MAGNETIC HYPERFINE INTERACTIONS IN GdAl₃

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We have studied the magnetic hyperfine interactions in GdAl₃ using $^{155}$Gd Mössbauer spectroscopy between the temperatures of 4 K and 90 K. Previous studies on GdAl₃ have shown that antiferromagnetic ordering occurs at 18 K, and that a fit of the susceptibility to $1/(T - \theta_p)$ yields a $\theta_p$ value of $-89$ K. The large ratio of $\theta_p$ to $T_N$ is indicative of magnetic frustration between competing ferro- and antiferromagnetic interactions, which may be due to a combination of the oscillatory nature of the RKKY interaction and the geometry of the hexagonal lattice. Our studies show that the saturation magnetic hyperfine field at the Gd site is $-24.0$ T, with the moments lying in the basal plane. The efg at the gadolinium site is $2.55(1) \times 10^{17}$ V cm$^{-2}$ which is considerably larger than the value predicted by a point charge calculation. This difference may indicate that there is a conduction electron contribution. A helical magnetic structure has been calculated from RKKY theory.

1. Introduction

The rare earth trialuminides from La to Gd (Except Eu) are isostructural and crystallize in the NiSn₃ structure (DO₁₉). Of these, the only compound for which a transition to an ordered magnetic state has been observed is GdAl₃, $T_N = 18$ K, $\theta_p = -89$ K, [1]. GdAl₃ is of interest because it is one of the endpoints of the system Ce₁₋ₓGdₓAl₃ which has shown an interesting interplay of spin-glass and heavy fermion properties [2]. The heavy fermion characteristic of this system persists up to 23% Gd as determined by specific heat measurements. This system also changes from antiferromagnetic to ferromagnetic and/or a spin glass state for $x \leq 0.5$. Mössbauer results on this system will be reported at a later date. The unusually large ratio of $\theta_p$ to $T_N$ of 4.9 is a good indicator that competing interactions and the geometry of the hexagonal lattice are frustrating magnetic order. Each Gd atom has 6 nearest neighbor Gd atoms in consecutive planes along the $c$-axis, (3 above and 3 below), at a distance 4.3 Å, two second nearest neighbors in the next plane along the $c$-axis at a distance of 4.6 Å, and six atoms within the same plane at a distance of 6.3 Å. Owing to this hexagonal symmetry,
it is evident that competing ferromagnetic and antiferromagnetic interactions are frustrating magnetic order.

2. Results

Mössbauer spectra were recorded at 4.5, 10, 13, 17, 18, 20, 54, 79 K using a single line source of $^{154}$SmPd$_3$ and a powdered absorber with effective thickness $T_a = 2.4$ at 4.5 K. The source temperature remained near 5 K. X-ray diffraction showed that less than 5% GdAl$_2$ was present in the sample. The recorded spectra, some of which are shown in fig. 1, were fitted by diagonalizing the full nuclear Hamiltonians [3]. The spectra recorded above 18 K show a temperature independent quadrupole splitting of 0.703(3) mm s$^{-1}$ which gives a resultant efg of $V_{zz} = 2.55 \times 10^{17}$ V cm$^{-2}$. Below 18 K the magnetic hyperfine field increases very quickly while the efg remains at the above value. The isomer shift remained constant at 0.43(1) mm s$^{-1}$ after correcting for SOD.

In the DO$_{19}$ structure, all Gd sites are equivalent and possess hexagonal symmetry. Therefore the ionic contribution, $V_{zz}^{i}$, lies along the c-axis and can be calculated, using the point charge model, from eq. (1).

$$V_{zz}^{i} = e q^{ion} = e^2 Z \left\{ a^{-3} \left[ 0.0065 - 4.3584(c/a - 1.633) \right] \right\}$$ (1)

$$V_{zz} = (1 - \gamma_{\infty}) V_{zz}^{i} + (1 - \gamma) V_{zz}^{c} + (1 - R) V_{zz}^{y}$$ (2)

For GdAl$_3$ we calculate $V_{zz}^{i} = 6.74 \times 10^{15}$ V cm$^{-2}$. The total efg, equation (2), was used with $\gamma_{\infty} = -80$, to obtain the contribution from the conduction electrons of $V_{zz}^{c}(1 - \gamma) = -2.93 \times 10^{17}$ V cm$^{-2}$, (assuming no orbital contribution in an S-state ion). This value is not expected since the conduction electron contribution should reinforce the ionic contribution, as in Gd metal where this contributes approximately 50% [4].

One important result is that the angle between $H$ and $V_{zz}$ is 90°. This indicates that the magnetic moments lie in the basal plane. We have used RKKY theory to determine the minimum exchange energy for the magnetic structure. The interaction between two rare earth ions can be expressed as an indirect one mediated between conduction electrons. NMR Knight shift results by van Diepen et al. [5], show that the use of RKKY theory yields encouraging results in describing the magnetic properties of this system. For RKKY, the interaction between magnetic ions can be written as

$$H = J(R_i - R_j) \hat{S}_i \cdot \hat{S}_j$$ (3)

$$J(R_i - R_j) = A \Sigma \phi(2k_i R_{ij}) e^{-\lambda/R_{ij}}$$ (4)

Here $A$ is a constant containing the exchange integral between a conduction electron and a 4-f electron, $\lambda$ is the electron mean-free path estimated to be approximately 12 Å in GdAl$_3$, and $R_{ij}$ is the distance between magnetic ions.
The quantity $k_f$ is the Fermi wave vector and $\phi$ is the familiar RKKY function. Let us examine the prediction of a simple model. By using eq. (3) and the fact that the magnetic moments are restricted to the basal plane, along with the
Fig. 2. a). The turn angle between consecutive planes for the lowest energy calculated from equations (3)–(4). The Fermi wave vector has been normalized to the free electron value of \( 1.648 \times 10^{-10} \, \text{m}^{-1} \). Calculations were carried out over 10 lattice translations in each direction, with \( \lambda = 12 \, \text{Å} \). b). Value of the exchange energy as a function of the angle between consecutive layers for \( k_f = 1.6779 \times 10^{10} \, \text{m}^{-1} \).
Fig. 3. Temperature dependence of the hyperfine field for GdAl₃. The solid line is the MFT calculation for $J = 7/2$.

The simplest antiferromagnetic model that all ions within one plane are ferromagnetically coupled and nearest neighbour planes are antiferromagnetically coupled to that plane, we have determined the minimum energy for a range of values of $k_f$ by allowing the moments in consecutive planes to be rotated an angle $\omega$ with respect to the plane below. Hence, $0^\circ$ corresponds to ferromagnetism and $180^\circ$ to simple antiferromagnetism. As can be seen from the results in fig. 2a, the structure is ferromagnetic for $k_f < 1.678 \times 10^{10}$ m$^{-1}$, and above this value the structure is helical yielding various values of $\omega$, including a pure antiferromagnetic state ($\omega = 180^\circ$).

Magnetization results [6], reveal a spin-flop transition at 6 T. However, this transition may in fact be a transition from a helical structure to a pure antiferromagnetic one as in holmium metal. This can be seen, for example, in fig. 2b where an increase in the energy can move the system to a new state of equilibrium at a different value of $\omega$. It must be kept in mind here that we have chosen the simplest model for use in the calculations and the actual structure may be more complicated. Neutron diffraction studies are clearly needed.

The temperature dependence of the magnetic hyperfine field is shown in fig. 3. The solid line is the result expected from Molecular-Field Theory for $J = 7/2$. This abrupt decrease in field close to 17 K is similar to that observed in the frustrated system MnO [7], ($\theta_p/T_N = 5.3$). The lack of agreement between our results and MFT may be attributed to the relief of magnetic frustration at the Néel temperature and the strong exchange interactions indicated by the magnitude of the paramagnetic Curie temperature. ESR experiments done by Coles et
al. [8], indicate a large increase in the linewidth between $|\theta_p|$ and $T_N$. They attribute this increase to frustration.

4. Conclusion

Our studies have revealed two important facts concerning the magnetic properties of GdAl$_3$; (1) the magnetic moment is confined to the basal plane regardless of temperature, (2) the relief of frustration at the Néel temperature produces a near discontinuous transition similar to that observed in MnO. In addition, application of RKKY theory yield some interesting properties of this system, most important being that the magnetic ground state may, in fact, be helical.

References