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Structure and magnetic properties of the pyrochlore $Ho_2Ru_2O_7$: A possible dipolar spin ice system

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Crystal structure, magnetic susceptibility, and magnetization measurements on the pyrochlore system $Ho_2Ru_2O_7$ show that it behaves as an Ising spin one-half system with an effective ferromagnetic interaction between the holmium spins. It may therefore constitute another example of spin ice magnetism observed in some Ho- and Dy-based pyrochlore oxides.

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One of the recent and interesting findings in the area of magnetism is the observation of the so-called spin ice behavior[1] in some pyrochlore oxides of the chemical formula $A_2B_2O_7$ where A is a rare-earth ion and B is a transition-metal ion. The crystal structure of these materials is face centered cubic and the atomic arrangement comprises of both A and B cations situated on the vertices of corner sharing tetrahedra. Although the nearest-neighbor Heisenberg exchange between the magnetic rare-earth ions is very weakly antiferromagnetic[2] there is no magnetic order down to the milli-K temperature range. However it has been shown that the dipolar interactions are also comparable but slightly larger than the nearest-neighbor exchange interactions giving rise to a net ferromagnetic exchange. The lowest-energy state of a system of Ising spins located on the vertices of a tetrahedral network, with effective ferromagnetic exchange, and with anisotropy consistent with cubic symmetry, was shown to consist of two spins pointing into the center of the tetrahedron (which is also the $\langle 111 \rangle$ crystallographic direction), and two spins pointing out, thereby making the $\langle 111 \rangle$ direction of the cubic system as the local anisotropy axis.[3] However, this state is macroscopically degenerate with a large measurable entropy equal to 1.68 J/mole and this was experimentally confirmed by Ramirez *et al.*[4] by measuring the magnetic specific heat. The spin configuration of these systems can be mapped onto the structure of crystalline ice which has hydrogen atom disorder due to a mismatch between the local bonding requirements of the water molecule and the crystal symmetry. To satisfy these requirements ice has a structure in which two hydrogen atoms move closer to, and two move away from the midpoint of the oxygen-oxygen distance, i.e., a two-in two-out configuration of the displacement of the midpoints, which themselves form a tetrahedral configuration. This state was shown[5] to have a macroscopic entropy due to the $(\frac{3}{2})^{N/2}$ number of ways in which the two-in two-out arrangement could be achieved in a sample containing N water molecules. The experimentally measured entropy for both the water ice system and the spin ice system were consistent with this and confirmed the presence of analogous frustration and disorder effects in them.

Until now three pyrochlore systems have been shown to have this unusual spin ice magnetic behavior: $Ho_2Ti_2O_7$, $Dy_2Ti_2O_7$, and $Ho_2Sn_2O_7$. The only magnetic species in all of them are the rare earth ions, with the other cation (Ti or Sn) having no magnetic moment. It is therefore of interest to investigate other similar pyrochlore materials that may show spin ice behavior. In this study we report crystal structure and magnetization studies on the $Ho_2Ru_2O_7$ pyrochlore system where the transition metal ion (Ru) also has a partially filled $4d$ shell and possesses a magnetic moment. Our structure and magnetization measurements show that this system also has properties similar to the other canonical systems in spite of the presence of a magnetic moment on the other tetrahedral sublattice. Ito *et al.*[6] first reported susceptibility, specific heat and neutron diffraction studies on $R_2Ru_2O_7$ ($R=$Y and Nd) pyrochlore systems. It was observed that below a magnetic transition temperature ($T_G=76.5$ and 145 K, for the Y and Nd systems, respectively) the Ru spins were ordered into an almost long-range ordered antiferromagnetic state. The spin structure of Ru ions for $Nd_2Ru_2O_7$ was deduced from neutron Rietveld analysis based on the assumption that the Nd^{3+} spins remained paramagnetic down to the lowest temperature of 10 K in their study. The integrated intensities of the magnetic reflections could be successfully explained on this basis with the magnetic moment values of $1.36\mu_B$ and $1.18\mu_B$ for Ru ions in $Y_2Ru_2O_7$ and $Nd_2Ru_2O_7$, respectively. This observation suggested that the Ru sublattice and rare earth sublattice were independent of each other and it was therefore of interest to further study the $Ho_2Ru_2O_7$ pyrochlore by magnetization studies and to compare its behavior with the other Ho-based pyrochlore systems. In this report we show that the magnetization in this system also saturates to about half the value expected for Ho^{3+} ions which has been considered as very strong direct evidence[1] of single ion anisotropy and spin ice behavior in the other three canonical systems known so far.

Polycrystalline samples were prepared by thoroughly mixing the requisite quantities of RuO_2 and Ho_2O_3 (99.9% purity), heating at 850 °C for 24 h, grinding and pelletizing, and then sintering at 1125 °C for 48 h. The samples were air quenched by pulling them out of the furnace after the heat treatment. X-ray diffraction work was carried out using a Philips PW1730 x-ray diffractometer. Magnetic measurements were done on a Quantum Design SQUID Magnetometer (Model MPMS2) in the temperature range 5–300 K.

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TABLE I. Atomic coordinates and thermal parameters for $Ho_2Ru_2O_7$ from Rietveld refinement in space group $Fd3m$. The reliability factor, goodness of fit indicator, and Durbin Watson statistic were $R_{wp}=7.76$, $S=2.65$, and $d1=1.32$. The thermal parameters for Ho were constrained to be equal to Ru and the thermal parameters of both oxygen sites were also constrained to be equal.

Atom	Site	x	y	z	B_{eq}
O1	48f	0.339(2)	0.125	0.125	0.563
O2	8b	0.375	0.375	0.375	0.563
Ho	16d	0.5	0.5	0.5	0.065
Ru	16c	0.0	0.0	0.0	0.065

A Rietveld analysis of the x-ray data was carried out in the space group $Fd3m$, using RIETAN-2000 (Ref. 7) and the refinement results are shown in Table I. The lattice parameter value of $a=10.1417(5)$ Å was in very good agreement with the earlier reported value of 10.142 Å.[8] The Ho atoms had an eightfold oxygen coordination with two oxygen atoms (O2) at 2.1957(1) Å and six oxygen atoms (O1) at 2.43(1) Å, whereas the Ru atoms had only six equi-distant oxygen atoms (O1) at 2.01(1) Å. The bond angle Ru-O(1)-Ru was 126.7° whereas the bond angles Ho-O(2)-Ho and Ho-O(1)-Ho were 109.5° and 95.3°, respectively. The eight oxygen ions around Ho thus form a trigonally distorted cube of D_{3d} symmetry with the trigonal axis of the cube lying along the $\langle 111 \rangle$ crystallographic direction whereas the six oxygen atoms around Ru formed a slightly distorted octahedron. Figure 1 shows the substructure formed by the corner linked tetrahedra formed by the Ho atoms.

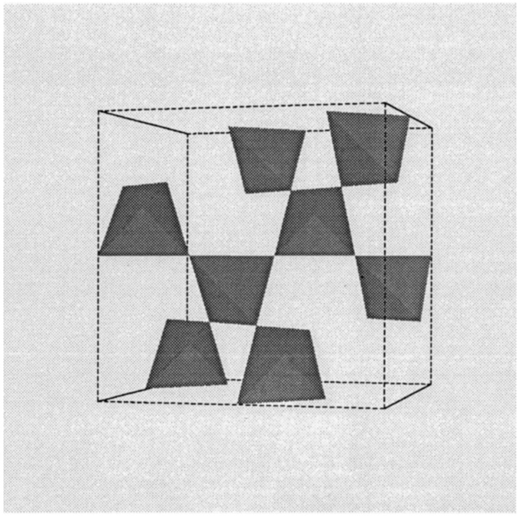

FIG. 1. Atomic arrangement of Ho ions in the pyrochlore structure of $Ho_2Ru_2O_7$. The network of corner sharing tetrahedara formed by the Ho ions is typical of the pyrochlore structure.

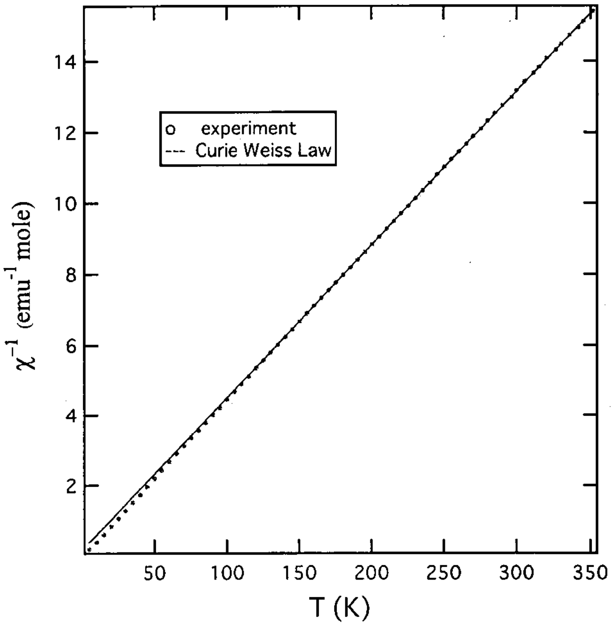

FIG. 2. Inverse susceptibility (χ^{-1}) as a function of temperature (T) after correction for demgnetization factor and Van Vleck paramagnetism. The solid line is Curie Weiss fit to data in the temperature interval 200–350 K.

Figure 2 shows the temperature dependence of inverse susceptibility measured in a field of 100 Oe between 5 and 350 K. The data was analyzed in the temperature range 200–350 K assuming a Curie-Weiss law $\chi=C/(T-\theta)$, where C is the Curie constant and θ is the Curie Weiss temperature. After correcting for Van Vleck paramagnetism and demagnetization factors[9] the effective magnetic moment per ion was determined to be 9.60(1) Bohr magnetons and $\theta=-4.0(5)$ K. Below about 200 K the inverse susceptibility curve starts deviating from linear behavior suggestive of a decrease in effective moment at lower temperatures. This was confirmed by measurement of magnetization versus applied field isotherms at low temperatures. Figure 3 shows the magnetization data at different temperatures up to a maximum field of 50 000 Oe. The magnetization data at low temperatures did not follow a Brillouin function dependence as expected for the $J=8$, $g_J=1.25$ ground state configuration ($^5I_8$) of the Ho^{3+} ion (Fig. 4). The magnetic moment per ion

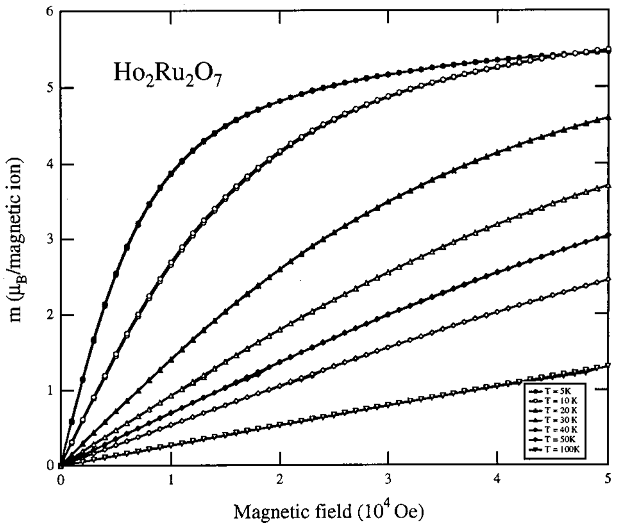

FIG. 3. Isothermal magnetization per nagnetic ion (m), as a function of applied field (H) at different temperatures.

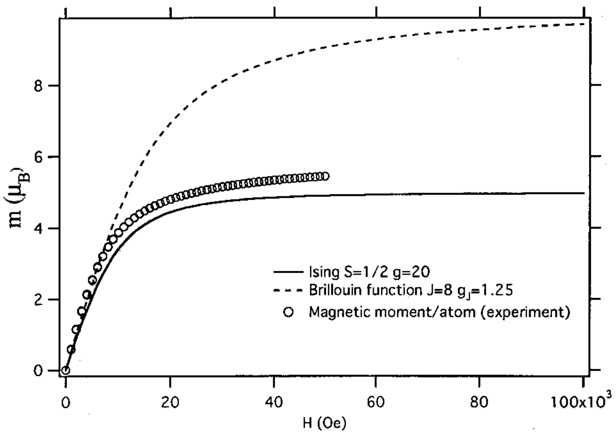

FIG. 4. The isothermal magnetization (m) per Ho ion at $T=5$ K, calculated on the basis of a Brillouin function dependence for free Ho^{3+} spins ($J=8, g_J=1.25$) and for Ising spins ($S=\frac{1}{2}, g_{\mathrm{eff}}=20$) using Eq. (1). The open circles are the experimentally observed data.

saturated to a lower value of about 5.4 Bohr magnetons per magnetic ion. This behavior shows the presence of a large single ion anisotropy effect due to the crystal field produced by the anisotropic local environment of Ho^{3+} ions. This magnetic behavior is also similar to that of the $Ho_2Ti_2O_7$ system and the observed magnetization behavior in this system also can be explained[9] by considering the system to be a one-dimensional Ising spin system ($S=\frac{1}{2}$) with an effective g factor equal to 20 in the $\langle 111 \rangle$ direction.

The magnetic moment per ion (m) for this model is given by[9]

$$m(H)=(1/gS)(k_BT/\mu_BH)^2\int_0^{g\mu_BHS/k_BT} x\tanh(x)\,dx, \tag{1}$$

where H is the applied field and T is the temperature. This equation was numerically integrated to get the field dependence of **m** and a comparison of the calculated result with the experimental data at 5 K is also shown in Fig. 4. In this analysis we have not taken into account the contribution of Ru magnetic moments to magnetization because the contribution to field dependence of magnetization from the antiferromagnetic ordered Ru subsystem is expected to be much smaller.

A complete understanding of the magnetic behavior of the $Ho_2Ru_2O_7$ system has to take into account the fact that the Ru^{4+} ions also form a network of corner sharing tetrahedra, and have a small magnetic moment ($S=1$), unlike the case of $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$, where Ti^{4+} ions do not have a moment. Ito *et al.*[6] observed that all the $R_2Ru_2O_7$ pyrochlore systems ($R=$rare earth and Y) showed a specific heat jump in the temperature range 75–160 K which was correlated with the rare-earth ionic size. Susceptibility and neutron diffraction studies were also reported on two of these systems viz. $Y_2Ru_2O_7$ and $Nd_2Ru_2O_7$ and irreversibility as well as magnetic ordering effects were observed at the temperatures of the specific heat jumps. This was attributed to an ordering of Ru moments into an ordered antiferromagnetic state but macroscopically exhibiting a spin-glass-like behavior due to geometrical frustration. In the $Ho_2Ru_2O_7$ system also our susceptibility data show a small irreversibility effect in zero field cooled and field cooled data (Fig. 5) below 95 K. This temperature is in very good agreement with the temperature of specific heat jump reported by Ito *et al.*[6] for this system. However, this implies a much larger Curie Weiss temperature than that deduced from the fit to the observed inverse susceptibility above 200 K. The contribution to total magnetic susceptibility from the lesser moment of Ru (as compared to Ho), as well as the large Curie Weiss theta value of the antiferromagnetic Ru sublattice, is therefore expected to be small as compared to the contribution from Ho moments. This is also borne out by looking at the measured susceptibility[6] of the $Y_2Ru_2O_7$ system, which has contribution from Ru moments only, and has absolute value about two orders of magnitude less than our system.

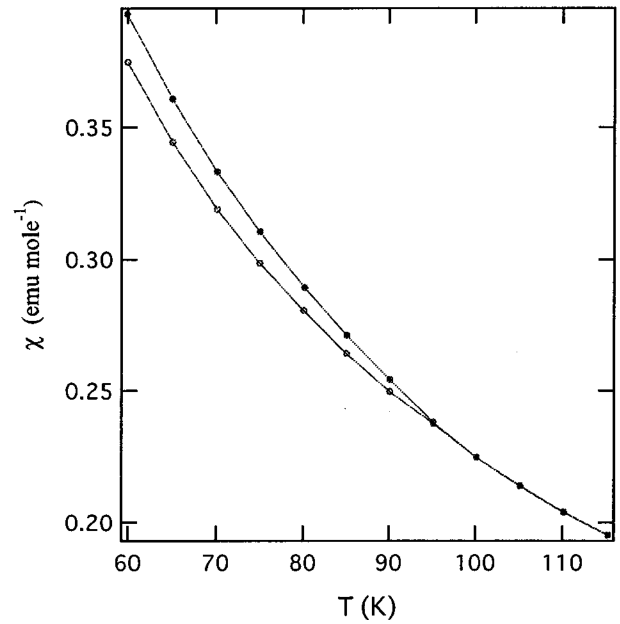

FIG. 5. Temperature dependence of susceptibility (χ) measured in zero field cooled state (open circles) and field cooled state (solid circles). The cooling field, as well as the measuring field, were 100 Oe.

We now discuss whether the exchange interactions in the Ho network also have characteristics of spin ice behavior similar to the other Ti-based pyrochlore systems. The two important energy scales for the spin ice system are the near-neighbor exchange between the Ising $\langle 111 \rangle$ moments (J_{NN}) and a dipolar energy scale $D_{\mathrm{NN}}=(\frac{5}{3})(\mu_0/4\pi)(\mu^2/r_{\mathrm{NN}}^3)$, where r_{NN} is the distance between the nearest Ho-Ho neighbors, μ is the magnetic moment of the Ho ion, and μ_0 is the free space permeability. These were combined[1] to define an effective nearest-neighbor energy scale J_{eff} as

$$J_{\mathrm{eff}}=J_{\mathrm{NN}}+D_{\mathrm{NN}}. \tag{2}$$

Subsequent to the important result of Bramwell and Harris,[3] who showed that the Ising spin system with single ion $\langle 111 \rangle$

anisotropy was frustrated, and gave spin ice ground state only for ferromagnetic near-neighbor interactions [or as long as the effective energy scale defined in Eq. (2) above was positive], it was further shown by Hertog and Gingras,[10] that the long-range dipolar interactions did not destroy the degeneracy of the spin ice state for $J_{\mathrm{eff}}/D_{\mathrm{NN}} \geqslant 0.09$. The experimentally observed value of Curie Weiss temperature obtained from fits to inverse susceptibility data at $T \gg \theta$ has contributions from exchange as well as dipolar interactions. The dipolar contribution depends on the shape of the grains and for spherical grains this contribution has been shown to reduce to zero.[11] As a simplifying approximation we assume spherical grains in our sample and attribute the Curie Weiss temperature to the exchange interaction alone. The near-neighbor exchange interaction estimated from the experimentally observed Curie-Weiss theta then has a small negative value $J_{\mathrm{NN}} = -0.9\ \mathrm{K}$ and the dipolar energy D_{NN} is estimated to be 2.37 K from the observed Ho-Ho distance (3.586 Å). The effective energy scale J_{eff} for the system is therefore positive and also satisfies the criterion of Hertog and Gingras[10] adequately.

The likely interaction between Ru and Ho moments is a small dipolar type interaction that is estimated to be about 0.24 K for Ho and Ru near-neighbor distances and moments. In the discussion above we therefore assumed that the magnetic behavior of the Ho and Ru subsystems at higher temperatures was independent of each other in a first approximation. It would be required to perform heat capacity and neutron diffraction studies at low temperatures to get more direct evidence for the establishment of the spin ice nature of the compound as well as the interaction between Ho and Ru spins.

In conclusion, we have shown that the $\mathrm{Ho_2Ru_2O_7}$ system has a crystal structure which gives large single ion $\langle 111 \rangle$ anisotropy, behaves as an Ising spin one-half system, and has effective ferromagnetic interaction between the holmium spins. It therefore has all the requisites of spin ice type behavior as observed for some of the other pyrochlore systems such as $\mathrm{Ho_2Ti_2O_7}$, $\mathrm{Dy_2Ti_2O_7}$, and $\mathrm{Ho_2Sn_2O_7}$ which exhibit spin ice magnetism.

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