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Spin dynamics in $\text{Ho}_2\text{Ru}_2\text{O}_7$

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Abstract

The spin relaxation processes within the pyrochlore $\text{Ho}_2\text{Ru}_2\text{O}_7$ have been investigated by neutron scattering and bulk property techniques. A single-ion process, that is thermally activated, dominates the spin–spin relaxation spectrum above 2 K. Assuming Arrhenius behaviour, we found an activation energy $\Delta = (329 \pm 6)$ K and characteristic relaxation time $\tau_0 = (5.2 \pm 0.3) \times 10^{-12}$ s in the paramagnetic state, akin to those found in the spin ice, $\text{Ho}_2\text{Ti}_2\text{O}_7$. At low temperature ($T < 95$ K) the activation energy lowers and below 20 K the entropy and ac susceptibility are similar to that observed in other spin ice compounds within a 10 kOe field.

Pyrochlore oxides, with the general formula $\text{A}_2\text{B}_2\text{O}_7$, have had a resurgence of interest to physicists and materials scientists over the past ten years due to the variety of physical properties that these materials exhibit. Pyrochlores have been studied as potential candidates for storing fissile waste materials [1]. Several ruthenate pyrochlores are potential cathodes for solid oxide fuel cells [2]. The rare-earth (RE) titanium-based pyrochlore compounds have been of particular interest to physicists studying geometrically frustrated magnetism [3–5].

In the rare-earth titanate compounds, the trivalent rare-earth ion, RE^{3+} , occupies the 16d site of the cubic structure with the space group $Fd\bar{3}m$, which forms a pyrochlore lattice of corner-sharing tetrahedra. Only the RE^{3+} ion possesses a magnetic moment. Experimental studies have shown that there is a very rich spectrum of magnetic ground states: $\text{Gd}_2\text{Ti}_2\text{O}_7$ develops a partially ordered long-range structure just below 1 K [6]; $\text{Tm}_2\text{Ti}_2\text{O}_7$ possesses a non-magnetic (i.e. spin singlet) ground state with an energy gap of about 120 K [7]; and $\text{Tb}_2\text{Ti}_2\text{O}_7$ has been shown to remain dynamic down to 17 mK and is referred to as a ‘co-operative’

paramagnet [8]. Probably the most studied pyrochlores in the past ten years are $\text{Ho}_2\text{Ti}_2\text{O}_7$ and its Dy analogue [4, 9–11]. Their ground states are well described by an Ising doublet, with a weak ferromagnetic nearest-neighbour exchange and long-range dipole interactions. In these systems, it is argued that the strong Ising-like single-ion anisotropy along [111] frustrates the development of long-range ferromagnetic order. This so-called ‘spin ice’ state is analogous to the Pauling hydrogen disorder of water ice (H_2O), where each spin is equivalent to a displacement vector, for the hydrogen ions, situated at the mid-point between nearest oxygen ions.

Anisotropy has been shown to play a major role in the frustrated spin ice materials [9], the cooperative paramagnet, $\text{Tb}_2\text{Ti}_2\text{O}_7$ [8], and $\text{Er}_2\text{Ti}_2\text{O}_7$ that shows order by disorder [12]. Strong crystal-field interactions produce this anisotropy. However, there is limited information in the literature on the crystal-field interactions in the rare-earth pyrochlores, probably because of the unusually high energies involved. Rosenkranz and collaborators [13] have studied the crystal-field Hamiltonian in the spin ice $\text{Ho}_2\text{Ti}_2\text{O}_7$, and have come up with a level scheme that not only explains the single-ion properties of Ho^{3+} in this environment, but also extrapolates well onto the other rare-earth ions. They found the ground state to be an almost pure $|8, \pm 8\rangle$ doublet separated by over 220 K from the next group of excited states.

$\text{Ho}_2\text{Ru}_2\text{O}_7$ has many bulk properties similar to the known spin ice compounds [14, 15], and until recently was considered a potential member of the spin ice family [16]. $\text{Ho}_2\text{Ru}_2\text{O}_7$ has the same crystal structure as the spin ice compounds with a 0.2% larger lattice parameter. Unlike in the titanates, the crystallographic 16c site possesses a magnetic species, complicating the spin–spin interactions and possibly disturbing significantly the crystalline electric field level scheme of the Ho^{3+} ion, with the presence of a molecular field. Previous studies on the ruthenates have shown that the $S = 1$, Ru^{4+} spin orders between ~ 70 and 160 K depending on the rare-earth ion, and that in $\text{Ho}_2\text{Ru}_2\text{O}_7$ this transition is at ~ 95 K [14, 15, 17]. Wiebe *et al* [16] then showed that the Ho^{3+} sublattice also orders, at 1.4 K. These two magnetic species form two independent lattices of corner-sharing tetrahedra that order into a structure similar to the short-range order seen in spin ice materials. Each magnetic moment is slightly tilted from the local easy axis, creating a long-ranged ordered ferromagnet. The authors reported that the sharp magnetic Bragg peaks, associated with the order of the $S = 1$, Ru^{4+} ions, were not resolution limited; however, a correlation length of over 200 Å (or 20 unit cells) was found. This ordered $1.2 \mu_{\text{B}}$ Ru^{4+} moment will create a small but finite internal field, which we suggest is equivalent to between 1/2 and 1 T of an external field being applied to the system (see below).

How does this ordered moment affect the fragile spin ice state? Does the internal field, associated with the ordered B sublattice, alter the Ho^{3+} environment significantly? In this paper we attempt to answer these questions using neutron scattering, ac susceptibility and specific heat.

Polycrystalline samples of $\text{Ho}_2\text{Ru}_2\text{O}_7$ were synthesized by a solid-state method using high-purity oxide starting materials. Stoichiometric proportions of Ho_2O_3 and RuO_2 were heated at 850 °C for 24 h, pressed into pellets, and then sintered at 1150 °C for 48 h. This sintering process was performed in a sealed quartz tube because of the high volatility of RuO_2 . Room-temperature x-ray diffraction revealed no impurity and a cubic lattice parameter, $a = 10.122$ Å. Inelastic neutron scattering was performed using the time-of-flight spectrometer SV-29 at the FRJ-2 reactor, Jülich, with 1.17 and 1.59 Å neutrons. The neutron spin-echo experiment was performed with an incident neutron beam of mean wavelength, $\lambda = 6.0$ Å and a 15% spread at the NCNR facility in Maryland. The beam polarization was maintained by a 1 Oe field. NSE data were taken at values of $|Q|$ between 0.4 and 0.7 Å⁻¹. XYZ polarization analysis was performed for each individual echo scan, at the same $|Q|$, in order to relate the echo amplitude

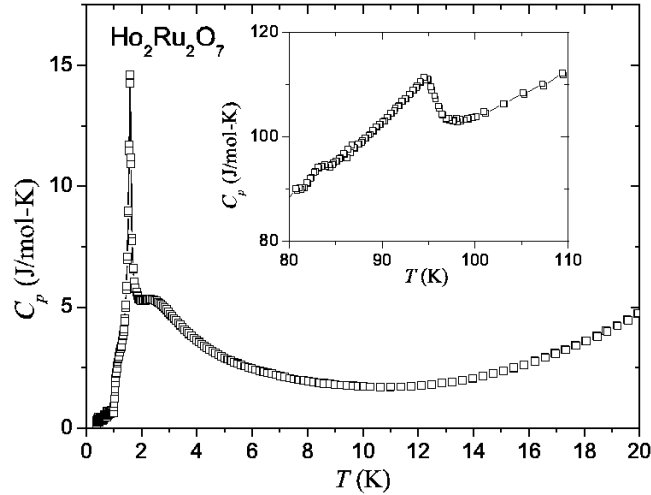


Figure 1. Specific heat of polycrystalline $\text{Ho}_2\text{Ru}_2\text{O}_7$ as a function of temperature around the Ru^{4+} (inset) and Ho^{3+} (main) ordering temperatures.

to the elastic magnetic-scattering intensity. This analysis separates magnetic scattering from coherent nuclear and incoherent spin and isotope scattering contributions that make up the total signal. Heat capacity measurements were measured using a thermal relaxation method above 0.35 K.

The temperature dependence of the specific heat, shown in figure 1, reveals two transitions. One at high temperatures, ~ 95 K (inset), was reported earlier by Ito *et al* [15] and is related to the ordering of the Ru sublattice. At lower temperatures ($T < 20$ K), a broad feature ubiquitous to many frustrated rare-earth systems is centred at ~ 3 K and a sharp, lambda-like transition exists at a slightly lower temperature. As we will discuss below, these features are related to the build-up of short- and long-range correlations between Ho spins respectively, and as far as we know have not been reported before. The broad feature is very reminiscent of that seen in $\text{Ho}_2\text{Ti}_2\text{O}_7$ and suggests that the Ho spin system tries to enter the spin ice state. Indeed, there is a considerable amount of missing entropy (see figure 5) in this system, similar to the other spin ices and first observed in $\text{Dy}_2\text{Ti}_2\text{O}_7$ [18]. However, the manifestation of a sharp lambda transition at a slightly lower temperature indicates these same spins overcome their frustration and undergo a transition into a long-ranged ordered state. This is confirmed by recent neutron diffraction [16] and advocates a difference in the local Ho environment.

In order to understand the nature of the magnetic order and the ground-state spin dynamics, it is important in any heavy rare-earth system to determine the single-ion crystal-field splitting. We therefore carried out inelastic neutron scattering measurements to investigate the crystalline electric-field energy levels of $\text{Ho}_2\text{Ru}_2\text{O}_7$. The point-group symmetry for the 16d site is trigonal and the degenerate $^5\text{I}_8$ energy levels of Ho are split into five E_g doublets and five singlets, exactly like that in $\text{Ho}_2\text{Ti}_2\text{O}_7$ [13]. Inelastic neutron scattering measures directly the energy levels of the crystal-field scheme. The modes are easily identifiable since they are independent of the momentum transfer, Q (being a single-ion effect), and their intensity follows the magnetic form factor appropriate for the species. The high-resolution INS performed by Wiebe and co-workers did not have the dynamic range to observe transitions out of the ground state to an excited level. Instead they looked at neutron energy gain data, where they observed transitions between excited CEF levels. What they label as F' in figure 4 of their paper [16] is a transition between the two levels shown in figure 2(C).

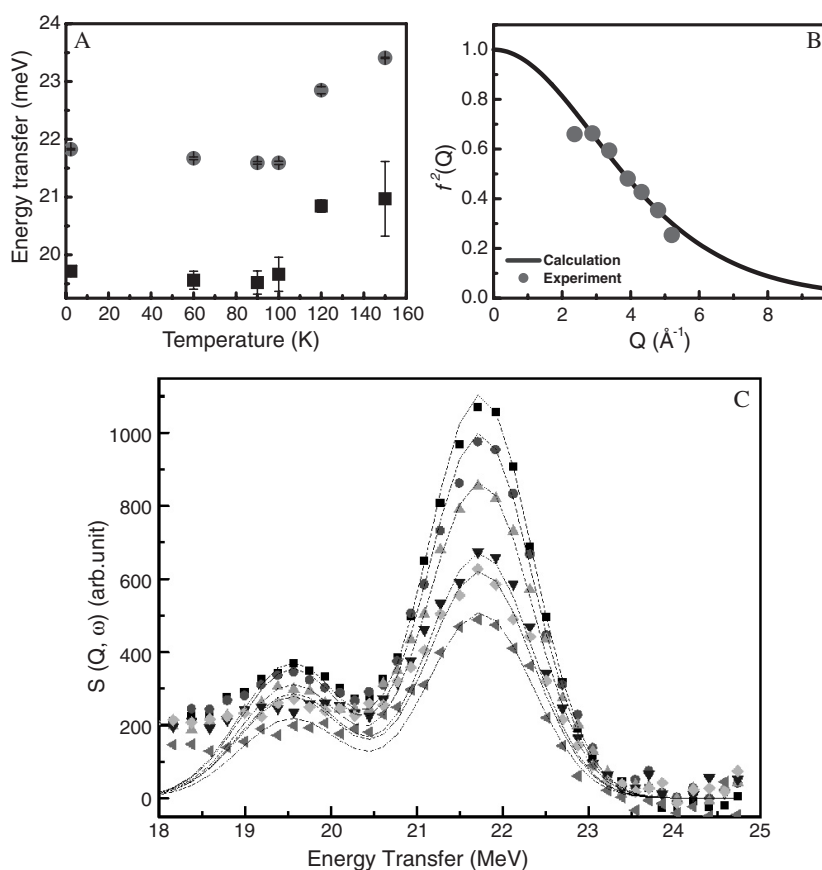


Figure 2. (A) The centre of mass of the two excitations (seen in (C)) as a function of temperature. These modes change substantially as the temperature is lowered below the Ru ordering temperature. (B) The intensity of the ~ 22 meV mode as a function of $|Q|$ at 90 K, plotted with the expected magnetic formfactor for paramagnetic Ho^{3+} spins. (C) Inelastic neutron scattering spectra of the first group of magnetic modes in $\text{Ho}_2\text{Ru}_2\text{O}_7$ taken at 90 K. From most to least intense the data were collected at 2.4, 3.3, 4.25, 5.1, 5.7, 6.3 and 6.9 \AA^{-1} . The lack of $|Q|$ dependence as a function of energy and the fact that the intensity follows the magnetic form factor for Ho^{3+} suggests that these excitations are associated with transitions between CEF levels.

In our time-of-flight experiment, no magnetic excitations out of the ground state were observed between 0 and 18 meV. A mode was observed around 10 meV, but the $|Q|$ dependence of this confirmed it as a phonon. As shown in figure 2, two $|Q|$ independent modes were observed around ~ 19.5 and 22 meV at 90 K. The energy gap to this first group of excitations is very similar to that seen in the original spin ice compounds, an indication that the energy scales are very similar. In spin ice compounds, this unusually large energy scale constrains the Ising-like moments to local $\langle 111 \rangle$ axes, which frustrates the dominant dipolar interactions in the system and leads to a frozen, non-collinear, spin disorder state below 1 K [10].

As mentioned above, in $\text{Ho}_2\text{Ru}_2\text{O}_7$ the spin frustration is overcome and long-range order sets in just below 2 K. We suggest that this must be due to the presence of the local field around the Ho^{3+} ion associated with the ordered Ru sublattice and the extra exchange path due to a magnetic species on the B-site of the cubic pyrochlore structure since the lattice parameters are so similar. To study this further we have performed a neutron spin echo (NSE) experiment. NSE

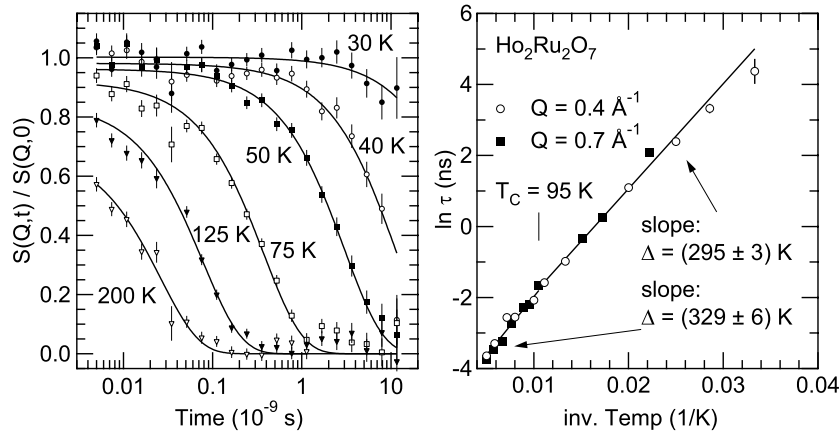


Figure 3. Measured spectra of $\text{Ho}_2\text{Ru}_2\text{O}_7$ at $Q = 0.4 \text{ \AA}^{-1}$ (left) and the dependence of the relaxation time on temperature (right) from two different positions in reciprocal space. The lines through the spectra on the left are a simple exponential, where the characteristic relaxation time is used in the Arrhenius plot on the right.

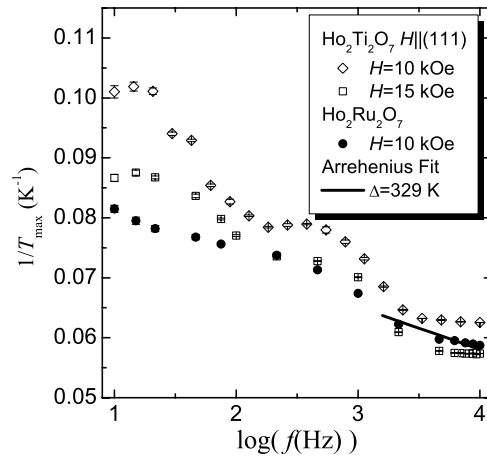


Figure 4. The relaxation process as observed from ac susceptibility measurements on a single crystal of the spin ice compound, $\text{Ho}_2\text{Ti}_2\text{O}_7$, and polycrystalline $\text{Ho}_2\text{Ru}_2\text{O}_7$ with various applied dc fields. This figure shows the peak position of the imaginary part of the ac susceptibility. An Arrhenius fit at high temperatures with a gap of 329 K is shown.

measures spatial and temporal correlation functions in matter. The quantity one measures is the intermediate scattering function, $S(Q, t)$, which can be easily related to the imaginary part of the generalized susceptibility. The dynamic range of the NSE technique is 10^{-12} – 10^{-7} s, which has been shown to be appropriate for the study of spin correlations in spin glasses, superparamagnetic particles and frustrated magnets [19–21], including $\text{Ho}_2\text{Ti}_2\text{O}_7$ [22].

Measurements at $|Q| = 0.4$ and 0.7 \AA^{-1} confirmed that the relaxation spectra measured by NSE were independent of $|Q|$ (see figure 3 (right)). This is not too surprising since neither Q -dependence was seen in the spin ice compounds studied [22] nor were collective modes seen in a high-resolution, inelastic neutron scattering (INS) study of $\text{Ho}_2\text{Ru}_2\text{O}_7$ by Wiebe *et al* [16]. The entire data set can be described well by an Arrhenius law with an attempt frequency of 1.6×10^{11} Hz, and an activation energy of $\Delta = 310 \pm 2$ K (not shown). By forcing a

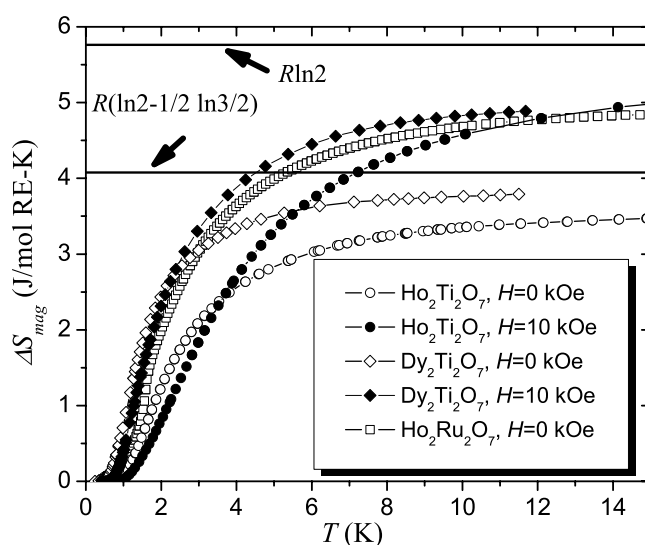


Figure 5. The magnetic entropy of $\text{Ho}_2\text{Ru}_2\text{O}_7$ at low temperatures in zero applied field. For comparison this plot also shows the magnetic entropy of the known spin ices in zero field (open symbols) and $\text{Ho}_2\text{Ti}_2\text{O}_7$ in 10 kOe (closed circles).

transition at 95 K, a statistically better fit can be achieved with activation energies of 329 ± 6 K and 295 ± 3 K above and below the transition respectively. This 34 K change in barrier height around 95 K is identical to the 3 meV (1 meV \equiv 11.6 K) change seen by INS to the first group of crystal-field levels. This characteristic energy is $\sim 20\%$ higher than the energy associated with the first group of crystal-field levels as determined by INS, suggesting that the effective barrier height is associated with more than just the gap between ground state and first excited crystal-field level. This discrepancy between the magnitude of the barrier and the gap to the first crystal-field level was also seen in $\text{Ho}_2\text{Ti}_2\text{O}_7$.

High-temperature ac susceptibility is also described well by an Arrhenius law with similar characteristic parameters. However, as the temperature is lowered below 20 K, the data deviate from this and become temperature independent. This is shown in figure 4 along with data from $\text{Ho}_2\text{Ti}_2\text{O}_7$, where an applied dc field is used to enhance the ac signal. The NSE data also deviate from the Arrhenius law at low temperatures. A temperature-independent process is often considered to be quantum mechanical in nature and has been discussed extensively in the spin ice compounds [22, 23]. As the temperature is lowered below 12 K the Arrhenius plot deviates from this plateau and again becomes temperature dependent. These data warrant lower temperature studies.

The missing low-temperature entropy (figure 5) is similar to that seen in spin ice when an external field of 1 T is applied, which implies that the internal fields associated with the ordered Ru sublattice are of this order. The relaxation processes in $\text{Ho}_2\text{Ru}_2\text{O}_7$ (figure 4) are also similar to those in the spin ice compound with an external 1/2 to 1 T of applied dc field. The transition to an athermal plateau region is rounded out due to the polycrystalline nature of the sample, but it is clear that the data are not explained by a single linear function.

Finally, another significant difference between $\text{Ho}_2\text{Ru}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$ is $S(Q, t)/S(Q, 0)$ as t approaches the low time limit of the NSE measurement window. In $\text{Ho}_2\text{Ti}_2\text{O}_7$ it has been shown that above 0.3 K this never reaches 1.0 as expected in a static system. A 5% loss in the signal is evident at temperatures above 300 mK [24], well below the spin ice freezing temperature (~ 2 K). It has been suggested that this slight inelasticity

is associated with a wobble around the easy Ising direction. In figure 3 it is clear that in Ho₂Ru₂O₇, $S(Q, t)/S(Q, 0)$ does not show this loss as $t \rightarrow 0$. This is usual when the Ho³⁺ ions order, but one might have expected it at higher temperatures, when the Ho ions are still dynamic and possess only short-range correlations. Wiebe *et al* [16] found the Ho³⁺ sublattice ordered with the moments pointing off the local $\langle 111 \rangle$ axis. This ‘pinning’, presumably due to the presence of the magnetic Ru sublattice, also affects the spin dynamics of the Ho ions in the regime where short-range, spin ice type, correlations exist.

To summarize, the presence of a magnetic B-site sublattice in the spin-ice compounds provides a way to relieve the frustration allowing the RE ions to order. Further studies with ordered and disordered magnetic B-site ions are now warranted. The internal mean field associated with the ordered Ru⁴⁺ ions clearly affects the CEF scheme and the spin dynamics over a wide range of temperatures. At low temperatures, even before the Ho sublattice orders, the wobble around the $\langle 111 \rangle$ easy axis is absent and at higher temperatures the single-ion properties of the Ho spins are changed.

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