^{166}Er Mössbauer study of Er$_2$Ge$_2$O$_7$

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Abstract

We have used ^{166}Er Mössbauer spectroscopy to investigate the recent proposal of a 5-fold local symmetry at the Er^{3+} site in Er$_2$Ge$_2$O$_7$. The measured ^{166}Er hyperfine field at 4.5 K is 663.7(5) T and the electric quadrupole coupling parameter (eQV_{zz}) is 6.4(1) mm/s. The proposed 5-fold local symmetry model predicts values of 436 T and 16.1 mm/s, respectively, based on magnetic susceptibility and optical absorption data, and is inconsistent with the observed ^{166}Er Mössbauer spectrum.
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1. Introduction

The tetragonal R$_2$Ge$_2$O$_7$ rare-earth (R) pyro-germanates have the space group P4$_1$2$_1$2 (#92) with 4 formula units per tetragonal cell. The R atoms occupy the 8b site which has triclinic point symmetry [1,2]. There have been many studies of the optical activity and magnetic susceptibility of the R$_2$Ge$_2$O$_7$ compounds and these data have been interpreted in terms of a 5-fold point symmetry (Tb [3], Dy [4,5], Ho [6], Er [7,8] and Tm [9,10]). The pentagonal-symmetry approach has had some success in interpreting the optical spectra and is obviously interesting from the viewpoint of greatly simplifying the crystal-field hamiltonian of the R site: pentagonal point symmetry reduces the R crystal-field hamiltonian from 27 terms to only 4.

As discussed in our previous paper on Tm$_2$Ge$_2$O$_7$ [11], the R site in R$_2$Ge$_2$O$_7$ is coordinated by 7 oxygens which form a distorted pentagonal bipyramid and when the oxygens are viewed along the *c*-axis their arrangement appears to exhibit the 5-fold rotational symmetry underlying the pentagonal crystal-field hamiltonian. However, when viewed from an orthogonal direction it is clear that the pentagonal bipyramid is far from ideal. Thus, the R-site point-group is triclinic and not pentagonal, although the pentagonal symmetry may be a very useful, simplifying approximation.

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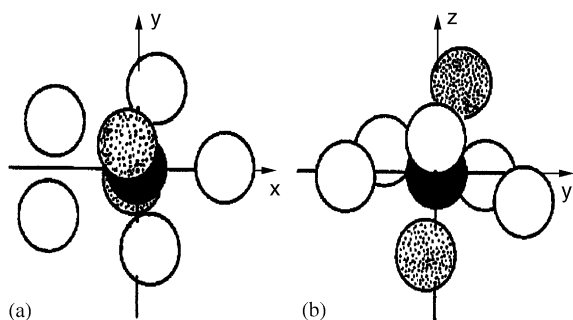*E-mail address:* j.cadogan@unsw.edu.au (J.M. Cadogan).

Fig. 1. Coordination polyhedron of oxygen atoms about the R site in $R_2Ge_2O_7$: (a) viewed along the c-axis; (b) side view. The R atom is solid black and two of the oxygen atoms are shaded to distinguish them from the 5 oxygen atoms comprising the basal plane of the distorted pentagonal bipyramid.

In Fig. 1 we show the arrangement of the 7 oxygen neighbours around the R atom in $R_2Ge_2O_7$ [11].

A common feature of the optical and magnetic susceptibility studies of the $R_2Ge_2O_7$ compounds is the fact that the 'pentagonal' crystal-field parameters were used to predict the hyperfine nuclear energy level schemes of the relevant R isotope, expected from the pentagonal point symmetry.

Our previous study of $Tm_2Ge_2O_7$ by ^{169}Tm Mössbauer spectroscopy [11] was in response to the work of Sengupta et al. [9] who had predicted the ^{169}Tm spectra. We demonstrated that the pentagonal symmetry crystal-field parameters, as published, could not reproduce the experimentally observed ^{169}Tm spectra and the temperature dependence of the electric quadrupole splitting. The main problem with the pentagonal model was that it predicted a doublet electronic ground state for the Tm^{3+} ion whereas our ^{169}Tm Mössbauer data clearly showed that the electronic ground state is in fact a singlet. In a subsequent paper, Das et al. [10] presented a reanalysis of their original $Tm_2Ge_2O_7$ data, in response to our work, and after correcting various errors in their pentagonal crystal-field model were able to obtain a singlet ground state and agreement with our experimental electric quadrupole splitting data.

In this paper, we turn our attention to the isostructural $Er_2Ge_2O_7$ compound. As before, we have used rare-earth isotope Mössbauer spectroscopy to check the nuclear energy level scheme predicted by Chattopadhyay et al. [8]. We find that the predictions of the pentagonal model, using the published crystal-field parameters determined from optical absorption and magnetic susceptibility work, do not match the experimental observations and we trust that our experimental data will provide useful quantitative information for the refinement of the pentagonal crystal-field approximation, as in the case of $Tm_2Ge_2O_7$.

2. Experimental methods

The $Er_2Ge_2O_7$ sample was prepared using the same process as in our study of $Tm_2Ge_2O_7$. Briefly, a stoichiometric mix of Er_2O_3 and GeO_2 was pressed into a pellet and calcined for 2 days at $1100°C$. The calcined sample was reground, pelletized and re-calcined at $1150°C$ for 2 days. The latter stage was repeated to make a total of three heat treatments. Powder X-ray diffraction patterns were obtained using Cu K_α radiation on an automated Nicolet–Stoe diffractometer.

The source for the ^{166}Er Mössbauer spectroscopy was made by neutron irradiation of $Ho_{0.4}Y_{0.6}H_2$ to produce $\sim 1\,GBq$ initial activity of the 27-h ^{166}Ho parent isotope. The ^{166}Er spectrum was obtained with both the sample and the source cooled to $4.5\,K$ in a helium-flow cryostat and the $80.6\,keV$ ^{166}Er gamma rays were detected using a high-purity Germanium detector. The spectrometer was operated in sine-mode and calibrated using the $819.45\,T$ magnetic splitting in $ErFe_2$ at $1.4\,K$. This calibration field is the average of the ^{166}Er Mössbauer measurement of $820.5(8)\,T$ by Hodges et al. [12] and the ^{167}Er NMR measurement of $818.4(10)\,T$ by Berthier and Devine [13]. The source half-linewidth on the $ErFe_2$ calibration was $2.49(4)\,mm/s$. The spectrum was fitted to the full nuclear hyperfine Hamiltonian using a non-linear least-squares routine. To facilitate comparison with other techniques we note that a Mössbauer *splitting* of $1\,mm/s$ in ^{166}Er corresponds to $64.973\,MHz$, $43.052 \times 10^{-27}\,J$, $3.1182\,mK$ or $0.00217\,cm^{-1}$.

3. Results and discussion

The magnetic ordering temperature of $Er_2Ge_2O_7$, determined by specific heat measurements [8], is 0.95(1) K. In Fig. 2a we show the ^{166}Er Mössbauer spectrum of $Er_2Ge_2O_7$ obtained at 4.5 K. The excited state and ground state nuclear spins associated with the 80.6 keV Mössbauer transition in ^{166}Er are 2 and 0, respectively, and the spectrum is a single, well-resolved, magnetically split pentet due to slow electronic relaxation between the two Er^{3+} states of the ground Kramers doublet. The magnetic hyperfine field is 663.7(5) T and the electric quadrupole coupling parameter (eQV_{zz}) is 6.4(1) mm/s. The half-linewidth is 2.83(5) mm/s. The free-ion hyperfine field of ^{166}Er, corresponding to a *fully-stretched* $|\langle J_Z \rangle| = 7.5$ electronic state is 770.5 ± 10.5 T [14] in a non-metal and thus we derive an 'effective' $|\langle J_Z \rangle|$ value of 6.46(1) for the Er^{3+} ion in $Er_2Ge_2O_7$. The isomer shift, relative to the source, is $-0.05(1)$ mm/s.

Chattopadhyay et al. [8] used a 5-fold crystal-field hamiltonian with crystal-field parameters deduced from their magnetic susceptibility and optical absorption data to predict the ^{166}Er Mössbauer spectrum of $Er_2Ge_2O_7$. Their predicted hyperfine field is 436 T, which is about two-thirds

Table 1
Observed and predicted Mössbauer line positions (mm/s) for ^{166}Er in $Er_2Ge_2O_7$ at 4.5 K

	Line 1	Line 2	Line 3	Line 4	Line 5
Observed (± 0.06 mm/s)	−49.03	−26.15	−1.66	24.43	52.15
Predicted	−28.77	−20.86	−11.96	22.26	39.17

of our measured value. They also predict an electric quadrupole parameter P of 43.5 MHz ($= 0.67$ mm/s) which converts to an electric quadrupole coupling parameter of $eQV_{zz} = 16.1$ mm/s, more than twice our measured value.

In Fig. 2 we also show the predicted ^{166}Er spectra based on the pentagonal model. The first predicted spectrum (Fig. 2b) is derived from the transition energies and nuclear energy level scheme given by Chattopadhyay et al. [8] whereas the second predicted spectrum (Fig. 2c) is derived from the predicted values of the hyperfine magnetic field and quadrupole parameter. Figs. 2b and c show clearly that the 5-fold crystal-field model, as published, does not reproduce the experimentally observed ^{166}Er Mössbauer spectrum. It is also evident that the two predictions of the pentagonal crystal-field model are mutually inconsistent.

The electronic ground state of the Er^{3+} ion in $Er_2Ge_2O_7$ was reported to be the Kramers doublet

$$\psi_0 = \mp 0.903 |\pm 11/2 \rangle \pm 0.176 |\mp 9/2 \rangle + 0.39 |\pm 1/2 \rangle, \tag{1}$$

which yields $\langle J_Z \rangle = \pm 4.7$ for the Er^{3+} ion in the ground Kramers doublet in $Er_2Ge_2O_7$, significantly smaller than our measured value of $|\langle J_Z \rangle| = 6.46(1)$.

In Table 1 we give the measured line positions of the five nuclear transitions between the excited and ground states of ^{166}Er in $Er_2Ge_2O_7$ at 4.5 K. For comparison, we also give the line positions predicted by the pentagonal crystal-field model [8], corrected for the small isomer shift (the line numbering is from lowest to highest energy i.e. left to right in the spectrum shown in Fig. 2).
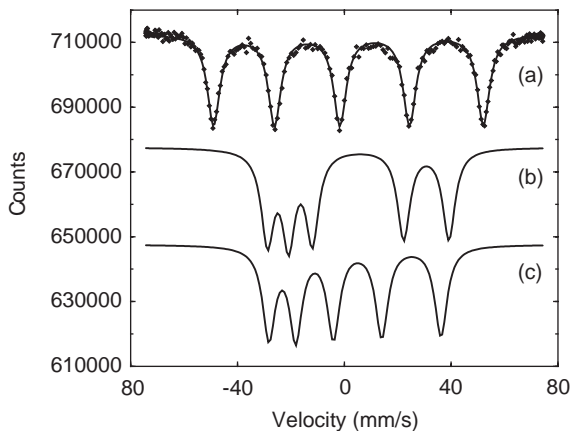

Fig. 2. ^{166}Er Mössbauer spectrum of $Er_2Ge_2O_7$ at 4.5 K: (a) is our fit as described in the text, (b) is the simulation using the line positions predicted by the pentagonal model [8] and (c) is the simulation using the hyperfine magnetic field and electric quadrupole parameter predicted by the pentagonal model [8].

3.1. Crystal-field model

As mentioned earlier, the point-symmetry of the R^{3+} site in the $R_2Ge_2O_7$ structure is triclinic [1,2] although a 5-fold model may be a useful, simplifying approximation when dealing with crystal-field effects. However, any model should show a systematic variation in its parameters as one changes the R^{3+} ion across a series of isostructural compounds. It is common practice, for instance, to assume that crystal-field lattice summations are effectively constant across a series. If we consider the values of the crystal-field parameters in the 5-fold model, tabulated by Jana et al. [3] for Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+} and Tm^{3+}, we observe a wide variation with no systematic behaviour across the $R_2Ge_2O_7$ series. Taking the published parameters [3] and dividing by the appropriate Stevens coefficients and electronic radial averages we obtain a set of crystal-field lattice summations which would be expected to show systematic behaviour across the series of $R_2Ge_2O_7$ compounds. In the standard crystal-field notation given by, for example, Hutchings [15], this amounts to the calculation of the A_{nm} lattice summation terms. The dominant second-order crystal-field lattice summation (A_{20}) takes the *relative* values -209, -281, $+74$, $+571$ and -134 across the series Tb–Tm. Clearly, these values show no systematic variation across this isostructural series.

3.2. Nuclear hyperfine hamiltonian

The fit to the measured ^{166}Er Mössbauer spectrum shown in Fig. 2a indicates that the nuclear hyperfine hamiltonian, comprising both magnetic dipole and electric quadrupole terms is effectively diagonal, since we obtain an excellent fit to the Mössbauer data without an asymmetry parameter or off-diagonal quadrupole terms. Thus, we may write (using standard notation)

$$H_{hf} = g_n\mu_N B_{hf} I_z + \frac{eQV_{zz}}{4I(2I-1)}(3I_z^2 - I^2) \qquad (2)$$

$$= aI_z + P(3I_z^2 - I^2) \qquad (3)$$

It is easy to show that a pentagonal point group at the Er^{3+} site produces a lattice electric field gradient which is diagonal. Furthermore, the standard asymmetry parameter η is zero. Thus, we may use the diagonal nuclear hamiltonian to deduce the values of the magnetic and electric quadrupole parameters a and P, respectively. This also provides us with an in-built check of the *physicality* or otherwise of a proposed fit to an ^{166}Er spectrum. Our fitted values of the hyperfine parameters show that such a diagonal hamiltonian in which the electric quadrupole term is basically a perturbation on the large magnetic term is valid. Within this procedure, the ^{166}Er Mössbauer line positions, relative to the small isomer shift, are

$$V_1 = -2a + 6P, \qquad (4)$$

$$V_2 = -a - 3P, \qquad (5)$$

$$V_3 = -6P, \qquad (6)$$

$$V_4 = +a - 3P, \qquad (7)$$

$$V_5 = +2a + 6P. \qquad (8)$$

These line positions provide us with two estimates for the magnetic hyperfine parameter a, which is proportional to the magnetic hyperfine field, namely

Expression	Observed	Predicted [8]
a (mm/s) $= \frac{1}{4}(V_5 - V_1)$	25.30 ± 0.03	17.0
a (mm/s) $= \frac{1}{2}(V_4 - V_2)$	25.29 ± 0.06	21.6

We can also obtain three estimates for the electric quadrupole parameter $eQV_{zz} = 24P$, namely

Expression	Observed	Predicted [8]
eQV_{zz} (mm/s) $= 2(V_5 + V_1)$	6.44 ± 0.24	$+21.0$
eQV_{zz} (mm/s) $= -4(V_4 + V_2)$	6.48 ± 0.24	-6.0
eQV_{zz} (mm/s) $= -4V_3$	6.44 ± 0.24	$+47.6$

The high degree of consistency between the hyperfine parameter values deduced from our experimental spectrum validates the use of the diagonal hyperfine hamiltonian shown in Eq. (2). On the contrary, the complete lack of consistency in the corresponding values deduced from the 5-fold crystal-field model and the published crystal-field parameters, in particular the values of the quadrupole parameter eQV_{zz}, demonstrate the unphysical nature of the predicted nuclear energy level scheme in ^{166}Er.

As in the case of $Tm_2Ge_2O_7$, it may be possible to derive a set of pentagonal crystal-field parameter values which not only explain the reported optical absorption data but also reproduce our ^{166}Er Mössbauer data. As mentioned earlier, the pentagonal crystal-field model may be a useful, simplifying approximation although the completely unsystematic variation of the pentagonal crystal-field parameters across the $R_2Ge_2O_7$ series reflects the fact that the point-symmetry of the R site in the $R_2Ge_2O_7$ structure is not pentagonal.

4. Conclusion

We have measured the ^{166}Er Mössbauer spectrum of $Er_2Ge_2O_7$ at 4.5 K, in response to the predictions based on a crystal-field model in which the Er atom occupies a site of 5-fold point symmetry. We find that the proposed pentagonal crystal-field model fails to reproduce the observed hyperfine interactions at the ^{166}Er nucleus, using the crystal-field parameters deduced from optical absorption measurements. The measured ^{166}Er hyperfine field at 4.5 K is 663.7(5) T and the electric quadrupole coupling parameter (eQV_{zz}) is 6.4(1) mm/s. The proposed 5-fold local symmetry model predicts quite different values of 436 T and 16.1 mm/s, respectively.

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