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An ^{166}Er-Mössbauer investigation of $ErNiAl_4$

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Abstract. A low temperature ^{166}Er-Mössbauer spectroscopy investigation of $ErNiAl_4$ reveals that the Er^{3+} ion's ground state Kramers doublet has $|\langle\pm| J_z |\pm\rangle|$ just 8% less than the fully-stretched value of J = 15/2. The persistence of a magnetically-split spectrum to well above T_N = 5.8 K is consistent with Orbach type paramagnetic relaxation that proceeds via the third excited crystal field level.

Introduction

The orthorhombic, intermetallic series $RNiAl_4$ (R = rare earth) exhibits interesting low temperature magnetic behaviour ([1] and references therein). This includes the dependence of the "easy" magnetisation axis on R (e.g. a-axis for Tb, Pr and b-axis for Ce, Nd) and the existence of multiple magnetic transitions as a function of both temperature and applied magnetic field [2,3]. The large inverse magnetocaloric effect observed for $TbNiAl_4$ [4] offers potential for low temperature magnetic cooling. It is expected that the strong magnetic anisotropies and hysteresis processes (such as those observed for $TbNiAl_4$) are driven by the crystal field (CF) interaction at the single R-site. Recent efforts to characterise the CF using inelastic neutron scattering (INS) have been directed at $ErNiAl_4$ [5]. One of the advantages of working with the Er^{3+} ion is that the CF scheme for its ground (J = 15/2) multiplet is comprised only of Kramers doublets. To assist with these efforts, ^{166}Er-Mössbauer spectroscopy has been employed here to determine the nature of the CF ground state doublet for Er^{3+} in $ErNiAl_4$, a useful additional criterion to be satisfied by the CF Hamiltonian that is eventually fitted to the INS spectra. $ErNiAl_4$ exhibits antiferromagnetic order below T_N = 5.8 K.

The crystal field scheme for Er^{3+} in $ErNiAl_4$

The orthorhombic C_{2v} (*mm*) point symmetry at the Er-site in $ErNiAl_4$ requires a CF Hamiltonian (Stevens operator equivalent notation) of the form

$$\mathsf{H}_{CF} = B_2^0 O_2^0 + B_2^2 O_2^2 + B_4^0 O_4^0 + B_4^2 O_4^2 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^2 O_6^2 + B_6^4 O_6^4 + B_6^6 O_6^6 \quad (1)$$

with the relatively large number of nine CF parameters to be determined experimentally. At liquid helium temperatures, there is negligible thermal population of the excited states. An INS spectrum recorded earlier at 8.6 K using cold neutrons revealed transitions to the excited states at 34.1(2) K, 85.3(2) K and 132(3) K as shown in Fig. 1(a). At that time, a semi-empirical approach (using rank 2 CF parameter estimates based on ^{155}Gd-Mössbauer results for $GdNiAl_4$ [2]) interpreted these three excited states in terms of a tentative CF Hamiltonian that implied a full CF splitting in excess of 450 K [5]. In order to identify transitions from the ground state to the highest CF levels, further INS measurements (with $E_{inc} \geq 40$ meV) will be undertaken at CNBC Chalk River. In the meantime, simple Pseudo-Voigt line fits ($\eta_{L\text{-}G} \approx 0.4$, 0.6 respectively) to the existing 8.6 K and 60 K INS spectra have identified a fourth excited CF level which is located at 148(2) K, as shown in Fig. 1(c).

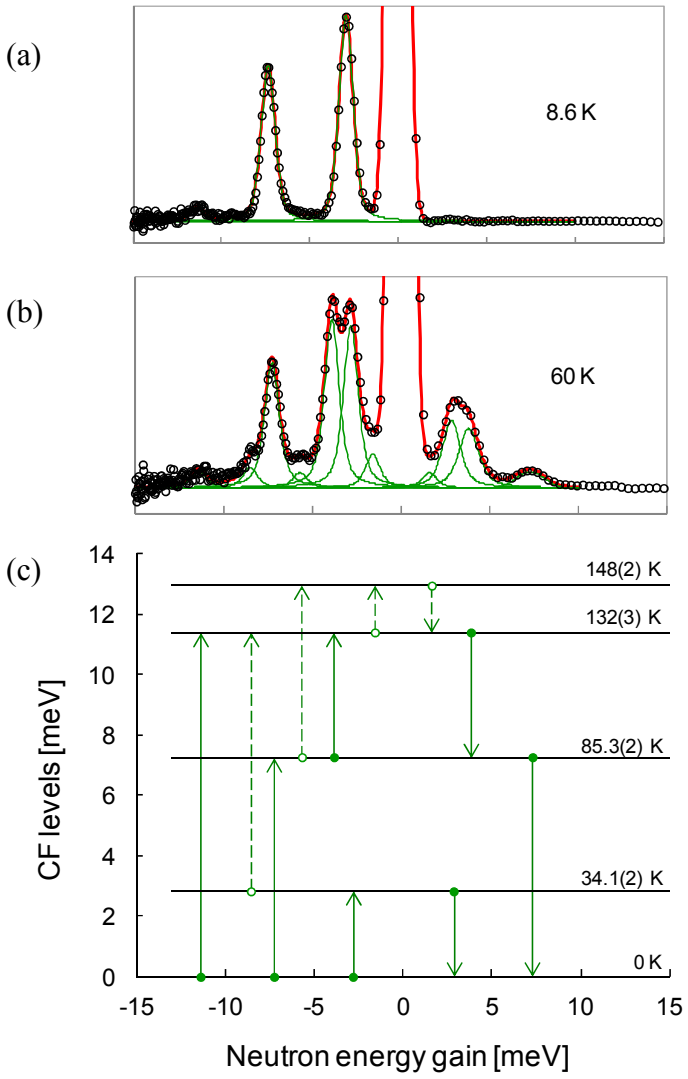

Fig. 1. Energy spectra of cold neutrons (E_{inc} = 20.5 meV) scattered from $ErNiAl_4$ at (a) 8.6 K and (b) 60 K. The fitted Pseudo-Voigt line shapes correspond to the transitions indicated by arrows in (c) which shows the energy levels proposed for 5 of the Er^{3+} CF scheme's 8 Kramers doublets.

^{166}Er-Mössbauer spectroscopy

Experimental details. The polycrystalline $ErNiAl_4$ was sampled from the material used for the previous INS measurements [5], and which was prepared as a set of smaller masses via repeated argon arc melting of high purity Er (99.9 %), Ni (99.99+ %) and Al (99.99+ %), followed by vacuum annealing (1300 K , 7 d). The lattice parameters are in excellent agreement with those reported earlier by Rykhal *et al.* [6]. The ^{166}Er-Mössbauer spectra were recorded at McGill University with both the source and the absorber (≈337 mg $ErNiAl_4$ cm^{-2}) mounted in a vertical configuration inside a Janis helium-flow cryostat. The source was prepared by neutron irradiation of $Ho_{0.4}Y_{0.6}H_2$ to produce ≈9 GBq of the ^{166}Ho parent isotope ($T_{½}$ = 26.9 h, E_γ = 80.56 keV).

Results and discussion. The ^{166}Er-Mössbauer spectra recorded for $ErNiAl_4$ are shown in Fig. 2 as a function of temperature. At 5 K, a typical magnetic spectrum is observed with 5 absorption lines of equal intensity and a splitting that corresponds to a magnetic hyperfine (hf) field of B_{hf} = 705(11) T acting at the ^{166}Er nucleus. Given the low Néel temperature, extra-ionic hf field contributions are expected to be negligible so that the hf field is proportional to the local expectation value of the 4f angular momentum according to

$$\frac{B_{\mathrm{hf}}}{B_{\mathrm{FI}}} = \frac{|\langle J_z \rangle|}{J} \qquad (2)$$

with a free ion field of $B_{FI}(Er^{3+})$ = 765.3 T [7]. The fitted hf field then corresponds to an expectation value of $|\langle J_z \rangle|$ = 6.9(2) which is just 8% less than the fully-stretched value of J = 15/2 = 7.5. This is consistent with slow relaxation (relative to the Larmor precession time) between the $|+\rangle$ and $|-\rangle$

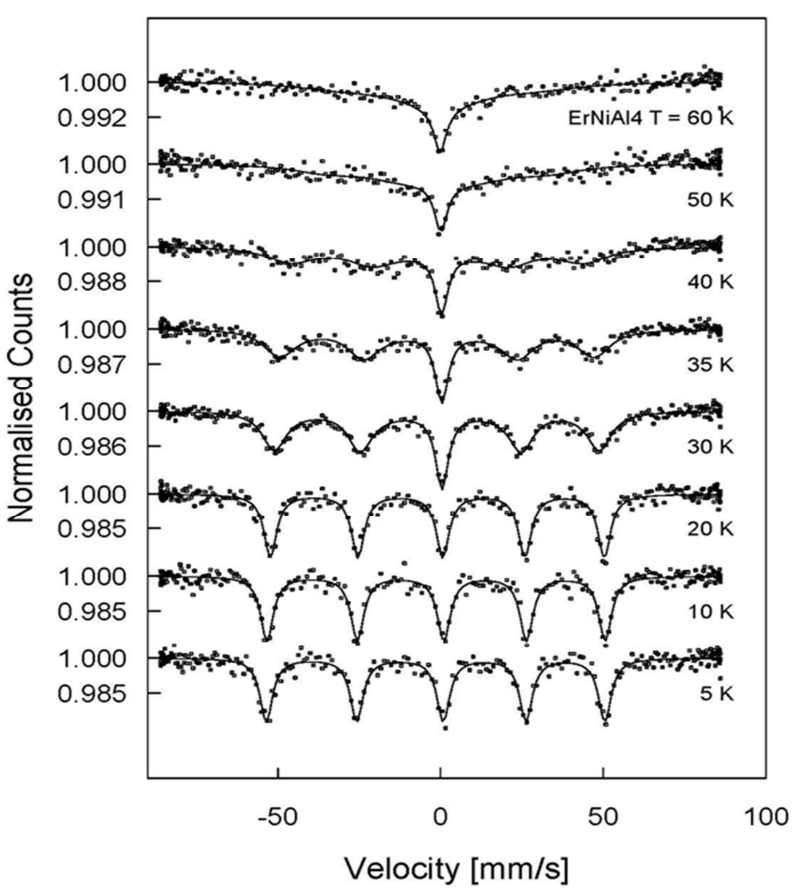

Fig. 2. ^{166}Er-Mössbauer spectra recorded as a function of temperature for $ErNiAl_4$. The solid curves were fitted using the relaxation theory of Nowik and Wickmann as decribed in the text.

components of the ground state Kramers doublet where $|\langle\pm| J_z |\pm\rangle|$ is close to 15/2. It is due to the influence of this slow paramagnetic relaxation that the spectrum retains its appearance to well above the Néel temperature of $T_N = 5.8$ K, eventually collapsing to a broadened single line at $T \geq 50$ K.

The spectra were fitted in terms of the relaxation model of Nowik and Wickmann [8] where the key parameter is the fluctuation time, τ, the average interval for switches between the $|+\rangle$ and $|-\rangle$ components of the ground state Kramers doublet. From Fig. 2, it is clear that the spectra are most sensitive to the fluctuation time for temperatures above 20 K and it is for this temperature range that the fitted fluctuation times are presented as a function of the inverse temperature in Fig. 3. The linear dependence of the semi-log plot confirms that

$$\tau^{-1} \propto \exp(-\Delta/T) \tag{3}$$

and the gradient provides an estimate of $\Delta \approx 125(5)$ K. Such exponential behaviour is consistent with spin-lattice relaxation of the Orbach type [9], involving a resonant 2-phonon process via an excited CF level at the energy of 125(5) K above the ground state. From Fig. 1, the best match is the third excited CF level at the slightly higher energy of 132(3) K.

Conclusion

Due to the influence of slow paramagnetic relaxation of the ground state Er^{3+} Kramers doublet, the ^{166}Er-Mössbauer spectrum for $ErNiAl_4$ retains the appearance of a low temperature, magnetically-split spectrum to well above the Néel temperature of 5.8 K. The $|\pm\rangle$ components of the doublet are almost fully stretched and the relaxation is determined to proceed via an excited CF level, identified as the third excited state at 132(3) K above the ground doublet.

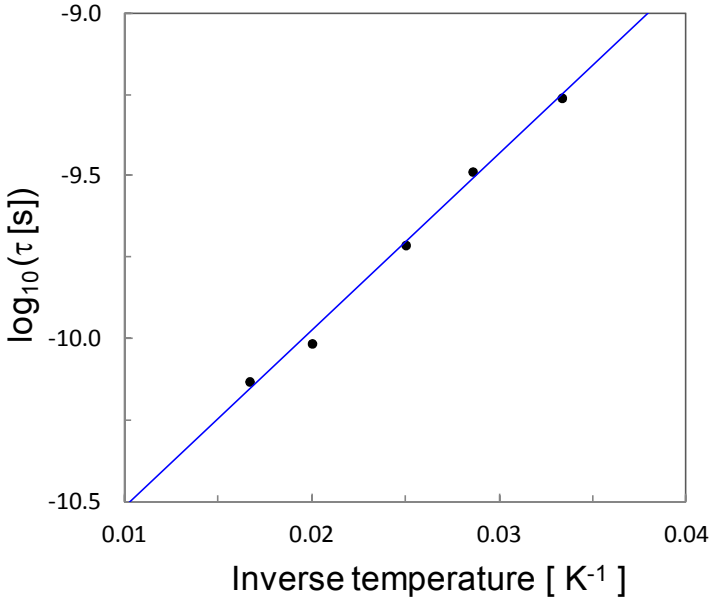

Fig. 3. Temperature dependence of the fluctuation time, τ, fitted to the ^{166}Er-Mössbauer spectra. By comparison, the fitted low temperature magnetic hf field of B_{hf} = 705(11) T corresponds to a Larmor precession time of $T_L \approx 0.6$ ns.

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