Magnetic Ground State of Dy^{3+} in $DyNiAl_4$

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Previously, the bulk magnetisation of polycrystalline $DyNiAl_4$ was found to reach barely half its saturation value with a 9 T applied field. New inverse paramagnetic susceptibility measurements confirm that only the Dy sub-lattice contributes magnetically and ^{161}Dy-Mössbauer spectroscopy yields a low temperature local Dy^{3+} moment close to its full free-ion value of 10 μ_B. The latter eliminates strong crystal field quenching as a mechanism and implies that a much larger applied field is needed for full ferromagnetic alignment.

1. Introduction

The orthorhombic, intermetallic series, $RNiAl_4$ (R = rare earth), exhibits a range of interesting magnetic behaviour [1] including the potential for low temperature, inverse, magnetic cooling [2,3]. Earlier specific heat measurements on polycrystalline $DyNiAl_4$ revealed phase transitions at T_N = 18 K and T_N'= 15 K [4]. Following trends observed across the $RNiAl_4$ series, it is expected that the Dy sub-lattice orders with an incommensurate magnetic structure at 18 K and eventually locks into commensurate antiferromagnetism at 15 K. The low temperature magnetisation curve suggested possible metamagnetic transitions near 2.5 T and 6.25 T and the peak entropy changes for the polycrystalline specimen were found to be comparable with those observed for single crystal $TbNiAl_4$ [4]. However, at the maximum applied field of 9 T the bulk magnetisation of 4.7 μ_B/f.u. corresponded to less than half of the maximum Dy^{3+} free-ion moment of 10 μ_B. It was uncertain whether crystal field quenching is responsible for a reduced local Dy^{3+} magnetic moment or whether increased applied fields are needed to overcome the antiferromagnetic exchange and the large magnetocrystalline anisotropy. In the new work reported here, inverse magnetic susceptibility and ^{161}Dy-Mössbauer spectroscopy have been employed to characterise the local magnetic moment at the Dy^{3+} site in $DyNiAl_4$.

2. Experimental details

Single phase specimens of polycrystalline $DyNiAl_4$ were synthesised by repeated argon arc melting of stoichiometric amounts 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 $DyNiAl_4$ 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.

^{161}Dy, 25.7 keV, Mössbauer spectra were collected in transmission mode using a room temperature ^{161}Tb:$^{160}GdF_3$ source. The source was activated at Australia's OPAL reactor (3d, 10^{13} n cm^{-2} s^{-1}) according to the reaction

$$^{160}\mathrm{Gd}\ (97\%\ \mathrm{enr}) \xrightarrow{n,g} {}^{161}\mathrm{Gd}\ (T_{1/2} = 3.7\mathrm{m}) \xrightarrow{b} {}^{161}\mathrm{Tb}\ (T_{1/2} = 6.9\mathrm{d}) \qquad (1)$$

In order to reduce the ^{24}Na activity arising from (n,α) activation of ^{27}Al in the source's press-sealed aluminium capsule, the source was allowed to decay for several days before use. The

$DyNiAl_4$ powder (≈36 mg/cm^2) and 48 μm thick reference Dy metal foil (≈41 mg/cm^2) absorbers were sandwiched between beryllium discs and cooled to 5 K in a liquid helium cryostat. The transmitted 25.7 keV gammas were counted using an argon gas-filled proportional counter.

As shown schematically in Fig. 1, a typical magnetically-split spectrum involves 16 allowed transitions between the ground (I_g = 5/2) and excited (I_e = 5/2) levels associated with the 25.7 keV resonance. In this work, the spectra were analysed in terms of a simple nuclear Hamiltonian of the form

$$H_{nucl} = H_{magnetic} + H_{quadrupole} = aI_z + P'[3I_z^2 - I(I+1)] \quad (2)$$

where $a(I) = B_{eff}\ \mu(I)/I$ represents the magnetic splitting, P′ is a (first order perturbation) quadrupole interaction term with the z-axis defined as the direction of the magnetic hyperfine field, B_{eff}. Based on high precision NMR measurements [5,6], the low temperature value of the ground state magnetic splitting for ^{161}Dy in Dy metal is $a(I_g)$ = 830.3(5) MHz which converts to 40.132(3) mm/s and provides a useful reference for the drive velocity calibration.

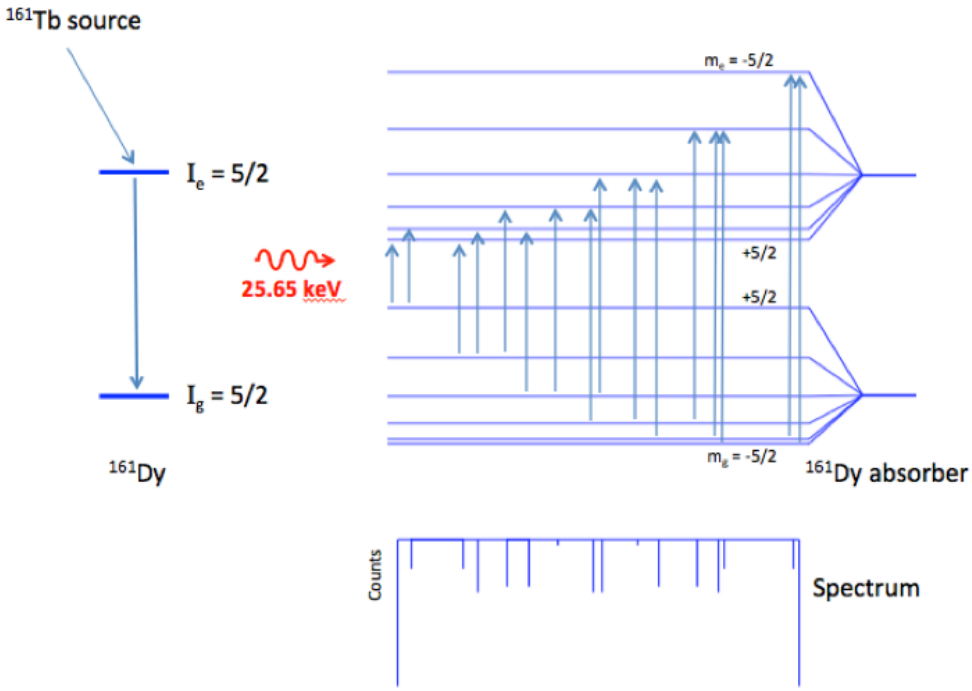

Fig. 1. Schematic of the ^{161}Dy, 25.7 keV transitions contributing to a typical magnetically-split Mössbauer spectrum.

3. Results and discussion

3.1 Paramagnetic susceptibility

The mass magnetisation data are shown in the inset at top left of Fig. 2. They are reasonably consistent with the earlier specific heat results [4]. 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. 2) exhibits Néel law dependence with $1/C_m$ = 1806.5 kg m^{-3} 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 μ_{eff} = 10.7(1) μ_B/f.u., in close agreement with the value of $\mu_{eff} = g_J\sqrt{J(J+1)}$ = 10.65 μ_B/Dy^{3+} expected for the Dy^{3+} ion with J = 15/2 and g_J = 4/3. This confirms that only the Dy sub-lattice contributes to the total $DyNiAl_4$ magnetism.

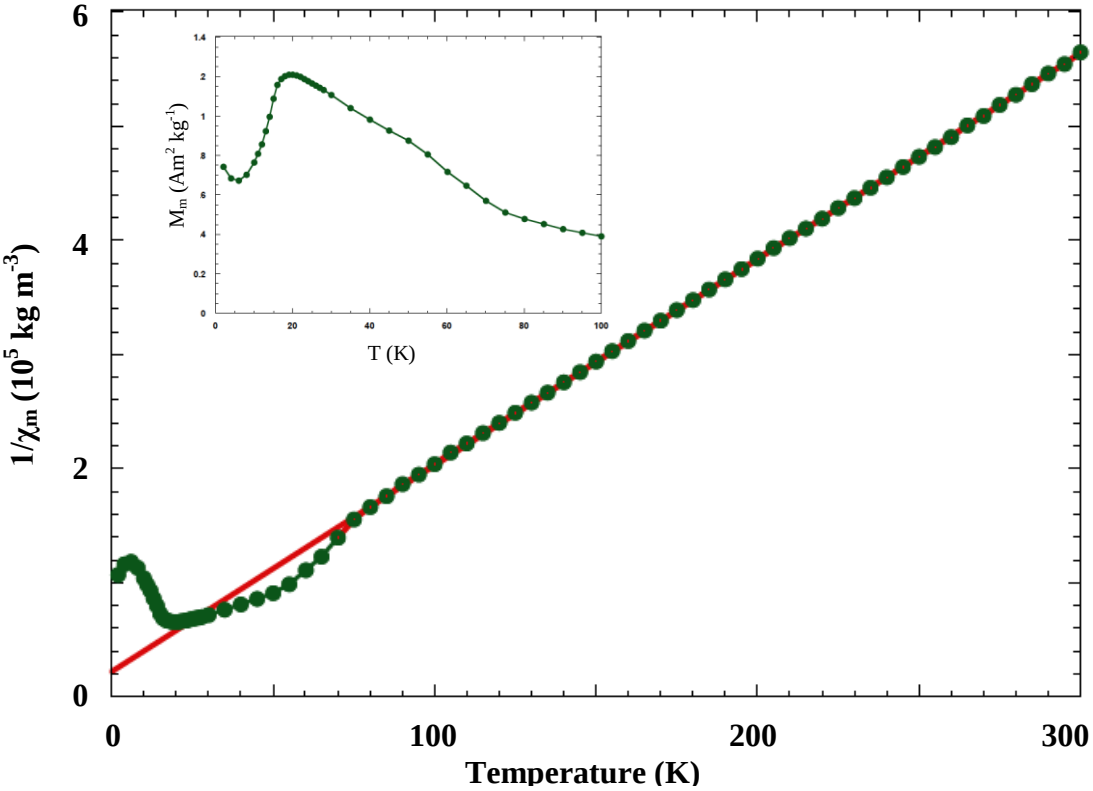

Fig. 2. Bulk magnetisation (insert) and inverse magnetic susceptibility (main figure) for $DyNiAl_4$ with an applied field of B_{app} = 0.1 T. The extrapolated straight line (solid red) is the line of best fit to the data for T > 70 K.

3.2 ^{161}Dy-Mössbauer spectroscopy

The ^{161}Dy-Mössbauer spectra recorded at 5 K for the reference Dy metal absorber and $DyNiAl_4$ are shown in Fig. 3 on the next page and the fitted hyperfine interaction parameters are presented in Table 1 below. The same drive velocity of v_{max} = 245.05 mm/s (calibrated using the known value of $a(I_g)$ = 40.13 mm/s for Dy metal) was employed for both spectra. The isomer shift, δ, is sensitive to the electron charge distribution at the nucleus and its large value of +2.7 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 $DyNiAl_4$ 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 $DyAl_2$ [7]. Using $\mu(I_g)$ = 0.4803(25) μ_B [8], the value of $a(I_g)$ fitted to the $DyNiAl_4$ spectrum corresponds to an effective hyperfine field of B_{eff} = 548(3) T. Compared with the free-ion field of $B_{eff}(FI)$ = 559.8 T, this implies a local Dy^{3+} electronic moment of 9.8 μ_B, which is very close to the full free-ion moment of 10 μ_B.

Table 1. Fitted 5 K values of the isomer shift δ (with respect to ^{161}Dy:$^{160}GdF_3$) and the parameters $P(I_g)$ and $a(I_g)$ as defined in (2).

	δ (mm/s)	$a(I_g)$ (mm/s)	$P(I_g)$ (mm/s)
Dy metal	2.7(2)	40.13	3.10(5)
$DyNiAl_4$	0.7(2)	38.73(4)	2.72(3)

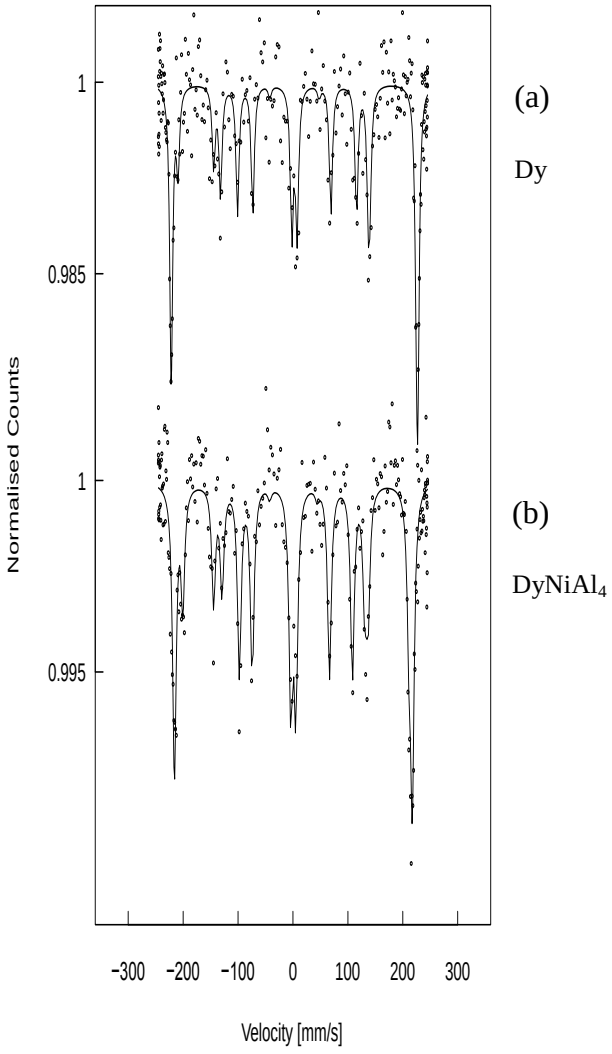

Fig. 3. ^{161}Dy-Mössbauer spectra recorded at 5 K for (a) reference Dy metal and (b) $DyNiAl_4$. The solid lines represent the theory fitted with parameters summarised in Table 1.

4. Conclusion

The local moment at the Dy^{3+} site in $DyNiAl_4$ is close to its maximum free ion value which rules out the possibility of significant crystal field quenching. Therefore, the relatively small value of bulk magnetisation achieved previously with an applied field of 9 T implies that a substantially larger field is needed to overcome the magnetocrystalline anisotropy.

Acknowledgments

This work was supported by AINSE, grant number ALNGRA14547.

References

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