Magnetic Ordering in the Spin-Ice Candidate Ho$_2$Ru$_2$O$_7$

C. R. Wiebe,$^{1,2}$ J. S. Gardner,$^{3,4}$ S.-J. Kim,$^1$ G. M. Luke,$^1$ A. S. Wills,$^5$
B. D. Gaulin,$^3$ J. E. Greedan,$^6$ I. Swainson,$^7$ Y. Qiu,$^{4,8}$ and C. Jones$^4$

$^1$Department of Physics and Astronomy, McMaster University, Hamilton, Ontario L8S 4M1, Canada
$^2$Department of Physics, Columbia University, New York, New York 10027, USA
$^3$Department of Physics, Brookhaven National Laboratory, Upton, New York, 11973-5000, USA
$^4$NIST Center for Neutron Research, Gaithersburg, Maryland, 20899-5682, USA
$^5$Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK
$^6$Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada
$^7$NPMR, NRC, Chalk River, Ontario K0J 1J0, Canada
$^8$Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, 20742, USA

(Dated: March 22, 2022)

Neutron scattering measurements on the spin-ice candidate material Ho$_2$Ru$_2$O$_7$ have revealed two magnetic transitions at $T \sim 95$ K and $T \sim 1.4$ K to long-range ordered states involving the Ru and Ho sublattices, respectively. Between these transitions, the Ho$^{3+}$ moments form short-ranged ordered spin clusters. The internal field provided by the ordered S=1 Ru$^{4+}$ moments disrupts the fragile spin-ice state and drives the Ho$^{3+}$ moments to order. We have directly measured a slight shift in the Ho$^{3+}$ crystal field levels at 95 K from the Ru ordering.

PACS numbers: 71.70.Ch, 75.10.-b, 75.25.+z

Frustration, a condition which describes the inability of a system to satisfy all of its individual interactions simultaneously, has become an important concept in the realm of condensed matter physics, being applicable to a wide range of phenomena such as high-$T_c$ superconductors, liquid crystal phase transitions, and protein folding. A renewed interest in geometrically frustrated magnets has resulted from this general interest in frustration and the discovery of new magnetic ground states. One of these new states is the spin-ice, which occurs on the pyrochlore lattice of corner sharing tetrahedra with weak ferromagnetic coupling between rare-earth ions subject to strong axial crystal fields. In particular, the ⟨111⟩ anisotropy of these sites promotes a “two-in, two-out” low temperature spin arrangement upon each tetrahedron, which is stabilized by dipolar interactions. The resulting ground state has a macroscopic entropy associated with the many ways that each tetrahedron can satisfy this condition independently of the other tetrahedra. The short-ranged order of the spins on each tetrahedra maps onto the problem of proton ordering in water ice. Pauling first realized the significance of the specific heat anomaly at the ice transition temperature as being due to the disorder at each oxygen site. An excellent agreement has been found between the spin ice model and physical properties including magnetization, specific heat, and neutron scattering experiments of the three spin ices, Dy$_2$Ti$_2$O$_7$, Ho$_2$Ti$_2$O$_7$ and Ho$_2$Sn$_2$O$_7$.

Recently, a new spin-ice candidate has been discovered by Bensal et al. - Ho$_2$Ru$_2$O$_7$. Whereas other spin ices of the formula $A_2B_2O_7$ only have one magnetic species on the A site, in Ho$_2$Ru$_2$O$_7$ both A and B sites are magnetic: Ho$^{3+}$ $J = 8$ spins and Ru$^{4+}$ S=1 spins. Previous studies on the closely related pyrochlores in the series R$_2$Ru$_2$O$_7$ (R = Y, Nd) have revealed that the Ru$^{4+}$ moments order at higher temperatures ($T \sim 100$ K). Ho$_2$Ru$_2$O$_7$ shows an anomaly in the magnetic susceptibility which agrees with these findings and suggests that the Ru$^{4+}$ moments order at $\sim 95$ K. However, this claim has not been verified until this work. This letter details the study of Ho$_2$Ru$_2$O$_7$ by neutron scattering to determine if the Ru$^{4+}$ moments order and, if so, to investigate the effect of the internal field on the Ho$^{3+}$ moments, which dominate the magnetic response. We will show that the Ru$^{4+}$ moments do order at $\sim 95$ K into a spin-ice like state of their own, while magnetic short range correlations develop between the Ho$^{3+}$ moments as the temperature is lowered further. The internal field associated with the Ru$^{4+}$ sublattice appears to be enough of a perturbation upon the Ho$^{3+}$ ions to induce a low temperature transition to a long-range ordered state at $\sim 1.4$ K which is not seen down to 50 mK of the other spin-ices.

We have made 20 g of Ho$_2$Ru$_2$O$_7$ powder with less than 1% excess Ru metal as determined by X-ray and neutron diffraction. The magnetic properties were measured between 2 K and 600 K using a commercial SQUID magnetometer. Elastic neutron diffraction measurements were performed with 2.37 and 2.0775 Å neutrons at Chalk River and NIST respectively from room temperature to 100 mK. Inelastic neutron scattering was performed using various wavelengths (3 to 9 Å) at the Disk Chopper Spectrometer (DCS) at NIST. Symmetry analysis calculations were carried out using the program SARA-Representational Analysis. Rietveld refinements were done using Fullprof.

High temperature susceptibility data was fitted to the Curie Weiss law and a Weiss temperature of -3(2) K was
FIG. 1: (a) Neutron scattering with 2.37 Å neutrons at T = 100 K and T = 20 K. The fits are to the crystal structure of Ho$_2$Ru$_2$O$_7$ (upper tick marks) and a magnetic structure (lower tick marks) described in the text. The residual of the 20 K fit is at the bottom of the plot ($R_p = 1.99$, $R_{wp} = 2.69$, $\chi^2 = 2.02$ at 100 K; $R_p = 2.82$, $R_{wp} = 3.73$, $R_{mag} = 40.9$, $\chi^2 = 3.73$ at 20 K). (b) The integrated intensity of the magnetic (111) reflection (as indicated in figure 1(a)). (c) $\psi_7$ and $\psi_8$ of the I.R. $\Gamma_3$, and the spin-ice state which arises from equal proportions of these basis vectors.

determined. This is in agreement with -4(0.5) K [9] found by Bensal et al. and is indicative of weak antiferromagnetic coupling. Assuming that the response is largely due to holmium, the Curie constant corresponds to an effective moment of 9.29(3) $\mu_B$, just short of the expected value for the Ho$^{3+}$ $^{5}I_8$ ion of 10.6 $\mu_B$ and again in agreement with Bensal et al.

Below 95 K, where a small field-cooled/zero-field-cooled divergence in the susceptibility data is seen, magnetic Bragg peaks appear which can be indexed with a $\mathbf{k} = 0$ propagation vector. These peaks are situated on top of diffuse magnetic scattering at low $Q$, which grows in intensity as one cools (see figure 2). This diffuse scattering is attributed to regions of short-ranged magnetic order (SRO) from the Ho$^{3+}$ species. Spin-ices have a characteristic diffuse scattering profile which is indicative of the ferromagnetic SRO (ie. an accumulation of scattering about $Q = 0$ [14]). However, an unambiguous determination of the nature of this scattering requires further study, preferably on single crystals. A slight broadening of the magnetic Bragg peaks with respect to the nuclear, and the reduced ordered moment with respect to expected $S = 1$ value (1.2(2) $\mu_B$ as compared to 2 $\mu_B$) indicates that not all of the Ru$^{4+}$ moments are ordered. From the (111) magnetic peak, one can estimate the correlation length of the Ru$^{4+}$ ordered spins to be ~ 250 Å, or about 25 unit cells. Further study of their ordering is not possible as the diffuse scattering is dominated by that of the much larger Ho$^{3+}$ moment.

The magnetic contribution to the powder neutron diffraction spectrum of Ho$_2$Ru$_2$O$_7$ below 95 K can be well described by ordering of the Ru$^{4+}$ moments according to the irreducible representation $\Gamma_9$ of the space group Fd$\overline{3}$m. [10] This irreducible representation has 6 associated basis vectors and may be thought of as involving a ferromagnetic structure along the $a$-axis, $\psi_7$, an orthogonal antiferromagnetic structure, $\psi_8$, and those related by alternative choices of the lattice axis (see figure 1). As neutron diffraction from a powder cannot distinguish the orientation of these structures with respect to the cubic axes, we restricted our analysis to the Hilbert space defined by $\psi_7$ and $\psi_8$. We note that equal proportions of $\psi_7$ and $\psi_8$ correspond to a spin ice state with the propagation vector $\mathbf{k} = 0$. At 20 K the ordering is found to be $0.881\psi_7 + 0.774\psi_8$, indicating that the Ru$^{4+}$ moments order with a spin ice-like local structure. It is
The Ho$^{3+}$ order according to the representation $\Gamma_8$ fitted by assuming that both the Ru$^{4+}$ and Ho$^{3+}$ ordered moments order at 90 K in Ho$_2$Ru$_2$O$_7$. Below 1.4 K, additional Bragg peaks appear in the diffraction data (figure 2). The data could only be well fitted by assuming that both the Ru$^{4+}$ and Ho$^{3+}$ moments order according to the representation $\Gamma_8$. Unlike the 20 K data, contributions from both Ru and Ho sublattices were required, and the final ordered moments are $1.8(6) \mu_B$ on the Ru and $6.3(2) \mu_B$ on the Ho. The Ru$^{4+}$ moments seem to be enhanced, but they are still within error of the 20 K values. The refined moments were oriented at 10° and 73° with respect to the uncompensated component indicating that the Ho$^{3+}$ ordering reduced the frustration of the Ru$^{4+}$ moments and increased their collinearity. The Ho$^{3+}$ moments themselves are more antiferromagnetic than ferromagnetic (with more $\Gamma_8$ character than $\Gamma_7$). Interestingly, the Ru$^{4+}$ moments orient themselves such that they cancel one component of the Ho$^{3+}$ spins, which in our definition is the a-axis. In the a-b plane, one can think of the two sublattices as being antiferromagnetically aligned, as shown in figure 2(d).

Bensal et al. concluded that in Ho$_2$Ru$_2$O$_7$, the long-range dipolar interactions among the Ho$^{3+}$ spins do not destroy the degeneracy of the spin-ice state, since the condition imposed by den Hertog and Gingras, $J_{eff}$ (effective nearest neighbor energy scale) / $D_{NN}$ (dipolar energy scale) $\geq 0.09$, is satisfied. However, we note that this is only true if the Weiss constant is adjusted for Van Vleck paramagnetism and demagnetization factors as found by Bramwell et al. for Ho$_2$Ti$_2$O$_7$. More precise measurements are needed on single crystals of Ho$_2$Ru$_2$O$_7$ to determine the Weiss constant (and thus, $J_{eff}$). Our experiments clearly show that the Ho$^{3+}$ moments do order, and do not form the spin-ice state.

High energy resolution inelastic neutron scattering was performed on 20 g of sample on the DCS. A representative spectrum at 220 K is shown in figure 3(b). The dispersionless features at finite energy transfer are a result of transitions between crystal field levels at higher energies than those measured on the DCS (E > 10 meV). Figure 3(a) shows that these excitations do not follow the form factor as predicted from isolated Ho$^{3+}$ moments, but they are modulated in $Q$ in a manner which follows the diffuse scattering seen at $\Delta E = 0$ meV. The scattering was performed on 20 g of sample on the DCS. A representative spectrum at 220 K is shown in figure 3(b). The dispersionless features at finite energy transfer are a result of transitions between crystal field levels at higher energies than those measured on the DCS (E > 10 meV). Figure 3(a) shows that these excitations do not follow the form factor as predicted from isolated Ho$^{3+}$ moments, but they are modulated in $Q$ in a manner which follows the diffuse scattering seen at $\Delta E = 0$ meV.

Below 1.4 K, additional Bragg peaks appear in the diffraction data (figure 2). The data could only be well fitted by assuming that both the Ru$^{4+}$ and Ho$^{3+}$ moments order according to the representation $\Gamma_8$. Unlike the 20 K data, contributions from both Ru and Ho sublattices were required, and the final ordered moments are $1.8(6) \mu_B$ on the Ru and $6.3(2) \mu_B$ on the Ho. The Ru$^{4+}$ moments seem to be enhanced, but they are still within error of the 20 K values. The refined moments were oriented at 10° and 73° with respect to the uncompensated component indicating that the Ho$^{3+}$ ordering reduced the frustration of the Ru$^{4+}$ moments and increased their collinearity. The Ho$^{3+}$ moments themselves are more antiferromagnetic than ferromagnetic (with more $\Gamma_8$ character than $\Gamma_7$). Interestingly, the Ru$^{4+}$ moments orient themselves such that they cancel one component of the Ho$^{3+}$ spins, which in our definition is the a-axis. In the a-b plane, one can think of the two sublattices as being antiferromagnetically aligned, as shown in figure 2(d).

Bensal et al. concluded that in Ho$_2$Ru$_2$O$_7$, the long-range dipolar interactions among the Ho$^{3+}$ spins do not destroy the degeneracy of the spin-ice state, since the condition imposed by den Hertog and Gingras, $J_{eff}$ (effective nearest neighbor energy scale) / $D_{NN}$ (dipolar energy scale) $\geq 0.09$, is satisfied. However, we note that this is only true if the Weiss constant is adjusted for Van Vleck paramagnetism and demagnetization factors as found by Bramwell et al. for Ho$_2$Ti$_2$O$_7$. More precise measurements are needed on single crystals of Ho$_2$Ru$_2$O$_7$ to determine the Weiss constant (and thus, $J_{eff}$). Our experiments clearly show that the Ho$^{3+}$ moments do order, and do not form the spin-ice state.

High energy resolution inelastic neutron scattering was performed on 20 g of sample on the DCS. A representative spectrum at 220 K is shown in figure 3(b). The dispersionless features at finite energy transfer are a result of transitions between crystal field levels at higher energies than those measured on the DCS (E > 10 meV). Figure 3(a) shows that these excitations do not follow the form factor as predicted from isolated Ho$^{3+}$ moments, but they are modulated in $Q$ in a manner which follows the diffuse scattering seen at $\Delta E = 0$ meV.
induce ordering upon the Ho\textsuperscript{3+} site and drive the system to order. It has been suggested that the dominant interaction is dipolar at low temperatures, with an interaction energy scale of 0.24 K.\textsuperscript{[9]} This is reasonable to assume, given the localized nature of the \textit{f} electrons of Ho\textsuperscript{3+}. Superexchange pathways are likely to be complicated between the two magnetic sublattices.

In conclusion, we find that Ho\textsubscript{2}Ru\textsubscript{2}O\textsubscript{7} is not a spin-ice, and has two magnetic ordering transitions; with Ru\textsuperscript{4+} and Ho\textsuperscript{3+} ordering at \(\sim 95 \) K and \(\sim 1.4 \) K, respectively. The magnetic properties of the rare earth pyrochlores are the result of a delicate balance between single ion anisotropy, exchange, and dipolar coupling.\textsuperscript{[2]} Although other rare earth pyrochlores such as Er\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}\textsuperscript{[22]} and Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}\textsuperscript{[23]} order, it is found that the corresponding structures vary considerably due to the roles played by these complicated interactions. We suggest that the Ho\textsuperscript{3+} ordering found in Ho\textsubscript{2}Ru\textsubscript{2}O\textsubscript{7} is due to the small internal field produced by the Ru\textsuperscript{4+} ordering. The subtle change in the Ho\textsuperscript{3+} crystal field scheme that we have observed is convincing evidence for this hypothesis.

C. R. Wiebe would like to acknowledge support from NSERC in the form of a PDF. The authors would like to thank the financial support of NSERC, EMK, and CIAR. This work utilized facilities supported in part by the National Science Foundation under Agreement No. DMR-0086210. Work at Brookhaven is supported by the Division of Material Sciences, U. S. Department of Energy under contract DE-AC02-98CH10896. The authors are also grateful for the technical support of the NPMR staff at Chalk River, and Ross Erwin at NIST.

FIG. 5: Schematic of the crystal field levels in Ho\textsubscript{2}Ru\textsubscript{2}O\textsubscript{7} (adapted from Rosenkranz \textit{et al.}\textsuperscript{[21]}). The transitions \( F' \) and \( G' \) are noted. As the Ru\textsuperscript{4+} moments order, the crystal fields are split slightly. The schematic is not to scale and the splitting is exaggerated for clarity.

| Temperature (meV) | Above 95 K | Below 95 K |
|------------------|------------|------------|
| 20 meV           | \( A_s \)  | \( F' \)   |
| 10 meV           | \( E_s \)  | \( F' \)   |
| 0 meV            | \( E_s \)  | \( F' \)   |

[1] J. E. Greedan, Chem. Mater. \textbf{10}, 3058 (1998).
[2] S. T. Bramwell \textit{et al.}, Science \textbf{294}, 1495 (2001).
[3] B. C. den Hertog \textit{et al.}, Phys. Rev. Lett. \textbf{84}, 3430 (2000).
[4] A. P. Ramirez \textit{et al.}, Nature \textbf{399}, 333 (1999).
[5] L. Pauling, J. Am. Chem. Soc. \textbf{57}, 2680 (1935).
[6] A. L. Cornelius \textit{et al.}, Phys. Rev. B \textbf{64}, 060406 (2001).
[7] O. A. Petrenko \textit{et al.}, Phys. Rev. B \textbf{68}, 012406 (2003).
[8] S. T. Bramwell \textit{et al.}, Phys. Rev. Lett. \textbf{87}, 047205 (2001).
[9] C. Sensal \textit{et al.}, Phys. Rev. B \textbf{66}, 052406 (2002).
[10] M. Ito \textit{et al.}, J. Phys. Chem. Solids \textbf{62}, 337 (2001).
[11] J. R. D. Copley \textit{et al.}, Chem. Phys. \textbf{292}, 477 (2003).
[12] A. S. Wills, Physica B \textbf{276}, 680 (2000), program available from \url{ftp://ftp.ill.fr/pub/dif/sarah/}
[13] J. Rodriguez-Carvajal, Physica B \textbf{192}, 55 (1993).
[14] H. Kadowaki \textit{et al.}, Phys. Rev. B \textbf{65}, 144421 (2002).
[15] Data analysis was completed with DAVE, which can be obtained at \url{http://www.ncnr.nist.gov/dave/}
[16] We follow the labeling scheme used by Kovalev in Ref.\textsuperscript{[17]}
[17] O. V. Kovalev, \textit{Representations of the Crystallographic Space Groups} Edition 2 (Gordon and Breach Science Publishers, Switzerland, 1993).
[18] N. Taira \textit{et al.}, J. Solid State Chem. \textbf{176}, 165 (2003).
[19] S. T. Bramwell \textit{et al.}, J. Phys. Cond. Matt. \textbf{12}, 480 (2000).
[20] J. S. Gardner \textit{et al.}, Phys. Rev. B \textbf{64}, 224416 (2001).
[21] S. Rosenkranz \textit{et al.}, J. Appl. Phys. \textbf{87}, 5914 (2000).
[22] J. D. Champion \textit{et al.}, Phys. Rev. B \textbf{68}, 020401(R) (2003).
[23] J. D. M. Champion \textit{et al.}, Phys. Rev. B \textbf{64}, 140407(R) (2001).