LETTER TO THE EDITOR

Dynamical crossover in 'hot' spin ice

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Abstract
The magnetic dynamics of the spin ice material $Ho_2Ti_2O_7$ in its paramagnetic
('hot') phase have been investigated by a combination of neutron spin echo
and ac-susceptibility techniques. Relaxation at high temperatures ($T > 15$ K)
is proved to occur by a thermally activated single-ion process that is distinct
from the process that dominates at lower temperatures (1 K $< T < 15$ K). It
is argued that the low-temperature process must involve quantum mechanical
spin tunnelling, as quasi-classical channels of relaxation are exhausted in this
temperature range. Our results resolve a mystery in the physics of spin ice:
why has a 15 K ac-susceptibility peak been observed in $Dy_2Ti_2O_7$ but not in
$Ho_2Ti_2O_7$ or $Ho_2Sn_2O_7$?

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In a magnet, the thermal motion of the atomic magnetic moments or 'spins' can usually
be pictured classically, even though it is strictly determined by quantum mechanics. Some
exceptions exist, such as $LiHoF_4$ [1], its relative $LiHo_\delta Y_{1-\delta}F_4$ [2], and the single-molecule
magnets [3], in which the spin can be thought of as confined to a double-well potential of
depth D arising from the crystalline electric field (CEF). At temperatures $T \ll D$, quasi-
classical spin reorientations are precluded, but spin relaxation may still occur. By analogy
with molecular systems, direct transitions of this sort, between degenerate $|\pm M_J\rangle$ states on

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either side of the barrier, are referred to as 'spin tunnelling'. In the single-molecule magnets direct and thermally assisted tunnelling is observed, while the weak quantum relaxation in LiHoF$_4$ is strongly enhanced by an applied transverse field. Schemes exist to harness such effects for quantum computation [4], but as D is small ($\sim$10 K for LiHoF$_4$ [5] and $\sim$50 K for Mn$_{12}$ [6]) the temperatures involved are low, with 'classical' processes dominating at $T > 1$ K.

In the 'spin ice' materials Ho$_2$Ti$_2$O$_2$ [7, 8] Dy$_2$Ti$_2$O$_7$ [9], and Ho$_2$Sn$_2$O$_7$ [10], the magnetic rare-earth ions R^{3+} occupy a cubic pyrochlore lattice of corner-linked tetrahedra [11]. The R^{3+} ground state is an almost pure CEF doublet separated by over 200 K from the first excited state [12], indicating that $D/k_B > 200$ K is much larger than in other magnets [1–3]. The Ising-like moments ('spins') are constrained to local $\langle 111 \rangle$ axes, which frustrates the dominant dipolar interactions in the system and leads to frozen, non-collinear, spin disorder below $\sim$1 K. The spin ice state is analogous to the Pauling hydrogen disorder of water ice (H$_2$O), with each spin equivalent to a hydrogen displacement vector situated on the mid-point of an oxygen–oxygen line of contact [11].

Our study was motivated by the frequency-dependent (ac-) susceptibility investigations of Matsuhira *et al* [13, 14] and Snyder *et al* [15, 16], which revealed a rich spectrum of dynamics in the spin ice materials. All spin ice compounds show a distinct susceptibility peak at $\sim$1 K which gives a frequency shift consistent with an activation energy of $\sim$20 K [12, 13]. For Dy$_2$Ti$_2$O$_7$ [14–16], a further, unexpected peak in the ac susceptibility at $\sim$15 K is consistent with a Debye-type exponential relaxation process with activation barrier $\sim$210 K. However, the 15 K peak was not reported for the Ho compounds [16], suggesting mysterious differences within the series.

In this letter we isolate these spectral properties and, where possible, identify their origin. To do this, we use the elegant technique of neutron spin echo (NSE) [17], which involves a beam of spin-polarized neutrons executing a fixed number (say N) of spin precessions prior to striking the sample. The sense of the precession is then reversed by static magnetic fields near to the sample position. After N further precessions the original polarization is restored, unless scattering processes in the sample have produced a phase shift. A phase shift to the individual neutron due to inelasticity in the sample will be in most cases detected by a loss of the average scattered beam polarization, because N is proportional to the wavelength, which is spread by 16% FWHM around the mean value.

The neutron polarization is thus a measure of the sample response. In fact, the NSE technique directly establishes the dynamic correlation function $S(Q, t)$, known in scattering theory as the 'intermediate'-scattering function. The quantity $S(Q, t)/S(Q, 0)$ describes the relaxation of the Fourier components of the sample magnetization after a weak perturbation or random thermal fluctuation has displaced them from equilibrium.

In this way, the NSE technique can reveal the physical origin of spin dynamics in a way that bulk ac-susceptibility measurements cannot. This is because $S(Q, t)$ contains all the information, both spatial and temporal, about spin correlations. The dynamical range of the NSE technique is $\tau \sim 10^{-14}$–10^{-7} s, which has proved to be an appropriate timescale for revealing the spin dynamics of spin glasses and superparamagnetic particles [17–19]. By Fourier transformation, the NSE signal can be related to the imaginary part of the generalized susceptibility $\chi''(Q, \omega)$ which can be extrapolated to $\nu < 10^5$ Hz for comparison with the bulk ac susceptibility (either $\chi''(0, \omega)$ or $\chi'(0, \omega)$ by Kramers–Kronig inversion).

2. Experimental results

Figure 1(a) shows the normalized relaxation function $F(Q, t) = S(Q, t)/S(Q, 0)$ measured for a polycrystalline sample of Ho$_2$Ti$_2$O$_7$ on the IN11 instrument at the Institut Laue-Langevin,
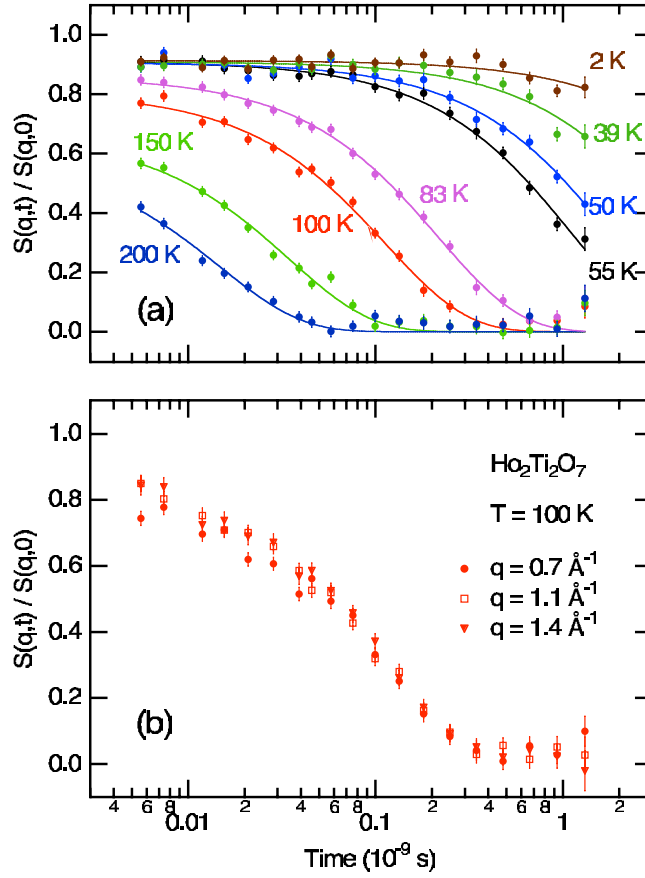
Figure 1. NSE results for $Ho_2Ti_2O_7$: (a) integrated over all Q and fitted to an exponential function; (b) as a function of Q, indicating negligible Q-dependence.

Grenoble, using a neutron wavelength of $\lambda = 5.5$ Å. The spectrometer was calibrated with a reference sample that does not show dynamics on the timescale of this experiment. At all temperatures between 0.05 and 200 K the measured relaxation can be fitted with excellent precision to a simple exponential function:

$$F(Q, t) = (1 - B) \exp\{-\Gamma(T)t\}, \tag{1}$$

where $B = 0.09 \pm 0.01$. The fact that B is finite, that is $F(Q, t) \neq 1$ at $\sim 10^{-12}$ s, proves the existence of relaxation processes at short timescales beyond the resolution of the NSE technique. We suggest that these very fast processes might be associated with small incoherent oscillations of the spins about their $\langle 111 \rangle$ easy axes. Such processes cannot relax the more important magnetic fluctuations associated with spin reversals, and hence are unable to provide complete relaxation of the system. We do not comment on them further in this letter.

The frequency $\Gamma(T)$ can be fitted to an Arrhenius expression $\Gamma(T) = 2\Gamma_h \exp(-E_a/kT)$ with attempt frequency $\Gamma_h = 1.1 \pm 0.2 \times 10^{11}$ Hz (~ 5 K) and activation energy $E_h = 293 \pm 12$ K. The relaxation was found to be Q-independent (figure 1(b)), an important clue to its origin (see below). For the rest of the letter we shall refer to this exponential relaxation as the 'high' process, referring to its typical temperature range, with subscript 'h'.
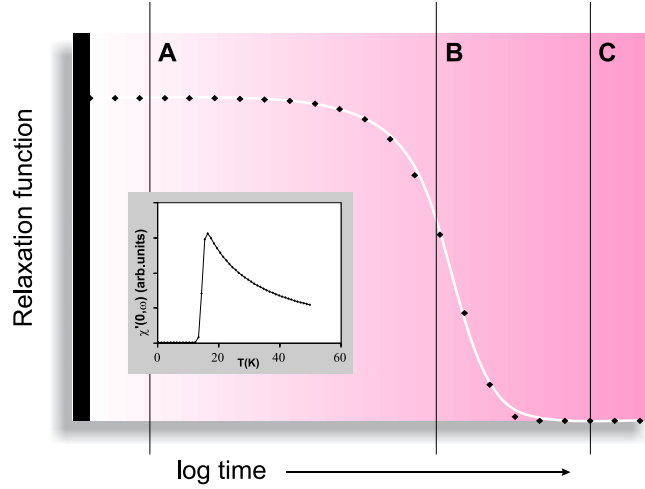
Figure 2. Inset: the extrapolated ac susceptibility $\chi'(0, 10^3$ Hz) corresponding to the 'high' process measured by the NSE technique, showing a peak at $\sim$15 K. Main figure: the schematic relaxation function in the ac-susceptibility time window, showing how the 15 K peak is revealed in the spin ice materials. Vertical lines A, B, C denote the 'cut-off' of $S(Q, t)$ due to the 'low' process. A: the peak is not present, as all relaxation is due to the low process and χ' changes smoothly through 15 K. B: the peak is just observed, as in $Dy_2Ti_2O_7$. C: the peak is clearly observed, as all relaxation is due to the high process. An applied field reveals the peak by shifting the cut-off to longer times (case C), while diamagnetic dilution eliminates it by shifting the cut-off to shorter times (case A). Note that under certain experimental conditions, the relaxation may not occur in the ac-susceptibility time window.

By Fourier transforming the relaxation function as described above (and approximating the 'detailed balance' factor of neutron scattering as $k_B T/\hbar\omega$) we find

$$\chi(Q, \omega) = \chi(Q)\{\Gamma(T)^2/(\Gamma(T)^2 + \omega^2) + i\omega\Gamma(T)/(\Gamma(T)^2 + \omega^2)\}. \qquad (2)$$

This function can be used to extrapolate the NSE response, from which ac susceptibility versus temperature curves can be derived; $\chi(Q = 0)$ can be well approximated as $\sim 1/T$ in the relevant temperature range. As illustrated in figure 2 (inset), this analysis implies that a susceptibility peak should be observed around 15 K. As one was not previously observed in low field, we have performed measurements on single-crystal samples of $Ho_2Ti_2O_7$ in an external field of up to 1 T applied along a cubic $\langle 111 \rangle$ direction. The results (figure 3) reveal the presence of the expected peak in finite field; in fact, when χ'' is normalized to $\chi(0)$, it can be seen even in very low field. Its frequency shift implies the expected activation barrier of $\sim$250 K.

Below $\sim$15 K, χ' continues to increase and our data confirm the presence of a $\sim$1 K peak [13] associated with an activation energy $E_l \approx 20$ K and attempt frequency $\Gamma_l \times 10^{10}$ Hz ($\sim$0.5 K). If we could extrapolate this process into the NSE time window, it would be visible above $\sim$4 K. It is not, so the process cannot exist on timescales much shorter than $\sim$10^{-5} s and must be only weakly temperature dependent at $T > 4$ K (the analysis of [13], figure 4, also supports this conclusion). Henceforth we will call it the 'low' process, in reference to its temperature scale, with subscript 'l'. As the high process appears in the ac-susceptibility time window above $\sim$15 K, we conclude that the relaxation is of the high type up to the ac-susceptibility timescale, where the low process acts as a 'cut-off' to drive $S(Q, t)$ prematurely to zero. This interpretation is inescapable, given that the two processes compete to relax the same set of thermal fluctuations, as shown by the fact that the high process drives $S(Q, t)$ to
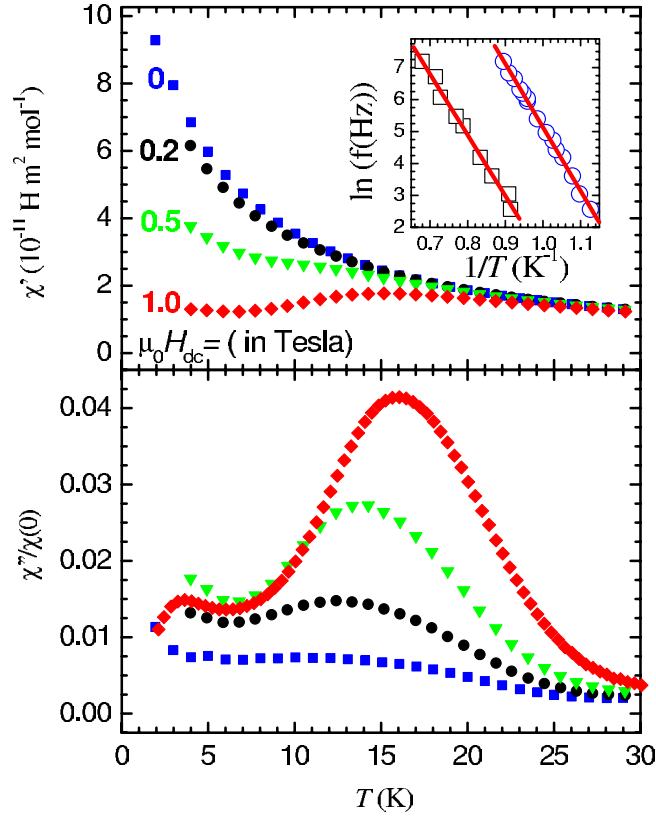
Figure 3. ac-susceptibility results for $Ho_2Ti_2O_7$. Main figure: measured with a field of 1 T applied along [111], revealing a ~15 K peak (upper panel: χ'; lower: $\chi''/\chi(0)$). Inset: an Arrhenius plot for the frequency shift of the ~1 K peak in polycrystalline $Ho_2Ti_2O_7$ (☐) and $Ho_{1.9}La_{0.1}Ti_2O_7$ (O) showing how doping increases the attempt frequency Γ_1 for the low-temperature process.

zero rather than some finite value, as would be the case if the two processes acted on physically distinct sets of spin fluctuations. This means that whichever of the two processes is the faster at a given temperature relaxes *all* thermal fluctuations in the spin system (except those on a very fast timescale, noted above). The NSE results likewise rule out additive contributions to $S(Q,t)$ or χ; the behaviour below 15 K reflects a change of spin-relaxation mechanism, not the gradual appearance of second, independent, contribution to the susceptibility.

The low process (which may include several processes) thus accounts for the increase in susceptibility below ~15 K and the peak at ~1 K. In order to 'see' a 15 K peak in $\chi(\omega)$, the low process has to be at sufficiently low frequency (i.e. long times) for the high process to provide significant relaxation in the ac-susceptibility frequency window (see figure 2). An applied field 'slows down' the low process, to reveal the peak. We have discovered that doping has the opposite effect: 5% diamagnetic dilution of the Ho sublattice leads to a remarkable 100-fold increase in Γ_s while E_s remains constant (figure 3 (inset)).

With regard to $Dy_2Ti_2O_7$ [14–16], it is now clear that the appearance of the 15 K peak in this material reflects a slower intrinsic rate of the low process, as explained in figure 2. In this material, diamagnetic dilution [15, 16] again speeds the low process up, thus eliminating the 15 K peak. This doping effect has previously been interpreted [15, 16] as evidence of a cooperative high-temperature process. Although that is a logical deduction from the data

presented in [15, 16], it is not consistent with our NSE results (at least for the Ho analogue of this material) that have established that the appearance or disappearance of the 15 K peak depends on the *relative* rates of the two processes. The slower intrinsic low-temperature dynamics in $Dy_2Ti_2O_7$ might correlate with the lower energy scale for spin ice freezing [11], or the fact that Dy, unlike Ho, is a Kramers ion.

3. Physical interpretation of the results

The high process has two properties that identify its origin:

  (i) it has activation energy close to the first group of CEF levels at 240–340 K [12];
 (ii) it gives rise to Q-independent scattering indicating negligible two-spin correlations.

These two facts establish that it is a single-ion spin flip mechanism, either quasi-classical (a Debye process) or by thermally assisted quantum tunnelling via one or more crystal field level. The characteristic attempt frequency of $\sim 10^{11}$ Hz (~ 5 K) is significantly less than $k_B D/\hbar$, which might imply a quantum mechanical transition matrix element of much less than unity entering into the quasi-classical expression.

Below 15 K, fast Arrhenius-type relaxation is replaced by slow, weakly temperature-dependent relaxation. In a molecular system this would typically be interpreted as indirect evidence of quantum tunnelling, either resonant or thermally assisted. Here the low process remains only weakly temperature dependent down to $T < 4$ K where it becomes thermally activated, with E_l much less than D and closer to the energy scale of the dipolar interaction, ~ 2.35 K per near neighbour bond [11]. The gradual spin ice freezing below 4 K corresponds to development of a mean field, which splits the Ho^{3+} ground state. Therefore, the spin configurations that facilitate the low process are thermally populated only in the 'hot' paramagnetic phase ($T > 4$ K), where Ho^{3+} ground state degeneracy remains.

The classical barrier, $D > 200$ K, is insurmountable below 15 K, so spin relaxation in this regime *must* occur by quantum tunnelling. We suggest that the most likely origin is the unusually strong, slowly fluctuating, dipolar field arising from neighbouring spins fixed at 109.5°. The resulting torque cannot be easily minimized because of the geometric frustration. The transverse component of this effective field (i.e. off-diagonal terms in the dipolar interaction) will mix higher $|M_J\rangle$ states into the $|\pm 8\rangle$ ground state doublet, facilitating a finite rate of spin inversion. An applied field, similar to the system freezing, will suppress these channels by removing degenerate spin configurations, while defects appear to increase the number of suitable channels. It is easy to imagine defect-assisted processes in spin ice: for example, flipping of a spin chain bounded by two defects is allowed by the ordering rules [11]. Furthermore, defects are relevant in water ice [20] and have been discussed in relation to closed-loop excitations [11, 21, 22] in the dipolar spin ice model. In general, it is possible that there are several low-temperature processes, perhaps involving spin clusters, as predicted for spin glasses [23].

In conclusion, $Ho_2Ti_2O_7$ presents a very different scenario to other quantum magnets [1–3], as here the tunnelling dynamics are an intrinsic consequence of the geometric frustration that prevents magnetic ordering. Cooperative quantum tunnelling occurs over a broad range of unusually high temperatures, from $T \approx 1$–15 K, while a single-ion process dominates above 15 K. The complementarity of the ac-susceptibility and NSE techniques has thus allowed us to elucidate the main relaxation processes in the 'hot' paramagnetic phase of $Ho_2Ti_2O_7$ and the other spin ices, which we believe may represent a remarkable new class of quantum dynamical magnet.

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