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Bulk Magnetic and Neutron Diffraction Data for the Pyrochlore $Yb_2V_2O_7$: Evidence for Ferromagnetic Coupling between Yb^{3+} and V^{4+} Moments

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Bulk magnetic data for the pyrochlore material $Yb_2V_2O_7$ have been redetermined and compared with existing literature values. Susceptibility data from 300 to 77 K can be interpreted in terms of Curie–Weiss behavior above about 170 K, yielding the parameters $C_m = 6.0\ cm^3\ mole^{-1}\ K^{-1}$ and $\theta_c = -20$ K. This θ_c is slightly more negative than values reported previously. The saturation moment at 4.2 K is 5.3 $\pm$ 0.1 μ_B, significantly greater than that reported previously. The magnetization versus temperature curve shows evidence for the ferromagnetic ordering of the V^{4+} sublattice at 73 K and the ferromagnetic ordering of the Yb^{3+} sublattice at about 30 K. The shape of the magnetization–temperature curve is most easily interpreted in terms of ferromagnetic coupling between the V^{4+} and Yb^{3+} sublattices. Neutron diffraction data at 7 and 100 K confirm the ferromagnetic model and yield a value of 1.7 $\pm$ 0.2 μ_B for the Yb^{3+} moment. This reduced moment (free ion = 4.0 μ_B) is consistent with crystal-field parameters found for the isostructural $Yb_2Ti_2O_7$ which has a similar lattice constant.

Introduction

There are few known examples of compounds which are simultaneously ferromagnetic and semiconducting. Recently, a number of groups have investigated the pyrochlore, $Lu_2V_2O_7$, and have shown that it falls into this category (*1–5*).

Whereas there exists good agreement among the various groups about the basic magnetic properties of $Lu_2V_2O_7$, there are a number of discrepancies in the literature regarding the properties of the isostructural material, $Yb_2V_2O_7$. Bazuev *et al.* (*1*) reported inverse susceptibility data from 300 to 77 K which had an inflection at 190 K separating two linear regions. Very different Curie–Weiss parameters were derived for $T < 190$ K and $T > 190$ K. On the other hand Shin-ike *et al.* (*2*) reported Curie–Weiss behavior for $Yb_2V_2O_7$ from 300 to 77 K with no inflection at 190 K and reported a different set of Curie–Weiss parameters. These results are summarized in Table I. Later Bazuev *et al.* (*3*) reported bulk magnetization data as a function of temperature and applied field. From these results they suggested that $Yb_2V_2O_7$ might exhibit ferromagnetic coupling between Yb^{3+} and V^{4+} moments although an absolutely firm interpretation cannot be made from the experimental evidence.

In this work we have undertaken a comprehensive examination of the magnetic properties of $Yb_2V_2O_7$. We have remeasured the susceptibility and bulk magnetization and in addition have used neu-

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TABLE I

SUMMARY OF MAGNETIC SUSCEPTIBILITY DATA FOR $Yb_2V_2O_7$

C_M (cm^3 mole^{-1} K^{-1})[a]	θ_c (K)	Reference
4.6(300–190 K)	+10	(*1*)
2.9(190–77 K)	+69	(*1*)
5.2(300–77 K)	+11	(*2*)
6.0(300–170 K)	−20	This work

[a] A theoretical C_m assuming a spin-only contribution of 0.37 per V^{4+} and a free ion contribution of 2.57 per Yb^{3+} is 5.88.

tron diffraction to determine the magnetic structure directly.

Experimental

The sample of $Yb_2V_2O_7$ was prepared by reducing $YbVO_4$ with a CO/CO_2 buffer gas at 1400°C. Details of the preparation are found in (*6*). The lattice constant of this material, $a_0 = 9.950(2)$ Å, is in good agreement with values reported in (*1, 6*).

The magnetic data were collected using a nickel-calibrated, vibrating-sample magnetometer. Temperatures were measured with a gold–iron and chromel thermocouple.

The neutron powder diffraction data were collected at the McMaster Nuclear Reactor using a triple-axis spectrometer operating in the double-axis mode with a neutron wavelength of 1.40 Å. Data were collected in steps of 0.2° of 2θ. Approximately 7 g of the sample was placed in a cylindrical vanadium sample holder with a diameter of 7 mm. Data were collected at 7 and 100 K. Temperatures were maintained using a modified Displex refrigerator system and measured using a calibrated gold–iron and chromel thermocouple.

Results and Discussion

We began by reinvestigating the susceptibility versus temperature curve in an effort to clarify the discrepancy in previous reports (*1, 2*). Our results along with those from (*1*) are given in Fig. 1. The two sets of data are similar in form but differ in detail; in particular there is a deviation from Curie–Weiss behavior below about 170 K, but our low-temperature data are not linear. The Curie–Weiss constants derived from our data are listed in Table I along with those from previous investigations. Our C_m values are in reasonable agreement with those of Shin-ike (*2*) and with a free-ion C_m, but θ_c is more negative than reported previously. Note that θ_c for $Lu_2V_2O_7$, where only the vanadium sublattice is ferromagnetically ordered, is +83 K. As suggested in a preliminary account of this work (*4*), the negative θ_c value coupled with the hyperbolic shape of the inverse susceptibility curve is not inconsistent with a ferrimagnetic model for $Yb_2V_2O_7$.

Our saturation magnetization data are shown in Fig. 2 along with those from (*3*). Note that our value, 5.3 ± 0.1 μ_B is significantly greater than the 4.7 μ_B reported by Bazuev. A ferrimagnetic model, antiparallel coupling between free-ion Yb^{3+} moments (4.0 μ_B) and V^{4+} moments (0.94 μ_B), yields 6.14 μ_B while a ferromagnetic model (parallel coupling) yields 9.8 μ_B.

Magnetization versus temperature data

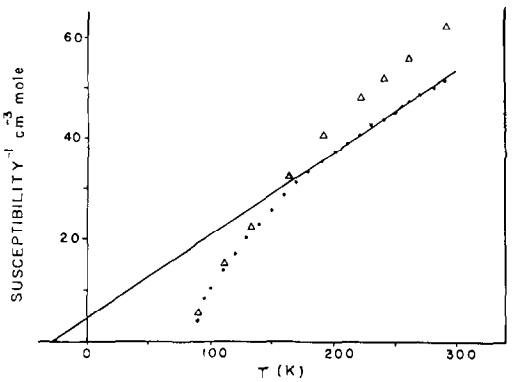

FIG. 1. Inverse susceptibility data for $Yb_2V_2O_7$ from 300 to 80 K. △, Bazuev *et al.* (*1*); •, this work.

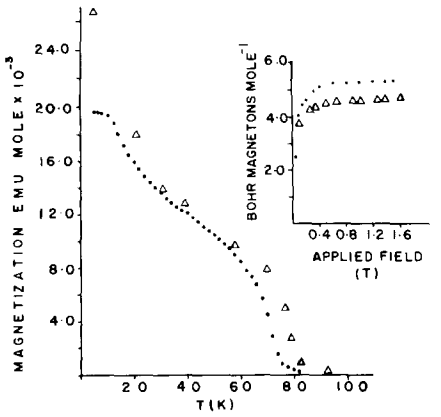

FIG. 2. Magnetization versus temperature for $Yb_2V_2O_7$. △, Bazuev *et al.* (*3*) applied field, 1.26 T; •, this work, applied field, 0.12 T. Inset: Magnetization versus applied field for $Yb_2V_2O_7$ at 4.2 K. △, Bazuev *et al.* (*3*); •, this work.

are also shown in Fig. 2. Again our data are in reasonable agreement with those of Bazuev et al. (*3*). Evidently, our data indicate saturation below 10 K while those of Bazuev *et al.* do not. The shape of this curve deviates from that of a simple Brillouin function below 30 K.

As suggested by Bazuev *et al.* (*3*), the simplest explanation for the data of Fig. 2 is ferromagnetic (parallel) coupling between the Yb^{3+} and V^{4+} sublattices assuming that the Yb^{3+} sublattice orders at about 30 K and the V^{4+} sublattice at 73 K, the same critical temperature as $Lu_2V_2O_7$ (*3*, *5*). A colinear ferrimagnetic model would predict a decrease in net magnetization below the ordering temperature for the Yb^{3+} sublattice. A difficulty with the ferromagnetic model is that the Yb^{3+} moment, calculated (assuming a V^{4+} moment of 0.94 μ_B) from the data of Fig. 2, is 1.7 ± 0.1 μ_B from our data or 1.3 μ_B from those of (*3*). Either moment is much reduced from the free-ion value of 4.0 μ_B. This reduced moment could result from crystal field interactions at the rate earth site or could be the apparent result of a canted or more complex arrangement of the Yb^{3+} and V^{4+} moments. In addition, while there exists ample precedent for ferrimagnetic ordering between $4f^n$ and $3d^n$ species, e.g., the rare earth iron garnets, no definitive evidence has been reported for ferromagnetic coupling in any compound known to us. Given only the evidence from bulk magnetic measurements on powder samples it is difficult to choose among alternative models; reduced-moment ferromagnetic, complex moment arrangement, and also the ferrimagnetic model which cannot be ruled out with certainty.

Neutron diffraction experiments were performed in order to distinguish between the possible models. A powder pattern taken at 7 K is shown in Fig. 3. All peaks can be indexed on the room temperature pyrochlore cell, space group $Fd3m$, a_0 = 9.95 Å. The absence of extra reflections rules out a complex moment arrangement and leaves only the colinear ferro- and ferrimagnetic models. Comparison with a room-temperature pattern (not shown) indicated that the intensities of only a few 7-K reflections were measurably enhanced.

Lacking a polarized neutron source and given the low neutron flux of the available reactor, we redetermined, at much longer counting times and therefore with greater

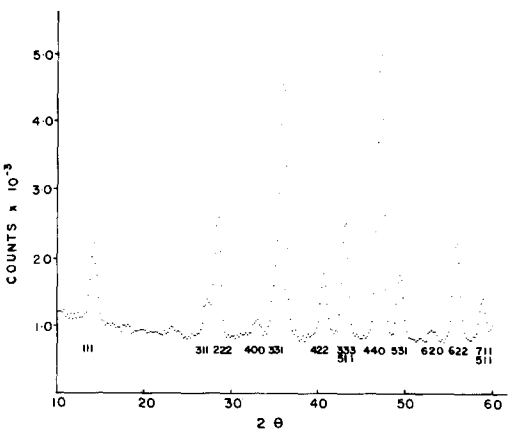

FIG. 3. Neutron powder diffraction data for $Yb_2V_2O_7$ at 7 K.

accuracy, the intensities of four reflections at 7 and 100 K. These data, together with the differences I_{hkl}(7 K) − I_{hkl}(100 K) = I_{hkl}(MAG), are listed in Table II. These values are compared with calculated I_{hkl}(MAG) for a ferromagnetic and a ferrimagnetic model. The scale factor was determined from the 100-K data and published values for the neutron scattering lengths (*7*). For both models the vanadium moment was taken to be 0.94 μ_B as determined from saturation magnetization data for $Lu_2V_2O_7$. Form factors for V^{4+} and Yb^{3+} were taken from (*8*) and (*9*), respectively. The ferromagnetic model assumes a Yb^{3+} moment of 1.7 μ_B and the ferrimagnetic model a moment of 3.4 μ_B, consistent with saturation magnetization data. Although the standard errors on I_{OBS}(MAG) are large, the data are in clear agreement with the ferromagnetic model. The ferrimagnetic model predicts that I_{111}(MAG) will be the strongest magnetic reflection whereas the ferromagnetic model predicts I_{111}(MAG) to be about one standard error and in fact the experimental value can be classed as unobserved. Agreement factors, $R = (\Sigma|F_{OBS} - F_{CALC}|)/\Sigma F_{OBS}$, are also listed and indicate the clear superiority of the ferromagnetic model. The magnitude of the Yb^{3+} moment determined from the three observed reflections is 1.7 ± 0.2 μ_B, in good agreement with our saturation magnetization data for $Yb_2V_2O_7$.

Having established the ferromagnetic model, we must consider a mechanism for the reduction of the Yb^{3+} moment below the free-ion value. Bazuev suggested that the crystal field quenches the orbital component of the moment in analogy with *d*-group transition metal ions (*3*). As spin-orbit coupling is generally much greater than the crystal field for the lanthanide ions this explanation is untenable. At present there exists no information regarding the crystal field at Yb^{3+} in $Yb_2V_2O_7$ but there have been two studies of crystal fields in the isostructural $Yb_2Ti_2O_7$ (*10, 11*). The point symmetry at the rare earth site in pyrochlore is $\bar{3}m$ and the nearest-neighbor coordination geometry consists of six equatorial O^{2-} forming a chair-like conformation with two axial O^{2-} at a much closer distance (*12*). Townsend and Crossley (*10*) analyzed the crystal field in terms of an essentially cubic Hamiltonian treating the trigonal distortion through an added second-order term:

$$\mathcal{H}_{CF} = B_2^0O_2^0 - B_4^0(O_4^0 - 20(2)^{1/2}O_4^3) + B_6^0\left(O_6^0 + \frac{35(2)^{1/2}}{4}O_6^3 + \frac{27}{8}O_6^6\right).$$

A best fit to magnetic susceptibility data is provided by the set of parameters $B_2^0 = 0$ K, $B_4^0 = -1.0$ K, and $B_6^0 = -0.006$ K. Interestingly, the fit is reported to be insensitive to the value of B_2^0. This zero value for

TABLE II

NEUTRON INTENSITY DATA FOR $Yb_2V_2O_7$ AND CALCULATED MAGNETIC INTENSITIES FOR FERROMAGNETIC AND FERRIMAGNETIC MODELS

hkl	I_{OBS} (100 K)	I_{OBS} (7 K)	I_{OBS} (MAG)	I_{CALC} (FERRO)	I_{CALC} (FERRI)
111	473 ± 8	471 ± 8	−2 ± 11	13	359
222	619 ± 7	716 ± 7	97 ± 11	102	120
400	89 ± 7	147 ± 7	58 ± 9	52	67
440	1729 ± 8	1767 ± 8	38 ± 12	36	78
	$R = \frac{\Sigma\|F_{OBS} - F_{CALC}\|}{F_{OBS}}$		—	R = 12%	R = 83%

the second-order term is surprising in view of the pronounced axial symmetry at the rate earth site. Point-charge calculations (*13*) and experimental values for the B_2^0 term from Mössbauer effect measurements on the closely related phases, $Er_2Ti_2O_7$ (*14*) and $Dy_2Ti_2O_7$ (*15*), indicate that the second-order term is far from negligible. Magnetization (*16*) and heat capacity data for $Dy_2Ti_2O_7$ and $Er_2Ti_2O_7$ (*17*) have been interpreted in terms of a lowest-lying $\pm |M_J(\mathrm{MAX})>$ doublet and highly anisotropic g-values, a situation best understood if the B_2^0 term is actually the dominant crystal-field parameter. The above evidence suggests that analysis of susceptibility data may not provide much information about the energy levels and wave functions of Yb^{3+} due to the crystal-field interaction in pyrochlores.

Dunlap *et al.* derived an entirely different set of crystal-field parameters from an analysis of the field dependence of ^{170}Yb Mössbauer data at 4.2 and 1.6 K (*11*). Using a Hamiltonian appropriate to $\bar{3}\,m$ symmetry,

$$\mathcal{H}_{CF} = B_2^0O_2^0 + B_4^0O_4^0 + B_6^0O_6^0 + B_6^6O_6^6,$$

and ignoring the sixth-order terms, the Mössbauer spectra can be fit using $B_2^0 = +21.0$ K and $B_4^0 = 0.2$ K. In the absence of a magnetic field, internal or external, the ground state for Yb^{3+} is a $|\pm\frac{3}{2}\rangle$ doublet separated by 18 K from $|\pm\frac{1}{2}\rangle$, 120 K from $|\pm\frac{3}{2}\rangle$, and 750 K from $|\pm\frac{7}{2}\rangle$. In $Yb_2V_2O_7$, an internal field will also be present. If the axes of the crystal field and the internal field are coincident, the ground state will be $|-\frac{3}{2}\rangle$ and the magnetic moment will be $\langle-\frac{3}{2}|gJ_z|-\frac{3}{2}\rangle = 1.71\ \mu_B$. This compares well with the Yb^{3+} moment determined from both magnetization and neutron diffraction data.

It is noteworthy that the crystal-field ground state found by Townsend and Crossely is $\Gamma_7 = \frac{1}{2}[3^{1/2}|\pm\frac{5}{2}\rangle - |\mp\frac{3}{2}\rangle]$. By inspection the magnetic moment is $\langle\Gamma_7|gJ_z|\Gamma_7\rangle = 1.71\ \mu_B$, identical to the value from the $|\pm\frac{3}{2}\rangle$ ground state. Thus both crystal-field schemes give a ground state magnetic moment consistent with the measured value.

The curvature in χ^{-1} vs T for $Yb_2V_2O_7$ (Fig. 1) may be due in part to the Boltzmann population of crystal-field excited states of Yb^{3+}. The Yb^{3+} contribution to the susceptibility above T_c was estimated by computing the difference, $\chi_{Yb_2V_2O_7} - \chi_{Lu_2V_2O_7}$. Values for $\chi_{Lu_2V_2O_7}$ were taken from (*5*). Calculated susceptibilities per Yb^{3+} ion based upon both sets of crystal-field parameters proposed for $Yb_2Ti_2O_7$, Dunlap *et al.* (*11*) and Townsend and Crossely (*10*), were compared with $\chi_{Yb^{3+}}$ measured as above. Neither model gave a very satisfactory fit to the data. This is not surprising as exchange effects will surely be important over the temperature range investigated. A more detailed investigation of exchange interactions and crystal-field states in $Yb_2V_2O_7$ and other members of this series is currently underway.

Conclusions

$Yb_2V_2O_7$ is shown to be ferromagnetic from neutron diffraction data. The Yb^{3+} moment was found to be $(1.7 \pm 0.2\ \mu_B)$ in good agreement with the value of $1.7 \pm 0.1\ \mu_B$ from magnetization measurements. The low-saturation moment for Yb^{3+} can be understood in terms of a $|\pm\frac{3}{2}\rangle$ or a Γ_7 ground state doublet. To our knowledge this is the first neutron diffraction evidence for ferromagnetic coupling between rare earth and transition metal moments in insulating or semiconducting materials.

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