CRYSTAL FIELD AND EXCHANGE INTERACTIONS IN DyT_4Al_8 ($T = \text{Fe}$ and Mn)

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ABSTRACT

We investigated the magnetic excitations in polycrystalline samples of hard magnet related compounds DyFe_4Al_8 and DyMn_4Al_8 by neutron spectroscopy. For both compounds the magnetic spectra at energies below 40 meV are dominated by the response of the Dy^{3+} ions. In DyMn_4Al_8 we observed pure crystal-field transitions within the Dy^{3+} $J=15/2$ ground multiplet which is split into 8 doublets under the low point-group symmetry of $4/\text{mmm}$. In DyFe_4Al_8 the Dy crystal-field-split states are perturbed by the molecular fields of the ordered Fe sublattice.

INTRODUCTION

A new class of hard-magnet related materials, RFe_4Al_8 ($R = \text{Tb}, \text{Dy}$)¹⁻³, which belongs to the ThMn_{12} structure type has gained much interest recently. In many cases the hard magnetic materials are intermetallic compounds of transition metals (e.g., Fe), rare earths (R) and additional nonmagnetic elements. The technologically important magnetic properties of such compounds (high Curie point, large crystalline and magnetic anisotropy, and easy magnetization direction, etc.) are determined by the microscopic properties of the R and T ions. These microscopic properties are controlled to a large extent by the effects and interplay of crystal and molecular fields. Therefore, an understanding of the systematics of various magnetic interactions involving the f- and d-electrons is one of the most important aspects in materials research of hard magnetic systems.

The RFe_4Al_8 materials is complementary to the well-known $\text{R}_2\text{Fe}_{12}\text{B}$ hard magnets. However, unlike the $\text{R}_2\text{Fe}_{12}\text{B}$ materials of which the crystal structure consists of two crystallographically distinct R sites and six Fe sites, RFe_4Al_8 has a simpler body-centered tetragonal crystal structure (space group $I4/\text{mmm}$) where the R and Fe atoms occupy a unique point symmetry of $4/\text{mmm}$ (positions 2a) and $2/\text{m}$ (8f), respectively. Moreover, by replacing the Fe with nonmagnetic Mn, the effects of crystal fields on a single R-ion in the paramagnetic phase and the additional R-R interaction in the ordered phase can be investigated without the complication of the f-d magnetic interactions.^{4,5} This makes the RT_4Al_8 ($T = \text{Fe}$ and Mn) system an attractive candidate for a systematic study of f-d magnetism of hard magnetic materials in progressing complexity from single-ion crystal-field effects to cooperative spin dynamics. In this paper we report the progress of a neutron-scattering study of magnetic excitations in DyMn_4Al_8 and DyFe_4Al_8 .

The Dy and T ($T = \text{Mn}$ and Fe) atomic positions in the unit cell of RT_4Al_8 are illustrated in Fig. 1. The magnetic structures of these compounds have been investigated by several workers.^{1,3,6-8} In DyMn_4Al_8 where the Mn d-electrons do not play a role in the magnetism of the solid, the Dy-Dy magnetic coupling via indirect exchange interactions is very weak, as indicated by the absence of magnetic ordering down to liquid helium temperatures.² In DyFe_4Al_8 , on the other hand, an ordering of the Fe magnetic moments parallel to the a-b plane with superimposed antiferromagnetic and ferromagnetic components was found near 77 K. At 4.2 K the Fe moments evolve to a spiral structure with a periodicity of about 60 Å with a propagation vector along the [110] direction. At the same time, a ferromagnetic ordering of the Dy moments develops, apparently induced by the Fe molecular fields. The Dy moment at 4.2 K was estimated to be $3.8 \pm 0.4 \mu_B$ per Dy ion. No incommensurate structure component of the Dy sublattice has been observed at low temperatures down to 4.2 K.¹ Therefore, by studying the magnetic excitation spectra of DyMn_4Al_8 and DyFe_4Al_8 one may gain insights into the relative strengths and possibly the interplay of the crystal and molecular fields in this system.

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Figure 1. A schematic drawing of the atomic positions of Dy and T (T = Fe or Mn) in the unit cell of DyT_4Al_8 . The Al atoms are not shown.

EXPERIMENTAL DETAILS

About 12 g each of polycrystalline powders DyMn_4Al_8 and DyFe_4Al_8 were prepared first by high-frequency electromagnetic induction melting the metals in an Ar atmosphere while the melt was turned over several times. The material was then wrapped in a Ta foil and annealed at 800°C under vacuum for a week. The sample was checked by x-rays and determined to have the desirable crystal structure with no observable impurity phases. The inelastic neutron-scattering scattering experiments were carried out using the High-Resolution Medium-Energy Chopper Spectrometer (HRMECS) at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. The sample was sealed inside an aluminum cell in the shape of a slab (of dimensions 7.5 cm X 10 cm) oriented at a 45° angle with the incident neutron beam. Such a geometry together with a thin (< 0.5 mm) sample minimizes the adverse effects of multiple scattering and neutron absorption by the sample. The sample was cooled by a closed-cycle helium refrigerator and the temperature was controlled to within about 0.5 K. The energy resolution ΔE in full width at half maximum of the spectrometer varies from about 4% of the incident energy E_0 in the elastic region to about 2% near the end of the neutron energy-loss spectrum.⁹ Two incident neutron energies of 20 and 40 meV were chosen for the measurements of magnetic excitations over the 0 - 35 meV region while maintaining good resolution. Background scattering was removed from the data using a combined empty-cell and neutron-absorber (Cd) runs. The measurement of elastic incoherent scattering from a vanadium standard provided intensity normalization between detectors and calibration of the observed scattering functions to absolute units of scattering cross section.

RESULTS AND DISCUSSION

The observed scattering functions $S(E)$ for DyMn_4Al_8 with E_0 of 20 and 40 meV are shown in Figs. 2 and 3, respectively. The inelastic ($E \neq 0$) spectra consist mainly of magnetic excitations since the data, obtained from low scattering angles ($< 20^\circ$), correspond to small wavevectors Q ranging from 1 to $3 \text{ \AA}^{-1}$. For small Q phonon scattering is expected to be weak and to show no sharp features (for powder samples). In DyMn_4Al_8 , the Hund's rule ground-multiplet, $^6\text{H}_{15/2}$, of the Dy^{3+} ions is split into eight doublets of $4\Gamma_6 + 4\Gamma_7$ by the crystal fields. The strong elastic

Figure 2. The observed spectra of DyMn₄Al₈ at 15 and 70 K with an incident neutron energy of 20 meV.

peaks in Figs. 2 and 3 contain the elastic scattering within the ground (and low-lying) doublet states, and other peaks at nonzero energies arise from transitions between different crystal-field states. At low temperatures corresponding to energies much smaller than the energy separation between the ground state and next higher state, the spectrum consists of only excitations from the ground states to upper unoccupied states. As the temperature increases, such excitation intensities decrease due to the depopulation of the ground state, and additional transitions originated from the occupied excited states give rise to new peaks in both the neutron energy-loss (excitation) and energy -gain (de-excitation) spectrum. Therefore, the peaks at about 6.5 and 9 meV in the 15-K spectra are likely to be the energies of some crystal-field states of Dy ions. Although these two peaks are better resolved in the 20-meV spectra, their widths are considerably larger than the corresponding energy resolutions at these energies. Thus it is possible that these two peaks may actually contain multiple unresolved, closely spaced lines. At 70 K the 20-meV spectrum shows two new sharp peaks at about 2.2 and 4 meV. There is also an indication of additional intensities occurring at ~6 meV. Magnetic excitations at energies between 10 and 35 meV, if any, are too weak to be observed unambiguously. Moreover, information regarding other possible states at $E > 35$ meV is not available from the present 20- and 40-meV runs.

Figure 3. The observed spectra of DyMn_4Al_8 at 15 and 70 K with an incident neutron energy of 40 meV.

Since magnetic-dipole-type transitions between any of the Γ_6 and Γ_7 states are allowed, there are in principle up to seven excitations from the ground state at low temperatures. However, some excitations may have too small a transition strength to be observable in the spectrum. At elevated temperatures various combinations of crystal-field transitions occur, giving rise to the possibility of many complex spectra. In order to describe the crystal-field level scheme of the R ions in the RT_4Al_8 compounds using a single-ion crystal-field model, a set of five crystal-field parameters, B_{20} , B_{40} , B_{44} , B_{60} , and B_{64} , is needed. Obviously, the present rather limited data are insufficient to determine these five parameters without additional information. Moze and co-workers^{4,5,10} have measured the low-energy crystal-field spectra of isostructural compounds of RT_4Al_8 ($T = \text{Tb}, \text{Ho}$ and Er) by neutron scattering and reported a possible set of crystal-field parameters for the three R ions. Since the R-ion environments are similar in these compounds, one would expect a relationship among these parameters, such as the corresponding n th-order crystal-field parameters (under the spherical tensor formalism) scaling roughly according to $\langle r^n \rangle = \int r^n R(r) d^3r$ (where R is the rare-earth ionic radial wavefunctions). We therefore attempted to seek a consistent pattern within the parameter sets of the Tb, Ho and Er compounds given by Moze and co-workers^{4,5,10} and then using it to produce an initial parameter set for DyMn_4Al_8 . However, we failed to find such self-consistency among the parameters sets of Moze *et al.*^{4,5,10} Due to the lack of a consistent connection among the parameter sets and the unavailability of neutron spectra covering a wide enough interval of energies, we feel that the present understanding of the crystal-field level schemes in the RT_4Al_8 system in terms of a crystal-field model is incomplete. Nevertheless, the salient features in the magnetic excitation spectra of the Tb, Ho, Er and Dy compounds behave as according to a typical crystal-field split level structure.

All the data support the notion of a rather weak f-f interaction between the R ions in the RMn_4Al_8 system.

Next, the excitation spectra of DyFe_4Al_8 obtained with $E_0 = 20$ meV at 15 and 30 K are shown in Fig. 4. At these temperatures the canted antiferromagnetic structure of the Fe moments in an ordered state is well developed. Hence we expect a combined effect of crystal and molecular fields on the R-ion wavefunctions. On the other hand, the Fe molecular fields are not strong enough to induce an ordered structure of the Dy ions. In fact, we observed magnetic spectra for DyFe_4Al_8 somewhat resembling to the corresponding ones for DyMn_4Al_8 (see Figs. 2 and 4). The crystal-field peaks of DyMn_4Al_8 in the 6-10 meV region can be compared to the broad band shifted to a slightly higher energy around 11 meV in DyFe_4Al_8 . The elastic intensity is similar in both compounds. This suggests that the magnitude of the net molecular fields at the rare-earth sites, resulted from a sum of the antiferromagnetic and ferromagnetic components of the ordered Fe moments in the sublattice, is rather small, producing only a small splitting and energy shift of the crystal-field lines.

Figure 4. The observed spectra of DyFe_4Al_8 at 15 and 30 K with an incident neutron energy of 20 meV.

It is of interest to compare the rare-earth magnetic spectra of RFe_4Al_8 and $\text{R}_2\text{Fe}_{12}\text{B}$. In the latter compounds the Fe moments order ferromagnetically, producing a large molecular field at the rare-earth sites. As a result, the rare-earth crystal-field structure is severely suppressed, and the excitation spectra are dominated by the molecular-field induced Zeeman transitions.¹¹ Similar ferromagnetic orderings of the Fe moments have recently been reported by Schäfer *et al.*^{8,12} in $\text{RFe}_{4+x}\text{Al}_{8-x}$ where excess Fe atoms replacing Al at the 8j sites resulted in a ferromagnetic ordering of the Fe-spin sublattice. One would expect the rare-earth crystal-field structure be strongly modified in the $\text{RFe}_{4+x}\text{Al}_{8-x}$ ($x \approx 1$) materials. Clearly, more measurements

of the magnetic response of these R-Mn-Al and R-Fe-Al systems over a wide energy range that is comparable to the overall splitting of the Hund-rule ground-multiplet energies are necessary to clarify the nature of the interplay of f-d magnetism. Such neutron-scattering studies are currently in progress.

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REFERENCES

1. W. Schäfer, M. Grönefeld, G. Will, and T. Gal, *Mater. Sci. Forum* **27-28** (1988) 243.
2. K. H. J. Buschow, J. H. N. Van Vucht, and Van den Hoogenhof, *J. Less Common Metals*, **50** (1976) 145.
3. I. Felner and I. Nowik, *J. Phys. Chem. Solids*, **39** (1978) 951.
4. O. Moze, R. Caciuffo, and K. H. J. Buschow, *Solid State Comm.* **76** (1990) 331.
5. O. Moze, K. H. J. Buschow, T. Osborn, Z. Bowden, and A. D. Taylor, *Solid State Comm.* **772** (1989) 249.
6. O. Moze, R. M. Ibberson, and K. H. J. Buschow, *J. Phys.: Condens. Matter*, **2** (1990) 1677.
7. J. Gal, I. Yaar, E. Arbaboff, H. Etedgi, F. J. Litterst, K. Aggarwal, J. A. Pereda, G. M. Kalvius, G. Will, and W. Schäfer, *Phys. Rev.* **B40** (1989) 745.
8. W. Schäfer, W. Kockelmann, G. Will, P. Fischer, and J. Gal, *J. Alloys Compounds*, **207/208** (1994) 316.
9. C.-K. Loong, S. Ikeda, and J. M. Carpenter, *Nucl. Instr. Methods* **A280** (1987) 381.
10. O. Moze, in "Supermagnets, Hard Magnetic Materials", Ed. G. J. Long and F. Grandjean (Kluwer, The Netherlands, 1990) p. 499.
11. M. Loewenhaupt, I. Sosnowska, and B. Frick, *Phys. Rev.* **B42** (1990) 3866.
12. W. Kockelmann, W. Schäfer, G. Will, P. Fisher, and J. Gal, *J. Alloys Compounds*, **207/208** (1994) 311.

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