

## Magnetic ground state of Dy<sup>3+</sup> in DyNiAl<sub>4</sub>

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Previously, the bulk magnetisation of polycrystalline DyNiAl<sub>4</sub> was found to reach barely half its expected saturation value with a 9 T applied field. New inelastic neutron scattering and <sup>161</sup>Dy-Mössbauer spectroscopy results suggest that the crystal field splitting for Dy<sup>3+</sup> in DyNiAl<sub>4</sub> is dominated by B<sub>2</sub><sup>0</sup> with a low temperature local Dy<sup>3+</sup> moment close to its full free-ion value of ± 10 μ<sub>B</sub>. Considering that the magnetization for related single crystal specimens (e.g. for TbNiAl<sub>4</sub>) typically grows more rapidly with the applied field directed along the easy axis, the slower response for DyNiAl<sub>4</sub> powder must be due to a strong magneto-crystalline anisotropy hindering the moment realignment. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4972997>]

### I. INTRODUCTION

The orthorhombic, intermetallic series, RNiAl<sub>4</sub> (R = rare earth), exhibits a range of interesting magnetic behaviour (<sup>1,2</sup> and references therein), including the potential for low temperature, inverse, magnetic cooling<sup>3</sup> with DyNiAl<sub>4</sub> showing most promise for maximum entropy change.<sup>4</sup> Furthermore, the choice of rare earth is crucial in determining the magnetic anisotropy. In keeping with trends across the series, the Dy sub-lattice orders with an incommensurate magnetic structure at T<sub>N</sub> ≈ 18 K and locks into commensurate antiferromagnetism at T<sub>N</sub>' ≈ 15 K. At 2 K, the bulk magnetisation for a powder specimen of DyNiAl<sub>4</sub> was observed to grow steadily but attain a value of just 4.7 μ<sub>B</sub>/f.u. with an applied field of 9 T.<sup>4</sup> This is substantially less than the full free-ion moment of μ<sub>FI</sub> (Dy<sup>3+</sup>) = 10 μ<sub>B</sub>. We report here on new magnetic susceptibility, inelastic neutron scattering (INS) and <sup>161</sup>Dy-Mössbauer spectroscopy measurements directed at characterising the crystal field (CF) ground state and associated magnetic moment for Dy<sup>3+</sup> in DyNiAl<sub>4</sub>.

### II. EXPERIMENTAL DETAILS

Single phase, polycrystalline DyNiAl<sub>4</sub> was prepared by repeated argon arc melting of stoichiometric proportions of 99.9% pure Dy and 99.99% pure Ni and Al metal, followed by a vacuum anneal at 1030 °C for 7 days. Powdered DyNiAl<sub>4</sub> material was pressed into a pellet and mass magnetisation data were recorded down to 2 K in a field of 0.1 T using a Quantum Design PPMS. The <sup>161</sup>Dy, 25.7 keV, Mössbauer spectra were collected in transmission mode using a room temperature <sup>161</sup>Tb:<sup>160</sup>GdF<sub>3</sub> source. The absorber material (≈36 mg DyNiAl<sub>4</sub> per cm<sup>2</sup>) was sandwiched between beryllium discs and cooled in a liquid helium cryostat. A 48 μm thick reference Dy metal foil (≈41 mg Dy/cm<sup>2</sup>) was employed in separate measurements to calibrate the drive velocity. Finally, INS measurements were performed at ISIS using the Mari time-of-flight spectrometer with a 15 g

mass of finely ground DyNiAl<sub>4</sub> packed into a hollow cylinder of  $\approx 1$  mm annular width. Additional spectra were recorded for 20 g of YNiAl<sub>4</sub> in order to subtract an accurate phonon background.

### III. RESULTS AND DISCUSSION

The mass magnetisation data are shown in the inset at top left of Fig. 1. They are reasonably consistent with the earlier specific heat results.<sup>4</sup> With decreasing temperature, the magnetisation starts to decrease in the vicinity of  $T_N = 18$  K followed by an inflexion close to  $T_N' = 15$  K. More importantly, the high temperature inverse magnetic susceptibility (main plot in Fig. 1) exhibits Néel law dependence with  $1/C_m = 1806.5 \text{ kg m}^{-3} \text{ K}^{-1}$  and  $\theta_N \approx 12$  K, smaller than the observed Néel temperature of  $T_N \approx 18$  K. The Curie constant,  $C_m$ , corresponds to  $\mu_{\text{eff}} = 10.7(1) \mu_B/\text{f.u.}$ , in close agreement with the value of  $\mu_{\text{eff}} = g_J \sqrt{J(J+1)} = 10.65 \mu_B/\text{Dy}^{3+}$  expected for the Dy<sup>3+</sup> ion with  $J = 15/2$  and  $g_J = 4/3$ . This confirms that only the Dy sub-lattice contributes to the DyNiAl<sub>4</sub> magnetism.

The <sup>161</sup>Dy-Mössbauer spectra recorded at 5 K for the reference Dy metal absorber and DyNiAl<sub>4</sub> (Fig. 2) are typical magnetically-split spectra involving 16 allowed transitions between the ground ( $I_g = 5/2$ ) and excited ( $I_e = 5/2$ ) levels of the 25.7 keV resonance. In this work, the spectra were analysed in terms of a simple nuclear Hamiltonian of the form

$$\mathcal{H}_{\text{nucl}} = \mathcal{H}_{\text{mag}} + \mathcal{H}_{\text{quad}} = a\bar{I}_z + P'[3\bar{I}_z^2 - I(I+1)] \quad (1)$$

where  $a(I) = B_{\text{eff}} \mu(I)/I$  represents the magnetic splitting and  $P'$  is a (first order perturbation) quadrupole interaction term with the  $z$ -axis defined as the direction of the magnetic hyperfine field,  $B_{\text{eff}}$ . The fitted hyperfine interaction parameters are presented in Table I. The same drive velocity of  $v_{\text{max}} = 245.05 \text{ mm/s}$  (calibrated using the known value of  $a(I_g) = 40.13 \text{ mm/s}$  for Dy metal<sup>5,6</sup>) was employed for the two spectra. The isomer shift,  $\delta$ , is sensitive to the electron charge distribution at the nucleus and its large value of  $+2.7 \text{ mm/s}$  (relative to the ionic trifluoride source) observed for the Dy metal is due to the contribution from conduction electrons. The smaller isomer shift observed for DyNiAl<sub>4</sub> reflects a smaller conduction electron density relative to Dy metal. These observations at 5 K are similar to those reported at room temperature for Dy metal and DyAl<sub>2</sub>.<sup>7</sup> Using  $\mu(I_g) = 0.4803(25) \mu_B$ ,<sup>8</sup> the value of  $a(I_g)$  fitted to the DyNiAl<sub>4</sub> spectrum corresponds to an effective hyperfine field of  $B_{\text{eff}} = 548(3) \text{ T}$ . Compared with the free-ion field of  $B_{\text{eff}}(\text{FI}) = 559.8 \text{ T}$ , this implies a local

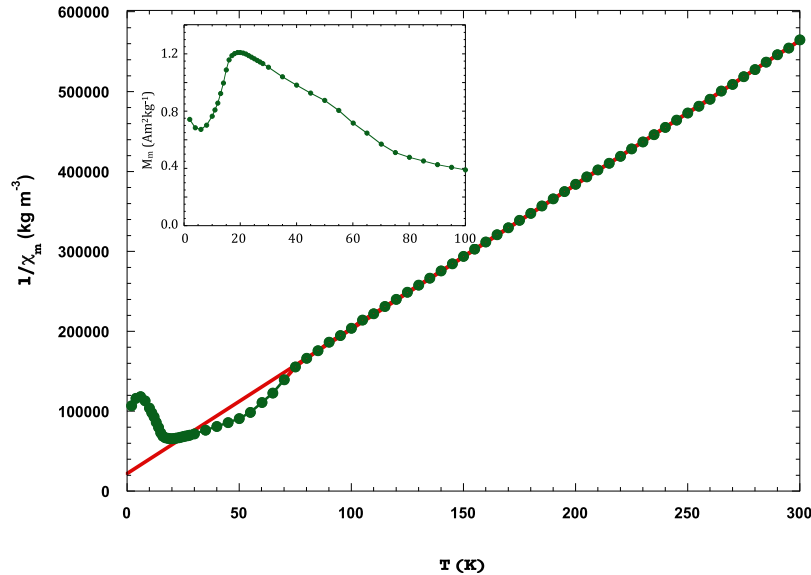


FIG. 1. Bulk magnetisation (inset) and inverse magnetic susceptibility (main figure) for DyNiAl<sub>4</sub> with an applied field of  $B_{\text{app}} = 0.1 \text{ T}$ . The extrapolated straight line (solid red) is the line of best fit to the data for  $T > 70 \text{ K}$ . The increase in magnetisation (inset) at about 60 K is due to a ferromagnetic DyAl<sub>2</sub> impurity phase ( $T_C = 62 \text{ K}$ ), too low in concentration to be identified in the x-ray diffraction pattern.

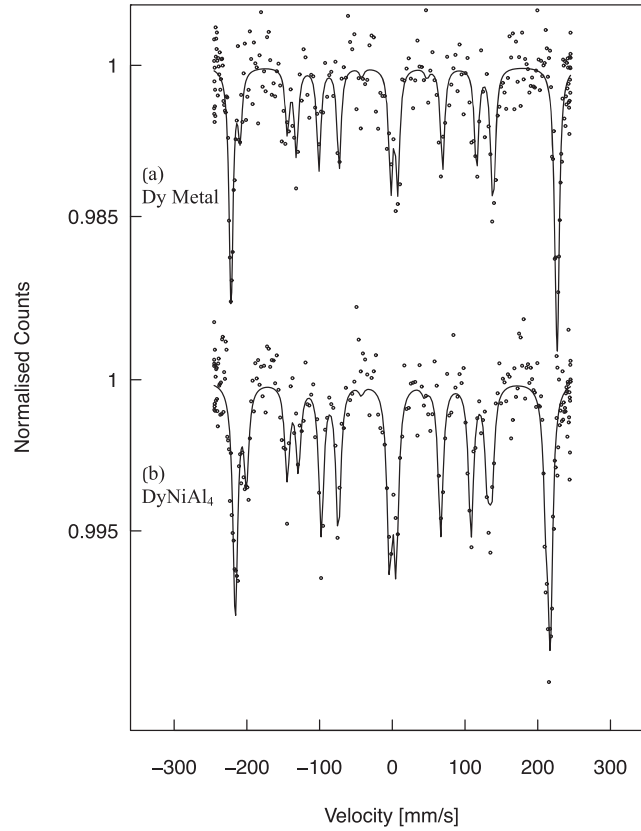


FIG. 2.  $^{161}\text{Dy}$ -Mössbauer spectra recorded at 5 K for (a) reference Dy metal and (b) DyNiAl<sub>4</sub>. The solid lines represent the theory fitted with parameters summarised in Table I.

Dy<sup>3+</sup> electronic moment of 9.8  $\mu_B$ , which is very close to the full free-ion moment of 10  $\mu_B$ . This is consistent with the previous  $^{166}\text{Er}$ - and  $^{169}\text{Tm}$ - Mössbauer investigations of ErNiAl<sub>4</sub><sup>9</sup> and TmNiAl<sub>4</sub> (unpublished), respectively, where the CF ground states were demonstrated to be “fully-stretched”, slowly relaxing (with respect to the Larmor precession frequency) doublets. In the case of TmNiAl<sub>4</sub>, the ground state is a pseudo-doublet.

The low temperature ( $T = 7$  K) neutron scattering intensity function,  $S(E, Q)$ , recorded for DyNiAl<sub>4</sub> using the Mari time-of-flight instrument (Fig. 3), features a well-defined absorption at 6.5 meV with a  $Q$ -dependent intensity and a possible further weak transition at about 11 meV. The trivalent Dy<sup>3+</sup> ion is a Kramers ion with  $J = 15/2$  and, for the relatively low orthorhombic symmetry at the rare earth site, the CF scheme is comprised of 8 Kramers doublets. At 7 K, only the lowest energy doublet will be populated. Normally, the orthorhombic site symmetry would require a complex CF Hamiltonian with 9 CF parameters

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

TABLE I.  $^{161}\text{Dy}$ -Mössbauer spectroscopy results for DyNiAl<sub>4</sub> at 5 K: isomer shift  $\delta$  (with respect to  $^{161}\text{Dy}$ : $^{160}\text{GdF}_3$ ) and the hyperfine interaction parameters  $P'(I_g)$  and  $a(I_g)$  as defined in (1).

	$\delta$ (mm/s)	$a(I_g)$ (mm/s)	$P'(I_g)$ (mm/s)
Dy metal	2.7(2)	40.13	3.10(5)
DyNiAl <sub>4</sub>	0.7(2)	38.73(4)	2.72(3)

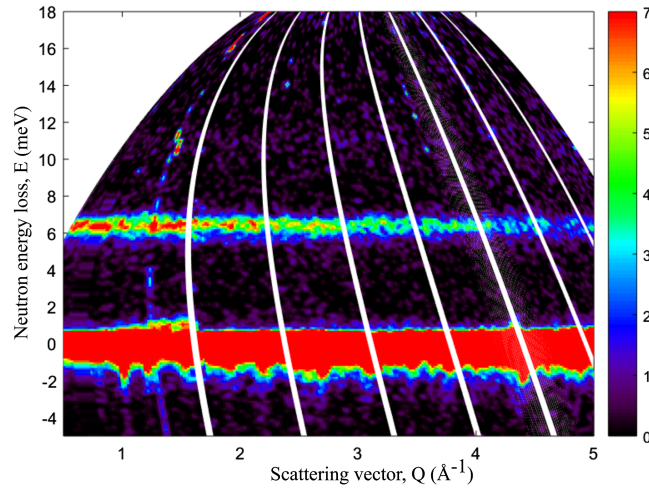


FIG. 3. Scattering intensity,  $S(E, Q)$ , recorded for  $\text{DyNiAl}_4$  at  $T = 7$  K using the Mari time-of-flight instrument with an incident neutron energy of 20 meV. Key neutron energy loss features are at 6.5 meV (intense and strongly  $Q$ -dependent) and 11 meV (very low intensity). The arc of intensity that passes upwards with high intensities at 6.5, 11, 16 and 18 meV is due to a faulty detector wire whose contribution was excluded from the plots shown in Fig. 4.

However, the lack of multiple observed transitions suggests a dominant  $B_2^0$  term that fully polarises the ground state into a  $|\pm 15/2\rangle$  doublet with a  $|\pm 13/2\rangle$  doublet at 6.5 meV as the next excited level.

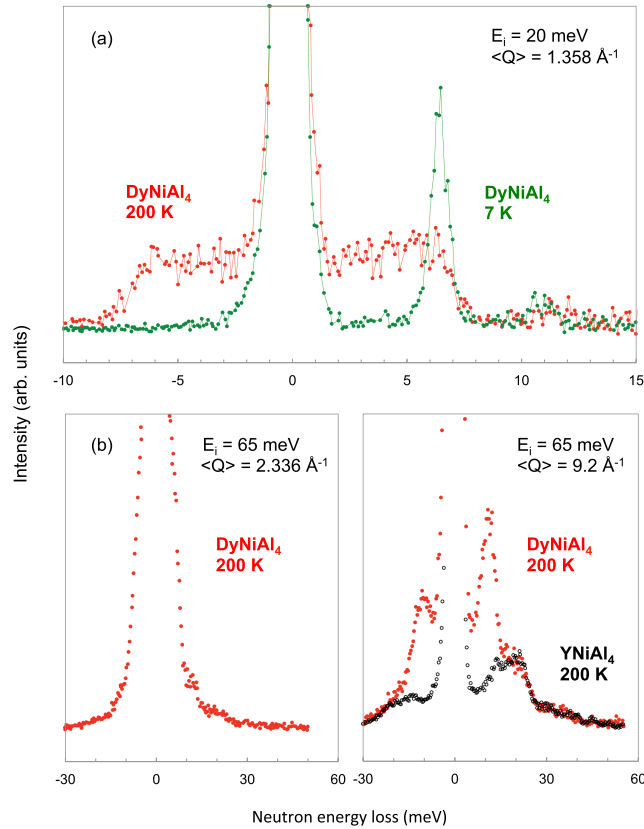


FIG. 4. Neutron energy loss spectra for  $\text{DyNiAl}_4$  at various temperatures and mean scattering angle values,  $\langle Q \rangle$ , derived from scattering intensity data,  $S(E, Q)$ , recorded on Mari for incident neutron energies of (a) 20 meV, and (b) 65 meV. The low  $Q$  ( $\langle Q \rangle = 1.358 \text{ \AA}^{-1}$ ,  $2.336 \text{ \AA}^{-1}$ ) and high  $Q$  ( $\langle Q \rangle = 9.2 \text{ \AA}^{-1}$ ) spectra were integrated over scattering angle ranges with means of  $\langle \phi \rangle = 22.29^\circ$  and  $110.05^\circ$ , respectively.

This simple proposal is further supported by the neutron energy loss spectra shown in Fig. 4(a). At  $T = 7$  K, the 6.5 meV transition is clearly dominant. However at 200 K there is effectively a continuum of spectral intensity extending from -6.5 meV through to +6.5 meV. Again, this could be accounted for with a single  $B_2^0$  CF term. For example, if  $B_2^0 \approx -0.143$  meV, then the Kramers doublets would be located at 0, 6, 11, 15.5, 18.9, 21.5, 23.4 and 25 meV with neutron-induced transitions  $\Delta m_J = \pm 1$  allowed between only the next-nearest levels. With thermal population of all of the levels at 200 K, this would generate the observed continuous block of transitions. The 16 transition energies would be equally spaced over the range of -6 to 6 meV.

Now consider more closely the low intensity peak that is observed at 11 meV in both Fig. 3 and 4(a). In the neutron energy loss spectrum recorded for  $E_i = 65$  meV at 200 K and low  $Q$  (Fig. 4(b) left panel), it is again present as a broad shoulder. Based on the above CF considerations it is possible therefore that it corresponds to a direct transition from the CF ground state to the second excited level. For the spectra recorded at 200 K and high  $Q$  (Fig. 4(b) right panel), it is observed that the purely phonon excitation spectrum of  $\text{YNiAl}_4$  matches closely with the higher energy range of the  $\text{ErNiAl}_4$  spectrum but not in the region of the 11 meV peak. Subtraction of the former from the latter reveals a well-defined 11 meV peak whose intensity appears to have increased. However, the intensity of a CF transition normally decreases with increasing  $Q$ . This puzzling behaviour suggests that a more complex process, such as a phonon-enhanced CF transition, is involved.

#### IV. CONCLUSION

Both the  $^{161}\text{Dy}$ -Mössbauer and inelastic neutron scattering data support the idea of a Kramers doublet ground state with fully-stretched  $J_z = \pm 15/2$ . Therefore, CF quenching can be ruled out. Considering that the magnetisation for related single crystal specimens (e.g. for  $\text{TbNiAl}_4$ ) typically grows more rapidly with the applied field directed along the easy axis, we conclude that the slower response for  $\text{DyNiAl}_4$  powder is due to a strong magneto-crystalline anisotropy that hinders the moment realignment.

#### ACKNOWLEDGMENTS

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