the interference of magnetic and nonmagnetic oscillators. This allows a determination of the higher-order multipole moments of rank 1 (dipole) to 6 (hexacontatetrapole). The strength of the Dy 4f multipole moments have been estimated as being up to 80% of the quadrupolar moment.

1. Introduction

Resonant x-ray Bragg diffraction (RXD), which is Bragg diffraction where the energy of the incident x-rays is tuned to a relevant absorption edge, has established itself as a powerful tool in modern solid state physics to investigate magnetic, orbital and charge ordering phenomena associated with electronic degrees of freedom. The data obtained from an RXD experiment can be interpreted using a model based on purely atomic quantities, neglecting, e.g., band and hybridization effects. Models based on atomic quantities have the advantage of being suited to the analysis of both x-ray and neutron diffraction experiments, as well as absorption, NMR (nuclear magnetic resonance), EPR (electron paramagnetic resonance), muon and Mössbauer spectroscopies [1]. The localized nature of rare earth 4f electrons makes them particularly suited to such analysis which conveniently relies upon quantities such as atomic tensors and operator equivalents with the many simplifications that these bring. In particular, any atomic observable may be decomposed into its $(2l + 1)^2$ multipole operator components $T_{q}^{x}$ (with $x = 0, \ldots, 2l$ and $q = -x, \ldots, x$, where $l$ is the orbital angular momentum quantum number corresponding to the electronic shell in question), and any atomic state may be represented by the set of nonvanishing multipole components $\langle T_{q}^{x} \rangle$ [2]. $\langle \cdots \rangle$ denotes the expectation value of the enclosed operator on the ground state of the electrons. The multipoles $\langle T_{q}^{x} \rangle$ are parity even. Additionally, they have the definite time signature $(-1)^{x}$, and we refer to time-odd multipoles as magnetic and time-even multipoles as charge. In rare earth compounds, the 4f electrons are not strongly coupled to the lattice and they may retain their degrees of freedom down to very low temperatures, and although ordered states of magnetic dipoles are relatively common, multipoles of rank 2 (quadrupole) or higher may order under favorable conditions [3]. Orbital ordering is usually labeled as simply antiferroquadrupolar (AFQ) or ferroquadrupolar.
(FQ) since higher-order multipoles are not well established by observations, despite the fact that for 4f electrons ($l = 3$) multipoles up to rank 6 can be present. In materials with a phase attributed to such ‘hidden’ ordering, exactly which multipoles dominate the transition to the ordered phase remains a rather controversial topic, as exemplified by the compounds Ce$_2$La$_{1-x}$B$_6$ [4], NpO$_2$ [5] and particularly URu$_2$Si$_2$ [6]. RXD is particularly useful in characterizing such orderings, and applications of this technique have produced both direct and indirect evidence of high-order multipole moments in Dy$_2$C$_2$ [7, 8], Ce$_2$La$_{1-x}$B$_6$ [9], and NpO$_2$ [10].

Dy$_2$C$_2$ has the highest known AFQ ordering temperature of any rare earth system with $T_Q = 24.7$ K and as such it has attracted much attention, as many other compounds where AFQ or FQ ordering is postulated order at temperatures of 5 K or less [2]. At room temperature, Dy$_2$C$_2$ exhibits the tetragonal structure $P4/mmb$ and undergoes a transition with small alternating shifts of pairs of B and C atoms along $c$ at $T_Q$ [11] which reduces the symmetry to $P4_2/mnm$ [12]. Below $T_K = 15.3$ K, antiferromagnetic (AFM) order with four distinct magnetic sublattices is observed, and the moment orientations are postulated to arise from the underlying orbital interaction [13]. Additionally, the crystal evolves a monoclinic lattice strain at $T_K$ [14]. While the properties of the combined AFM/AFQ phase (phase IV) of the similar compound HoB$_2$C$_2$ are postulated to arise from an octupole order parameter [14], the case for Dy$_2$C$_2$ is not as clear cut due to the presence of the aforementioned lattice strain, and the broader variations in its elastic properties at the AFM and AFM + AFQ transitions.

Due to the less stringent experimental constraints, most RXD studies of rare earth materials using x-rays probe the $L_{2,3}$ edges via an E1 dipole transition (2p → 5d) or an E2 quadrupole transition (2p → 4f). In most cases the information obtained from such a measurement is relatively indirect in the case of an E1 resonance, and has relatively low intensity in the case of an E2 resonance. Soft resonant x-ray diffraction (SRXD) at the rare earth M$_{4,5}$ edges probes the empty 4f valence states directly by exciting a dipole resonance (3d → 4f). SRXD experiments at the Dy M$_{4,5}$ edges have shown that the Coulomb (intra-atomic quadrupole) interaction between the 3d and 4f shells is significant [15]. The ordered quadrupole moment of the 4f shell in the intermediate state reshapes the observed 3d$_{5,2}$ and 3d$_{3,2}$ core hole charge density and leads to a splitting of the 3d energy levels. This splitting causes interference between different pathways of the scattering amplitude, allowing the observation of high-order multipole moments of the 4f shell that have rank 3, 4, 5 and 6: respectively the octupole, hexadecapole, triakontadipole, and hexacontatetrapole. Quantification of these higher-order multipoles allows the ground state of dysprosium to be expressed in terms of the associated state multipoles, and accordingly a better understanding of its electronic structure can be obtained.

In the present work, we probe the combined AFM/AFQ phase of Dy$_2$C$_2$ using the same core hole splitting formalism previously applied to the AFQ phase [15], with the structure factor extended to include magnetism. Phenomenological changes are introduced to mimic differences between magnetic resonances and nonmagnetic ones. The presence of magnetic ordering allows the measurement of odd rank multipoles (1, 3, 5) associated with the magnetic order, and it is observed that their presence changes the even rank ⟨$T_q$⟩.

2. Experimental results

A Dy$_2$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. The orbital ordering (000$\overline{4}$) reflection was recorded (without polarization analysis [16]) at the Dy M$_{4,5}$ edges of Dy$_2$C$_2$ at the RESOXS end-station of the SIM beam line at the Swiss Light Source, at an azimuthal angle of $116^\circ$ (0° azimuth corresponds to the $b$ axis in the scattering plane). 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.

The recorded energy profiles of the space group forbidden (000$\overline{4}$) reflection of Dy$_2$C$_2$ in the pure AFQ phase [15] and the AFM + AFQ phase are shown in figures 1(a) and (b), respectively. The integrated intensity was corrected for absorption, and the corrected curves are shown in figures 1(c) and (d). We draw particular attention to the qualitative difference between the high and low temperature spectra, due to the onset of magnetic ordering. In the AFQ phase, the energy profile is largely independent of the polarization of the incident x-rays to within a scale factor, which is to be expected for a resonance that contains only a single order parameter (in this case, the quadrupole), and the $\sigma$ channel is the most intense. Conversely, in the AFM + AFQ phase the structure in the energy profile is different for incident $\sigma$ and $\pi$ polarizations with the $\pi$ spectra containing an additional intensity contribution around 1285 and 1300 eV that is not present in the $\sigma$ spectra. This is indicative of a combination of magnetic and orbital scattering which interfere constructively or destructively as a function of energy. Moreover, in the AFM + AFQ phase the intensity measured in the $\pi$ channel is generally larger than the intensity measured in the $\sigma$ channel at the M$_4$ edge, as expected from a magnetic contribution to the scattering. The intensities of the $\sigma$ and $\pi$ spectra are of the same order of magnitude, as a consequence of the strong orbital contribution to the scattering.

3. Theoretical framework

It was demonstrated in a previous study [15] that the unique shape of the energy dependence of the (000$\overline{4}$) reflection is well described by the splitting of the 3d core states. This splitting results in multiple interfering resonators and consequently adds structure to the energy profile in analogy to the unusual energy profile of the resonance at the M$_4$ edge in NpO$_2$ [10]. The addition of magnetism to the multipolar Coulomb interaction in the combined AFM + AFQ phase further lifts the degeneracy of the 3d shell with respect to the magnetic quantum number $M$. Here $\tilde{J}$ and $\tilde{M}$ refer respectively to the total angular momentum and its projection for the 3d hole state, and $-\tilde{M} \leq \tilde{M} \leq \tilde{J}$. The intra-atomic quadrupole interaction splits the
different $|\vec{M}|$ levels, and the intra-atomic magnetic interaction lifts the remaining degeneracy in $|\pm |\vec{M}|$. The relative oscillator amplitudes are determined by the $4f$ wavefunction, which is characterized in terms of multipoles.

Following the theory for resonance enhanced scattering of x-rays [1, 17–20] and its extension to the AFQ phase of DyB$_2$C$_2$ [15] we modify the equations for the scattered x-ray amplitude to include contributions from the time-odd multipoles allowed in the presence of the magnetic order that develops below $T_N$. These resonances due to odd rank multipoles will interfere with the even rank ones either constructively or destructively. The x-ray scattering amplitude, the square of which is proportional to the x-ray intensity $d\sigma/d\Omega$, is formed from the product of two tensors [1]

$$f = \sum_{Q} X^K F^K = \sum_{K, Q} (-1)^Q X^K_{Q} F^K_{Q}$$

with $-K \leq Q \leq K$. $F^K_{Q}$ describes the electronic response of the sample and $X^K_{Q}$ is constructed from the polarization vectors of the incident and scattered x-ray beams, and is discussed explicitly in appendix A. $F^K_{Q}$ is expressed as

$$F^K_{Q} = (2K + 1)^{1/2} \sum_{q} D^K_{q} (\alpha, \beta, \gamma) I^K_{q}$$

where the Wigner $D$ tensor $D^K_{q} (\alpha, \beta, \gamma)$ rotates $I^K_{q}$ (which refers to local coordinate axes), onto the coordinates of the experimental reference frame used for $X^K_{Q}$ and $F^K_{Q}$ with Euler angles $\alpha$, $\beta$, and $\gamma$. The Dy site symmetry in the magnetic phase of $2/m$ restricts $q$ to $q = \pm 1, \pm 2$. $K = 2$ corresponds to quadrupoles (orbitals), while $K = 1$ corresponds to magnetic dipoles, and the $K = 0$ contribution corresponds to charge order, which is absent at the given Bragg reflection. $I^K_{q}$ describes the atomic resonance process which is commonly represented by a harmonic oscillator. In our previous work the standard theory was extended so that $I^K_{q}$ is a sum of several oscillators created by the splitting of the core state; the amplitude $A^K_{q} (\vec{J}, \vec{M})$ of each oscillator is labeled by the total angular momentum $\vec{J} = \frac{1}{2}, \frac{5}{2}$ and the magnetic quantum number $\vec{M}$ of the core hole created by the resonance process:

$$I^K_{q} = \sum_{J, M} r_{J} A^K_{q} (\vec{J}, \vec{M})$$

$$\epsilon^K (\vec{J}, \vec{M}) = [3M^2 - \vec{J} (\vec{J} + 1)] Q_{J} + g \vec{J} \cdot \vec{M} - H_{\text{int}}$$

where $E$ is the photon energy, $\Delta_J$ is the difference in energy between the degenerate 3d$_J$ shell and the empty 4f states and $\hbar / \sqrt{\epsilon^K (\vec{J}, \vec{M})}$ is the lifetime of the intermediate state. $\epsilon^K (\vec{J}, \vec{M})$ is the energy shift of the core levels due to the intra-atomic quadrupole interaction $Q_{\vec{J}}$ and the intra-atomic magnetic interaction created by the unpaired 4f electrons $H_{\text{int}}$.

There are six resonant oscillators at the $M_5$ edge ($\vec{M} = \pm \frac{5}{2}, \pm \frac{3}{2}$, $\pm \frac{1}{2}$) and four at the $M_3$ edge ($\vec{M} = \pm \frac{3}{2}, \pm \frac{1}{2}$). The oscillator amplitudes interfere and the branching ratio between the two edges is defined as a purely real mixing parameter $r_{J}$. $A^K_{q} (\vec{J}, \vec{M})$ is constructed from the structure factor of the chemical unit cell $\Psi^K_{q}$:

$$A^K_{q} (\vec{J}, \vec{M}) = (-1)^{J-M} \sum_{J} \left( \begin{array}{ccc} J & r & \vec{J} \\ -M & 0 & \vec{M} \end{array} \right) \times \sum_{x} \left( \begin{array}{ccc} K & r & x \\ -q & 0 & q \end{array} \right) R^K (r, x) \Psi^K_{q}$$

where the symbol in brackets is a $3j$ symbol [21] and $R^K (r, x)$ are reduced matrix elements, with $r = 0, 1, \ldots, 2J$, $x = |K - r|, \ldots, |K + r|$, and $q + x$ and $r + x$ are both even integers. The relevant reduced matrix elements $R^K (r, x)$ are listed in appendix C.

Figure 1. (a), (b) Diffractions intensities of the (004) reflection in DyB$_2$C$_2$ taken with incident $\sigma$ (vertical) and $\pi$ (horizontal) polarizations at 18 K and 12 K, respectively. ((c), (d)) The diffractions intensities of (a) and (b) corrected for absorption effects. Note: all data are normalized to $\sigma$ of the sample and $X^K$ discussed explicitly in appendix A.
The theory detailed in section 3 is used to fit the measured energy dependences for σ and π incident polarizations via a genetic algorithm global optimization and a pattern search refinement of this solution using the mean square error as a cost function. All fitted values have a statistical error of approximately 10%. The best fit is shown as the solid black line in figure 2 with the oscillator positions indicated by arrows, alongside a fit with the just the dipole \( \Psi_1 \) time-odd contribution (broken blue line) and a fit with all time-odd contributions \( \Psi_1 \) as well as the intra-atomic magnetic interaction \( H_{\text{int}} \) set to zero (the broken red line) which is unable to account for the ratio of the intensity \( \pi/\sigma \). Absorption is applied to the calculated spectra in order to compare them to the as-measured spectra where the features on either side of the central M 5 absorption edge and the value of \( T_{5/2} \) is largely independent to 4.5 eV for \( T_{5/2} \). The dependence on the higher rank 4f multipoles arises from the splitting of the core hole states, which results in the \( M \) dependence of the amplitudes of the different harmonic oscillators. Correspondingly, these amplitudes are influenced by contributions from higher rank 4f multipoles which would otherwise cancel due to symmetry imposed by the \( 3j \) symbols in (5). Therefore, the core hole splitting allows the measurement of higher rank multipoles through its spectral shape than would normally be expected for an E1 resonance.

### 4. Discussion

The theory detailed in section 3 is used to fit the measured energy dependences for \( \sigma \) and \( \pi \) incident polarizations via

### Table 1. Fitted parameters in the AFQ and AFM + AFQ phases of DyBi\(_2\)C\(_2\).

| Parameter | \( T = 18 \) K (AFQ) | \( T = 12 \) K (AFM + AFQ) |
|-----------|----------------------|----------------------|
| \( \Delta_{3/2} \) (eV) | 1287.7 | 1287.6 |
| \( \Delta_{5/2} \) (eV) | 1324.0 | 1323.9 |
| \( \Psi_1 \) | 1\( ^2 \) | 1\( ^2 \) |
| \( \Psi_1 \) | 1\( ^2 \) | 5.2 |
| \( \Psi_1 \) | 0.22 | 0.26 |
| \( \Psi_1 \) | 0.07 | 0.07 |
| \( \Psi_1 \) | 0.77 | 0.77 |
| \( \Psi_1 \) | 0.78 | 0.78 |
| \( \Psi_1 \) | 5.3 | 5.3 |
| \( \Psi_1 \) | 3.2 | 3.2 |
| \( \Psi_1 \) | 1.9 | 2.2 |
| \( \Psi_1 \) | 4.5 | 4.5 |
| \( \Psi_1 \) | 2 | 2 |
| \( \Psi_1 \) | 7.9 | 7.9 |
| \( \Psi_1 \) | 9.1 | 9.1 |
| \( \Psi_1 \) | 6.2 | 6.2 |
| \( \Psi_1 \) | 12.8 | 12.8 |

\( ^{a} \) This value is fixed to 1.
contributions $\Gamma_j^{1-4}$. $\Psi_j^1$ is normalized to 1 and the best fit for
the values of $\Psi_j^q$ gives $\Psi_j^1 = 0.22$, $\Psi_j^2 = 0.07$, $\Psi_j^3 = -0.34$,
$\Psi_j^4 = 0.77$, and $\Psi_j^5 = -0.78$. The dominant time-odd contributions
are the octupole and triakontadipole moments which is in accord with observations that the elastic properties
of DyB$_2$C$_2$ are similar to the related compound HoB$_2$C$_2$ for
which a strong influence from octupolar order is inferred [14].
We note in particular this is the first direct measurement of a
triakontadipole moment.

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 an absorption process. Resonant diffraction is sensitive to
the difference between electronic states and the conditions
for nonvanishing intensity depend only on local symmetries (of
the resonant atom) while absorption spectroscopy is sensitive
to the average difference between electron states, and the
conditions for nonvanishing terms must reflect the global
symmetry (Neumann’s principle) [24, 25]. 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 [26].
In the present theoretical framework the energy dependences
of the 4f$^{1-7}$ states are assumed to be independent of their
quantum numbers [1] and the effect of the 4f multiplet structure
is taken into account in an approximate way through the
effective widths $\Gamma_j^{1-4}$ which exceed the intrinsic lifetimes
of the excited states (normally expected to be of the order of
0.3 eV [23]) and describe the data surprisingly well. In this
way, much physical intuition regarding the associated
atomic quantities of interest (i.e. the atomic tensors $\langle T_j^q \rangle$)
is retained. This compares to recent numerical calculations [27]
which included a crystal field splitting of the 4f states and
the full multiplet structure, where a similar magnitude of $Q_j$
was found (although of different sign) but no information on
the $\langle T_j^q \rangle$ could be extracted from such a calculation.
This work further demonstrates that inclusion of the intra-atomic
Coulomb and magnetic interactions is a viable approach to
account for the multiple spectral features and their broad
distribution in energy.

5. Conclusion

DyB$_2$C$_2$ exhibits an ordered phase with both AFM and AFQ
order below $T_N = 15.3$ K. Soft resonant x-ray Bragg
diffraction experiments were performed at the Dy M$_4$,M$_5$ edges
and the energy dependence of the space group forbidden
$(00\frac{1}{2})$ reflection was measured in this low temperature
AFM + AFQ phase. The Dy 4f multipole moments of
rank 1 (dipole) to 6 (hexacontatetrapole) were measured and
their magnitudes were determined to be up to 80% of the
quadrupole (rank 2) moment. The (rank 3) octupole and the
(rank 5) triakontadipole moments are the dominant time-odd
contributions. The energy dependence of the $(00\frac{1}{2})$ reflection
was modeled successfully by including an intra-atomic core
hole interaction parameterized by quadrupole and magnetic
interactions. A pseudo-multiplet structure was also introduced,
allowing for the interference between oscillators that have
different properties under time reversal due to having different
excited state lifetimes.

Acknowledgments

This work was supported by the Swiss National Science
Foundation, and NCCR MaNEP. This work was partly
performed at the Swiss Light Source of the Paul Scherrer
Institute, Villigen, Switzerland.

Appendix A. Explicit relations for $X^K_Q$

The quantity $X^K_Q$ appearing in equation (1) is a spherical tensor
constructed from components of the incident and reflected
polarization vectors. It is described by equation (66) in [1],
and the values appropriate to the current study are

$$\sigma'\sigma: \quad X_0^2 = \left( \frac{1}{2} \right)^{1/2}$$
$$\pi'\pi: \quad X_0^3 = \frac{i}{\sqrt{2}} \sin(2\theta), \quad X_0^2 = \frac{1}{\sqrt{2}} \cos(2\theta), \quad X_0^1 = \frac{1}{2}$$
$$\sigma'\pi: \quad X_0^1 = \frac{1}{2} e^{i\theta}, \quad X_1^1 = -\frac{i}{2} e^{-i\theta}$$
$$\pi'\sigma: \quad X_0^1 = \frac{1}{2} e^{i\theta}, \quad X_1^1 = -\frac{i}{2} e^{-i\theta}$$

Due to the inability to measure the polarization of the outgoing
beam without severely attenuating the measured signal, the
spectra in figures 1 and 2 are combinations of the rotated
and unrotated channels. Specifically, $I_\sigma = I_{\sigma\sigma} + I_{\pi\sigma}$ and
$I_\pi = I_{\pi\pi} + I_{\sigma\pi}$.

Appendix B. Dy site symmetry and magnetic structure

The structure factor appropriate to the Dy site symmetry and
magnetic ordering

$$\Psi_q^\sigma = (1 – e^{i\pi}) (\langle T_q^\sigma \rangle – e^{i\frac{\pi}{2}} T_q^{–\sigma}) \quad (B.1)$$
does not account for the slight rotations of the magnetic moments
proposed in, for example, [28]. In the above case, we arrive at the following:

$$\Psi_q^\sigma = 4i (T_q^\sigma)^\prime$$ \quad (B.2)
$$\Psi_q^\sigma = -2i ((T_q^\sigma)^\prime’ - (T_q^\sigma)^\prime) \quad (B.3)$$

where $(\cdot \cdot \cdot)^\prime’$ and $(\cdot \cdot \cdot)^\prime$ represent the real and imaginary parts,
respectively. If we include the proposed rotations of $\pm 9^\circ$ away
from the site symmetry, we arrive at the following structure
factor:

$$\Psi_q^\sigma = (1 – e^{-i\pi}) (\langle T_q^\sigma \rangle – e^{i\frac{\pi}{2}} e^{-i\theta} T_q^{–\sigma}) \quad (B.4)$$

which gives

$$\Psi_q^\sigma = -i(0.62(T_q^\sigma)^\prime)’ - 3.90(T_q^\sigma)^\prime$$ \quad (B.5)
$$\Psi_q^\sigma = -i(1.98(T_q^\sigma)^\prime)’ - 1.69(T_q^\sigma)^\prime$$ \quad (B.6)
Table C.1. Reduced matrix elements $R^x(r, x)$ for $^6H_{15/2}$ and $n_b = 5$.

| $K = 1, \bar{J} = \frac{1}{2}$ | $r$ | 0 | 1 | 2 | 3 |
|---------------------------------|-----|----|----|----|----|
| $x = 0$                         | 0   | 0  | 0  | 0  | 0  |
| 1                               | $\frac{1}{35} \sqrt{11} \frac{9}{10}$ | 0  | $\frac{7}{35} \sqrt{11} \frac{9}{10}$ | 0  | 0  |
| 2                               | 0   | $\frac{1}{35} \sqrt{11} \frac{9}{10}$ | 0  | $\frac{7}{35} \sqrt{11} \frac{9}{10}$ | 0  | 0  |
| 3                               | 0   | 0  | 0  | $\frac{2}{35} \sqrt{11} \frac{9}{10}$ | 0  | 0  |
| 4                               | 0   | 0  | 0  | 0  | $\frac{2}{35} \sqrt{11} \frac{9}{10}$ | 0  |

Table C.2. Reduced matrix elements $R^x(r, x)$ for $^6H_{15/2}$ and $n_b = 5$.

| $K = 1, \bar{J} = \frac{1}{2}$ | $r$ | 0 | 1 | 2 | 3 | 4 | 5 |
|---------------------------------|-----|----|----|----|----|----|----|
| $x = 0$                         | 0   | 0  | 0  | 0  | 0  | 0  | 0  |
| 1                               | $\frac{1}{35} \sqrt{11} \frac{9}{10}$ | 0  | $\frac{7}{35} \sqrt{11} \frac{9}{10}$ | 0  | 0  | 0  | 0  |
| 2                               | 0   | $\frac{1}{35} \sqrt{11} \frac{9}{10}$ | 0  | $\frac{7}{35} \sqrt{11} \frac{9}{10}$ | 0  | 0  | 0  | 0  |
| 3                               | 0   | 0  | 0  | $\frac{2}{35} \sqrt{11} \frac{9}{10}$ | 0  | 0  | 0  | 0  |
| 4                               | 0   | 0  | 0  | 0  | $\frac{2}{35} \sqrt{11} \frac{9}{10}$ | 0  | 0  | 0  |
| 5                               | 0   | 0  | 0  | 0  | 0  | $\frac{2}{35} \sqrt{11} \frac{9}{10}$ | 0  | 0  |

Appendix C. Reduced matrix elements $R^K(r, x)$

$R^K(r, x)$ is calculated for the Dy$^{3+}$ ground state of $^6H_{15/2}$ using

$R^K(r, x) = (2\bar{J} + 1)(-1)^K(\sqrt{2x + 1} \times \sum_{a,b} \langle \frac{x}{a, b} | W^{(a, b)}(r, x) | \frac{x}{a, b} \rangle)

C.1
where the relation between $W^{(a,b)}$ and $W^{(a,b)x}$ is given by
\[
(\theta J|W^{(a,b)x})|\theta' J'\rangle = \left(\frac{(2J+1)(2K+1)(2J'+1)}{(2a+1)(2b+1)}\right)^{1/2} \times \sum_{S\ S'\ a\ L\ L'} \frac{(\theta|W^{(a,b)}|\theta')}{|\theta'|}.
\]  
\[W^{(a,b)}\] is a unit double tensor defined in accord with Judd [21], where $a$ is the rank of the spin component and $b$ is the rank of the orbital component. Its calculation is facilitated by the following equation:
\[\langle l^p a LS|W^{(a,b)}|l'^p a' L'S'\rangle = n[L, L', b, S, S', a] \times \sum_{a L S} (-1)^{L+L'+b+S+a+s+t} \frac{1}{L \ L' \ L}
\times \sum_{s S' a} \frac{1}{S \ S' \ S} \frac{(l^p a LS|[l'^p - a LS])}{(l^p a LS|[l'^p - a LS])}
\]  
where $(l^p a LS|[l'^p - a LS])$ is a coefficient of fractional parentage and values for it are tabulated for almost all electron configurations of interest in Nielson and Koster [29], along with values of $\langle \theta|V(K)|\theta'\rangle = \left(\frac{1}{2}(2S+1)\right)^{-1/2}\langle \theta|W^{(a,b)}|\theta'\rangle$. $s$ and $l$ are the spin and orbital angular momenta of the equivalent electrons coupled together in this process, and in the case of 4f electrons have the values 3 and $\frac{1}{2}$, respectively. The results for the calculation of the reduced matrix elements $R^*(r, x)$ for the Dy$^{3+}$ ion (which has $n_s = 5$ 4f holes) in the ground state $^6H_{15/2}$ are tabulated in tables C.2 and C.1.

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