Characterization of the crystal field interaction in rare earth intermetallics using Mössbauer spectroscopy

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Abstract. Mössbauer spectroscopy is a valuable tool for the characterization of the crystal field interaction at rare earth sites in a wide range of compounds. This overview focuses on the complementary role of the $^{116}$Tm- and $^{55}$Gd-Mössbauer resonances when investigating compounds with low magnetic ordering temperatures and highlights special issues that need to be kept in mind when working with intermetallics.

1. Introduction
The electrostatic charge distribution external to the 4f shell of a rare earth ion is responsible for the so-called crystal field (CF) interaction which removes the degeneracy of the 4f multiplet levels (as shown schematically in figure 1 for the Tm$^{3+}$ ion). Given that the 4f shell is well shielded by the outer closed 5s$^2$ 5p$^6$ shells, the CF interaction is small in comparison with the spin-orbit interaction and can be treated as a perturbation. For temperatures that are low ($\leq$ 2000 K) it is usual to express the CF Hamiltonian in terms of a multipole expansion of Stevens operator equivalents,$^1$$^2$$^3$$^4$$^5$$^6$$^7$$^8$$^9$$^{10}$

$$\mathcal{H}_{CF} = \sum_{m=-2}^{+2} B_{2}^{m} O_{2}^{m}(J) + \sum_{m=-4}^{+4} B_{4}^{m} O_{4}^{m}(J) + \sum_{m=-6}^{+6} B_{6}^{m} O_{6}^{m}(J)$$

acting on the ion’s (2J+1)-degenerate ground state multiplet. The characterization of the CF interaction is then reduced to a process of determining the relevant set of CF parameters, $B_{n}^{m} = \theta_{n}(1 - \sigma_{n})\langle r^{m}\rangle_{4f} A_{n}^{m}$. In this expression, the $A_{n}^{m}$ represent a bare estimate of the electrostatic interaction, the $\theta_{n}$ are reduced matrix elements, the $\sigma_{n}$ represent the shielding effect of the outer closed shells, and the $\langle r^{m}\rangle_{4f}$ are radial expectation values for the 4f shell [1-3].

Inelastic neutron scattering (INS) is the most direct experimental approach to the determination of the CF parameters. This is because the positions of the spectrum’s absorption lines are related to the CF-split energy levels and the intensities are related to their eigenfunctions [1]. However, characterization can also be achieved via the analysis of temperature-dependent data recorded for physical properties that depend on the thermal population of the CF levels. These include the bulk properties of specific heat and magnetic susceptibility as well as the quadrupole interaction at the rare earth nucleus, which can be monitored using Mössbauer spectroscopy. In practice, it has been found that it is advantageous to test proposed sets of CF parameters against data from two or more experimental techniques. This is particularly important for rare earth sites with low point symmetries. As the degree of symmetry decreases, the number of CF parameters needing to be determined increases from 2 (cubic symmetry) to 27 (triclinic). It is often the case that more than one non-
equivalent set of CF parameters will adequately describe the same set of experimental data. This brief overview considers the application of rare earth Mössbauer spectroscopy to the characterization of the CF interaction via monitoring the nuclear quadrupole interaction as a function of temperature. Mössbauer resonances commonly employed for this purpose include $^{169}$Tm (8.4 keV), $^{161}$Dy (25.7 keV), $^{166}$Er (80.6 keV) and $^{170}$Yb (84.3 keV). The first two have the advantage that their gamma energies are small and the recoil-free fraction is large over a wide temperature range. $^{169}$Tm has the additional advantage that Tm$^3+$ is a non-Kramers ion and is therefore less susceptible to paramagnetic relaxation effects that are often associated with Kramers ground state doublets. There will be a focus on the complementary roles of the $^{169}$Tm- and $^{155}$Gd-Mössbauer resonances. Most of the considerations apply equally well to the other resonances listed above.

2. The nuclear quadrupole interaction approach to CF characterization.

The electric field gradient (EFG) tensor acting at the rare earth nucleus can be expressed in its most general (lowest symmetry) form as

$$
\begin{pmatrix}
V_{xx} & V_{xy} & V_{xz} \\
V_{yx} & V_{yy} & V_{yz} \\
V_{zx} & V_{zy} & V_{zz}
\end{pmatrix}
= k_1 \begin{pmatrix}
3O_2^+ & \frac{1}{2}O_2^- & \frac{3}{2}O_2^+ \\
\frac{3}{2}O_2^- & O_2^- & 3O_2^- \\
\frac{3}{2}O_2^+ & 3O_2^- & O_2^+
\end{pmatrix}_{4f} + k_2 \begin{pmatrix}
B_2^{\text{latt}} \\
B_4^{\text{latt}}
\end{pmatrix}_{\text{latt}}
$$

(2)

where the temperature-dependent 4f contributions are due to the CF-induced distortion of the 4f shell and are proportional to the thermally averaged expectation values of the rank $n = 2$ Stevens operators. The temperature-independent, lattice contributions are due to the direct lattice EFG and are proportional to the rank 2 CF parameters. Note that some liberty has been taken with the highlighted elements of the tensors, in order to show that $(O_2^2)_{4f}$ and $B_2^{\text{latt}}$ contribute to the difference $V_{xx} - V_{yy}$. The factors $k_1$ and $k_2$ involve the Sternheimer shielding and antishielding parameters ($R_Q$ and $\gamma_\infty$, respectively), as well as the 4f-shell radial expectation values, $(r^{-3})_{4f}$ and $(r^2)_{4f}$. It is useful to combine these with the quadrupole moment, $Q$, to form the experimental “shielding parameters”

$$
\rho_{4f} = Q(1 - R_Q)(r^{-3})_{4f} \quad \text{and} \quad \rho_{\text{latt}} = Q(1 - \gamma_\infty)/(1 - \sigma_2)(r^2)_{4f}
$$

(3)

that are convenient for the purpose of analyzing temperature-dependent, quadrupole interaction data.

2.1. TmES and Tm$_2$O$_3$

The relationship between the CF interaction and the nuclear quadrupole interaction was first demonstrated in the seminal paper of Barnes et al. [2] that considered two non-metallic compounds.

Figure 1. Schematic diagram showing the relationship between alternative experimental CF characterization techniques for the special case of a pure CF interaction.
Figure 2. Quadrupole splitting, $\Delta E_Q$, versus temperature for $^{169}\text{Tm}$ ($I=3/2$ level) in Tm$_2$O$_3$. The solid squares [3] and diamonds [4] (red and green, respectively, on line) are data for the resolved monoclinic site doublet and the solid circles at higher temperatures are the original unresolved data of Barnes et al. [2]. The solid curve represents the shielding parameter fit using the CF parameter set due to Leavitt et al. [5].

The authors used $^{169}\text{Tm}$-M"ossbauer spectroscopy to record the quadrupole splitting, $\Delta E_Q$, over an extensive temperature range for the excited $I = 3/2$ state of $^{169}\text{Tm}$ in both thulium ethylsulphate (TmES) and Tm$_2$O$_3$. In each case, CF parameters had already been determined using optical spectroscopy. The impressive outcome was that they needed only to adjust the shielding parameters to match theoretical curves to the respective sets of experimental data. However, the resultant values of $\rho_{4f}$ were -15.1 b a 0$^{-3}$ for single hexagonal symmetry site of TmES and -17.1 b a 0$^{-3}$ for the dominant unresolved monoclinic symmetry site of Tm$_2$O$_3$. This discrepancy arose out of an assumption that the EFG tensor was diagonal [6] for both cases. For monoclinic symmetry the CF Hamiltonian involves $15$ CF parameters.

$$
\mathcal{H}_{\text{CF}} = B_{2}^{0}O_{2}^{2} + B_{2}^{2}O_{2}^{0} + B_{2}^{-2}O_{2}^{-2} + B_{4}^{0}O_{4}^{0} + B_{4}^{2}O_{4}^{2} + B_{4}^{-2}O_{4}^{-2} + B_{4}^{4}O_{4}^{4} + B_{4}^{-4}O_{4}^{-4} + B_{6}^{0}O_{6}^{0} + B_{6}^{2}O_{6}^{2} + B_{6}^{-2}O_{6}^{-2} + B_{6}^{4}O_{6}^{4} + B_{6}^{-4}O_{6}^{-4} + B_{6}^{6}O_{6}^{6} + B_{6}^{-6}O_{6}^{-6}
$$

(4)

In order to simplify the optical spectroscopy analysis process, it is commonly assumed that an appropriate rotation about the CF $z$-axis has been used to set $B_{2}^{-2}=0$. Although this reduces the lattice contribution of equation 2 to diagonal form, this is not so for the 4f contribution where the $(O_{2}^{-2})_{4f}$ term remains non-zero. A subsequent reanalysis [3] using revised CF parameters [5], resolved site data (figure 2) and a full EFG tensor diagonalization yielded a shielding parameter of $\rho_{4f} = -15.3$ b a$^{-3}$ for the monoclinic site of Tm$_2$O$_3$. Based on close agreement with the earlier value for TmES, it was recommended that $\rho_{4f} = -15.2$ b a$^{-3}$ and the theoretical value of $Q(I = 3/2) = -1.5$ b [7] be adopted for the $^{169}\text{Tm}$-M"ossbauer resonance [3].

2.2. The special case of the $^{155}\text{Gd}$-M"ossbauer resonance

For S-state ($L = 0$) ions, such as Gd$^{3+}$, the local CF has relatively little influence on the spherical charge distribution associated with the ground state multiplet. This means that there will be no 4f shell contribution to the EFG tensor at the $^{155}\text{Gd}$ nucleus (equation 2). Hence the $^{155}\text{Gd}$-M"ossbauer determination of the EFG tensor components can be exploited to estimate the rank 2 CF parameters, $B_{2}^{m}$, for another trivalent rare earth ion in a compound of the same isostructural series.
3. TmCu$_2$Si$_2$ as an instructive intermetallic case study

The system of ternary rare earth intermetallics RT$_2$X$_2$ (R = rare earth, T = transition metal, X = Si or Ge) continues to be studied because of the extensive array of compounds that form with the same body-centred tetragonal structure and their diverse range of physical properties. There is a single R site whose tetragonal D$_{4h}$ (4/mmm) symmetry requires the following CF Hamiltonian with just 5 CF parameters to be determined.

$$
\mathcal{H}_{CF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4
$$  (5)

TmCu$_2$Si$_2$ orders at 2.8 K so that the temperature-dependent quadrupole splitting shown in figure 3 was able to be recorded over a wide temperature range using the $^{169}$Tm-Mössbauer resonance [8]. At the time, it was observed that the low temperature maximum could be described using a small positive $B_2^0$ and relatively large negative values for $B_4^0$ and $B_4^4$. The data were then interpreted in terms of the CF parameters given in the first row of table 1. For this initial analysis, the lattice shielding parameter was set at $\rho_{latt} = -555$ b a$_0^{-2}$, based on the early work of Barnes et al. [2].

The CF parameters presented in row 2 of table 1 were fitted to the same data set using starting CF parameters converted from those determined for ErCu$_2$Si$_2$ by Gromychkin et al. [10] via INS. The conversion was made by adjustment of the R-specific components of the CF parameters according to

$$
B_n^m(Tm^{3+}) = \frac{\theta_n(1-\sigma_n)(r^n)s_f}{\theta_n(1-\sigma_n)(r^n)s_f} B_n^m(Er^{3+})
$$  (6)

Note that the new fitted $B_2^0$ is opposite in sign and larger in magnitude, while the rank 4 terms are significantly reduced in magnitude. This is a very different set of CF parameters but it provides an equally good description of the experimental $^{169}$Tm-Mössbauer data. The final two sets of CF parameters in table 3 were taken, respectively, from a combined INS/single-crystal magnetism investigation of TmCu$_2$Si$_2$ due to Kosaka et al. [11] and from a recent re-appraisal by Chatterji et al. [12] of all available TmCu$_2$Si$_2$ experimental data. They were then employed without modification to provide theory curves that are indistinguishable from the others in figure 3. The last three theory curves discussed were all calculated with the lattice $V_{zz}$ contribution fixed at the $^{155}$Gd-Mössbauer

| Table 1. Sets of CF parameters employed for the description of the TmCu$_2$Si$_2$ temperature-dependent $^{169}$Tm quadrupole splitting data. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $B_2^0$         | $B_4^0$         | $B_4^4$         | $B_6^0$         | $B_6^4$         |
| [K]             | [K]             | [mK]            | [mK]            | [mK]            |
| Stewart & Jukrowski (1982) | +.40            | -39.7           | -19.8           | -0.104          | +1.78           |
| Harker et al. (2002) based on Gromychkin et al. (1996) | -.98            | -4.81           | -11.4           | -0.020          | +1.14           |
| Kosaka et al. (1997) | -.118           | +.285           | -.553           | -.078           | +1.05           |
| Chatterji et al. (2003) | -1.15           | -.29            | -.565           | -.073           | +1.05           |

**Figure 3.** Theory curves for the TmCu$_2$Si$_2$ quadrupole splitting data (based on the CFparameters presented in table 1)
The clear message from this sequence of measurements and analyses for TmCu$_2$Si$_2$ is that a satisfactory fit of CF parameters to good quality quadrupole splitting data need not represent the only solution. To arrive at an unambiguous solution, it will almost certainly be necessary to test the outcome against other experimental techniques. It is also evident from the breakthrough brought about by the ErCu$_2$Si$_2$ INS work that CF parameters determined for one rare earth intermetallic can be converted to provide useful starting parameters for the CF analysis of a second isostructural compound.

4. ErNiAl$_4$ and a semi-empirical approach for dealing with low symmetry

The orthorhombic RNiAl$_4$ series is another intermetallic series that orders magnetically at low temperatures. It is of interest because of the intermediate magnetic phases that are observed both as a function of temperature and as a function of external magnetic field. For the orthorhombic C$_{2v}$ (mm) point symmetry of the single R site, the CF Hamiltonian requires 9 CF parameters to be determined. The CF Hamiltonian is given by

$$\mathcal{H}_{CF} = B^0_2O^0_2 + B^2_2O^2_2 + B^4_4O^4_4 + B^6_6O^6_4 + B^8_4O^8_4 + B^6_6O^6_6 + B^8_6O^8_6 + B^8_8O^8_8 + B^{10}_8O^{10}_8$$

In an effort to reduce the number of parameters that needed to be fitted, a semi-empirical approach was recently employed for a preliminary CF analysis of an INS spectrum that had been recorded for ErNiAl$_4$ using an incident neutron energy of 20.5 meV [15, 16]. The 8.6 K INS spectrum is shown in figure 4. Until further INS spectra are recorded using higher neutron energy, only 3 of the 7 excited CF levels are known with confidence.

The approach taken was to use the simple point charge model for the near-neighbour ions (figure 5) to estimate the within-rank ratios $r^m_n = B^m_n / B^n_n$ for the rank $n = 4$ and 6 CF parameters. For this purpose the CF axes $(x,y,z)_{CF}$ were chosen to align with the crystallographic axes $a$, $b$ and $c$, respectively. Next, the rank 2 CF parameters $B^4_4$ and $B^6_6$ were estimated using the EFG tensor values determined earlier from a $^{155}$Gd-Mössbauer spectroscopy investigation of isostructural GdNiAl$_4$ [17]. For orthorhombic point symmetry, the principal EFG axes are also aligned with the crystallographic axes but the particular orientation of the axes is unknown. This leads to 6 possible sets of $B^4_4$ and $B^6_6$ as shown in table 2 [16]. Finally, a grid search was performed over the values of the CF parameters $B^4_4$ and $B^6_6$ for each of the six possible $B^4_4 - B^6_6$ combinations. INS spectra were then simulated for the CF parameter sets that matched the known excited CF energies. The only close fit to the spectrum without further refinement (solid curve in figure 4) was obtained for the $(x,y,z)_{EFG} // (x,-z,y)_{CF}$ combination of $B^4_4$ and $B^6_6$ values with $B^4_4 = -6.83$ mK and $B^6_6 = -27.28$ $\mu$K.

**Figure 4.** CF theory fit (solid line) to the INS neutron energy loss spectrum for ErNiAl$_4$ (taken from reference [15]).

**Figure 5.** Local near-neighbour environment for the Er$^{3+}$ site in orthorhombic ErNiAl$_4$ (from [15]).
Table 2. The possible combinations of $B_{0}^{0}$ and $B_{2}^{0}$ for Er$^{3+}$ in ErNiAl$_{4}$ that are derived from the $^{155}$Gd-Mössbauer investigation of isostructural GdNiAl$_{4}$ (taken from reference [16]).

| $(x,y,z)_{EFG}$ // $(y,z,x)_{CF}$ | $(x,z,y)_{CF}$ | $(z,x,y)_{CF}$ | $(z,y,x)_{CF}$ | $(-y,x,z)_{CF}$ | $(x,y,z)_{CF}$ |
|-------------------------------|----------------|----------------|----------------|----------------|----------------|
| $B_{0}^{0}[K]$                | +0.432         | +0.432         | +0.199         | +0.199         | -0.631         | -0.631         |
| $B_{2}^{0}[K]$                | -0.829         | +0.829         | +1.065         | -1.065         | +0.233         | -0.233         |

This semi-empirical approach can also be applied to the CF analysis of $^{169}$Tm quadrupole splitting data where the $^{155}$Gd- and $^{169}$Tm-Mössbauer resonances then play complementary roles. However, for intermetallics the point-charge model calculations of the within-rank CF parameter ratios are, at best, an approximate indication of the true situation. These types of calculations are much more reliable for ceramic compounds where the ligands are generally of a single type with the same charge and, in the context of the superposition model, the within-rank ratios are determined largely by the angular arrangement of the ligands.

5. Concluding remarks
In conclusion, the conversion of CF parameters between isostructural rare earth intermetallics is a useful tool and the $^{155}$Gd- and $^{169}$Tm-Mössbauer resonances complement one another as a means of characterising the CF interaction. However, it is always wise to test the outcome against data obtained using other experimental techniques. Finally, the semi-empirical approach using theoretical calculations of within-rank CF parameters to reduce the number of free parameters is a useful first approximation, although it is likely to be more reliable for non-metallic compounds than for the rare earth intermetallics.

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