Quantum-Classical Reentrant Relaxation Crossover in $Dy_2Ti_2O_7$ Spin Ice

J. Snyder,[1] B. G. Ueland,[1] J. S. Slusky,[2] H. Karunadasa,[2] R. J. Cava,[2] Ari Mizel,[1] and P. Schiffer[1,*]

[1]*Department of Physics and Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania 16802, USA*

[2]*Department of Chemistry and Princeton Materials Institute, Princeton University, Princeton, New Jersey 08540, USA*

(Received 21 February 2003; published 5 September 2003)

We have studied spin relaxation in the spin ice compound $Dy_2Ti_2O_7$ through measurements of the ac magnetic susceptibility. While the characteristic spin-relaxation time (τ) is thermally activated at high temperatures, it becomes almost temperature independent below $T_{\text{cross}} \sim 13$ K. This behavior, combined with nonmonotonic magnetic field dependence of τ, indicates that quantum tunneling dominates the relaxational process below that temperature. As the low-entropy spin ice state develops below $T_{\text{ice}} \sim 4$ K, τ increases sharply with decreasing temperature, suggesting the emergence of a collective degree of freedom for which thermal relaxation processes again become important as the spins become strongly correlated.

DOI: 10.1103/PhysRevLett.91.107201 PACS numbers: 75.50.Lk

Geometrically frustrated magnetic materials, in which the geometry of the spin lattice frustrates the spin-spin interactions, have been shown to display a wide range of novel ground states [1,2]. There has been especially strong recent interest in the so-called "spin ice" pyrochlore materials (such as $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$) in which the rare-earth spins are highly uniaxial due to strong crystal fields [3]. Ferromagnetic and dipolar interactions between these spins on this lattice of corner-sharing tetrahedra are frustrated in a manner analogous to that of protons in ice leading to a variety of exotic behavior [4–16]. While the spin entropy freezes out only below $T_{\text{ice}} \sim 4$ K in $Dy_2Ti_2O_7$ [9], magnetic susceptibility studies show a strongly frequency-dependent spin freezing at $T \sim 16$ K [10,11]. In contrast to traditional spin glasses, the spin-freezing transition is associated with a very narrow range of relaxation times and thus represents a rather unusual example of glassiness in a dense magnetic system.

Here we report a study of the spin-relaxation processes in the spin ice compound $Dy_2Ti_2O_7$. We find that, while the characteristic spin-relaxation time is thermally activated at high temperatures, it becomes almost temperature independent below $T_{\text{cross}} \sim 13$ K. We interpret the data in terms of a crossover from thermal to quantum mechanical relaxation mechanisms, direct evidence for which is provided by data taken in an applied magnetic field. While most previous studies of such crossovers involve isolated moments, this material represents a unique example of quantum relaxation in a dense spin system with developing correlations. These correlations result in a highly unusual reemergence of thermally activated behavior for $T \lesssim T_{\text{ice}}$ as the collective degrees of freedom dominate the spin dynamics at low temperatures.

Polycrystalline $Dy_2Ti_2O_7$ samples were prepared using standard solid-state synthesis techniques [10,17]. X-ray diffraction demonstrated the samples to be single phase, and Curie-Weiss fits done to the high temperature susceptibility were consistent with $J = 15/2$ Dy^{3+} ions. We study the magnetization (M) and the resultant dc susceptibility ($\chi_{\text{dc}} = dM/dH$) measured with a Quantum Design SQUID magnetometer, as well as the real and imaginary parts (χ' and χ'') of the ac susceptibility (χ_{ac}) measured with either the Quantum Design physical properties measurement system or a simple inductance coil in a dilution refrigerator at low temperatures.

In Fig. 1, we show the temperature dependent susceptibility at different frequencies. We find that χ_{dc} increases monotonically with decreasing temperature, but $\chi'(T)$ and $\chi''(T)$ display a frequency-dependent spin freezing [10,11]. While magnetic site dilution studies [10] indicated that this freezing was associated with the development of spin-spin correlations, recent data suggest that it may instead be a single-ion effect [15]. As demonstrated in the inset of Fig. 1(b), the frequency dependence of T_f can be fit to an Arrhenius law, $f = f_0 e^{-E_a/k_B T_f}$ where $f_0 \sim 10^9$ Hz and $E_A \sim 200$–300 K, which is the energy scale set by the crystalline field [3,10,11]. The Arrhenius law behavior indicates that the spin-relaxation processes are thermally driven for $T \gtrsim T_f$, and an extrapolation suggests that one should observe $T_f \sim 8$ K for frequencies of order 10 mHz, the time scale of the nominally static magnetization measurements. The absence of observed irreversibility in the magnetization in this temperature range implies that the characteristic relaxation time does not continue to follow the Arrhenius law to lower temperature [10,11].

The spectrum of spin-relaxation times can be determined from the frequency dependence of χ'', which we have measured as a function of temperature and field (Fig. 2). For a single characteristic relaxation time, τ, $\chi''(f)$ has a well-defined form with a maximum at $f = 1/\tau$ [18]. Experimentally, in a glassy system, one typically finds broadening associated with a spread of relaxation times, but $\chi''(f)$ for $Dy_2Ti_2O_7$ in zero magnetic field is only slightly broader than the single-τ form for our entire temperature range [10], indicating the existence of

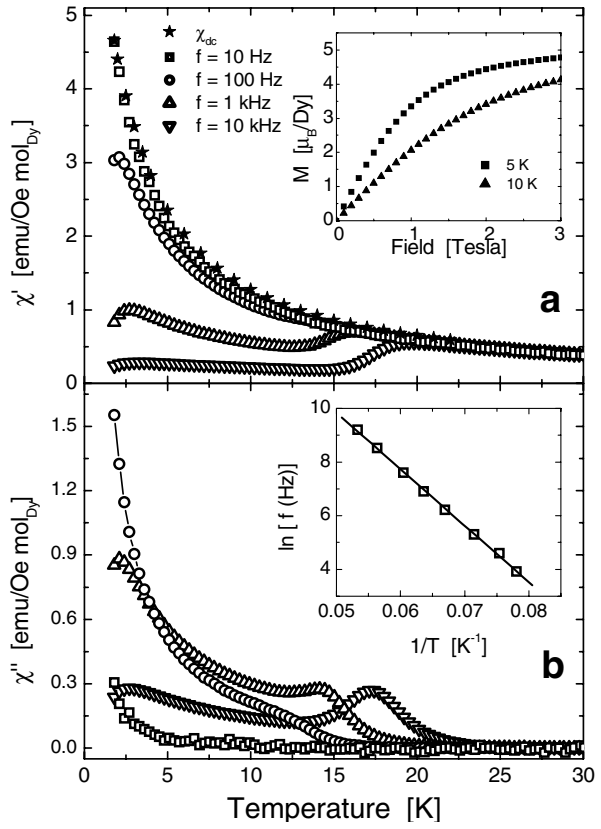

FIG. 1. Temperature dependence of the magnetic susceptibility for $H = 0$. (a) The dc susceptibility and real part of the ac susceptibility (χ'). Inset: the dc magnetization versus applied field. (b) The imaginary part of the ac susceptibility (χ''). Inset: the measurement frequency versus inverse freezing temperature, fit to an Arrhenius law.

a temperature dependent characteristic spin-relaxation time with a narrow distribution at any given temperature. The spectrum does broaden somewhat in a magnetic field (especially near $H = 0.5$ T and $T \sim 12$ K, as discussed below), but there is a clear local maximum to $\chi''(f)$ for almost our entire temperature and magnetic field range, which we take to indicate the characteristic relaxation time, τ, where $\tau = 1/f_{\max}$. While the form of the peak in $\chi''(f)$ is somewhat broadened relative to the ideal case and there is a broad background underneath the peak at the lowest temperatures and highest fields, the resultant uncertainty in the determination of the peak frequency does not qualitatively change the temperature or magnetic field dependence of τ, and thus does not affect the discussion below.

As shown in Fig. 3, the temperature dependence of τ for $T > T_{\text{ice}}$ is quite striking. Above a crossover temperature, $T_{\text{cross}} \sim 13$ K, τ is thermally activated, as expected from the Arrhenius behavior of T_f. Below T_{cross}, however, we find that τ is almost temperature independent ($\tau \sim 5$ ms at $H = 0$) down to $T \sim T_{\text{ice}}$. The weak temperature dependence raises a new question of how the spins are relaxing for $T < T_{\text{cross}}$, since $\tau(T)$ is not consistent with a

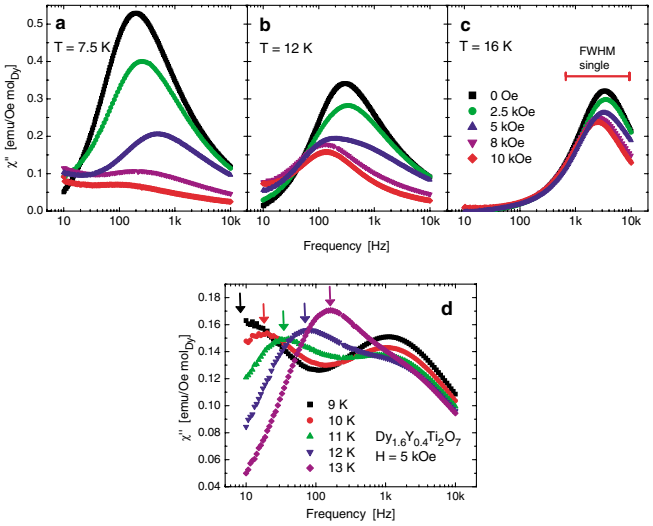

FIG. 2 (color online). (a)–(c) The frequency dependence of the imaginary part of the ac susceptibility (χ''). The peak magnitude decreases monotonically with increasing field. The bar in the 16 K plot shows the full width at half maximum of the theoretical response of a system with a single relaxation time. (d) Similar data at $H = 5$ kOe in a sample diluted with 20% Y on the Dy site. The data show two distinct peaks, confirming the existence of two separate relaxation processes. The colored arrows indicate the temperature dependent (classical relaxation) peak which moves down in frequency with decreasing temperature.

thermally activated process (which would require an unphysically weak energy barrier of $E_A < 2$ K). Since the Hamiltonian of this pure ordered system is relatively simple, it is difficult to imagine how any combination of thermal processes could result in the observed $\tau(T)$. We conclude instead that the relaxation process for $T_{\text{ice}} < T < T_{\text{cross}}$ is through quantum tunneling between the

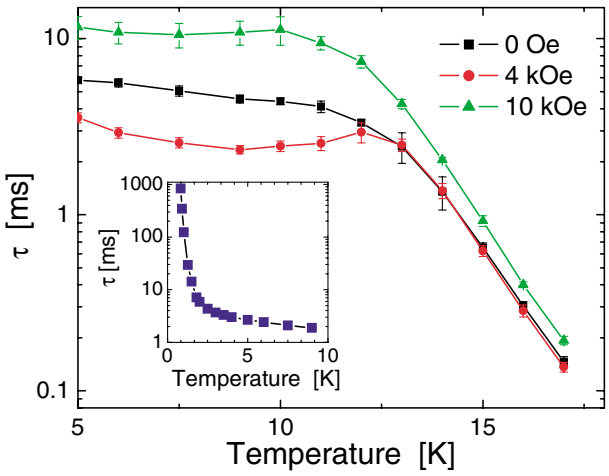

FIG. 3 (color online). The characteristic relaxation time, τ, as a function of temperature at various applied fields. Inset: $\tau(T)$ at $H = 0$ for a sample potted in epoxy down to $T < 2$ K [19].

two accessible Ising states, as has been suggested for different Dy systems [20], other systems in which the relaxation rate changes from being thermally activated to almost constant [21], and for $Ho_2Ti_2O_7$ from neutron spin echo studies [15].

As indicated by the three $\tau(T)$ curves in Fig. 3, the application of a magnetic field [22] significantly affects the spin-relaxation process. Importantly, the application of a field also confirms the coexistence of classical and quantum spin-relaxation processes near $T_{\rm cross}$, as can be seen in the $\chi''(f)$ data taken at $T = 12$ K and $H = 5$ kOe [Fig. 2(b)]. At that field, the relative efficiency of the two relaxation processes is such that the peak of $\chi''(f)$ has both a maximum and a broad shoulder, indicating the existence of two different relaxation processes. This coexistence is even more apparent in the data of Fig. 2(d) taken on a sample diluted with Y on the Dy sites [10] in which the two relaxation modes have similar efficiencies at $H = 5$ kOe but better-separated frequencies (presumably due to the altered spin-spin and spin-lattice interactions, not chemical inhomogeneity since the shoulder is observed in the pure compound [23]). These data clearly demonstrate the evolution with decreasing temperature from a temperature dependent (classical relaxation) peak to a temperature independent (quantum relaxation) peak.

As shown in Fig. 4, the relaxation time has a nonmonotonic dependence on magnetic field. For small fields ($H < 5$ kOe), τ decreases with increasing field, but for larger fields $\tau(H)$ increases and then saturates (the field required for saturation increases with decreasing temperature). We interpret the measured $\tau(H)$ in terms of a simplified spin Hamiltonian: $H = -DS_z^2 - g\mu_B\vec{S}\cdot\vec{H}_{\rm applied} - g\mu_B\vec{S}\cdot\vec{H}_{\rm dipole}$ where D represents the local anisotropy, $\vec{H}_{\rm applied}$ is the applied dc field, $\vec{H}_{\rm dipole}$ is the local dipolar field, and we neglect the relatively weak exchange interactions [5]. Given the four different

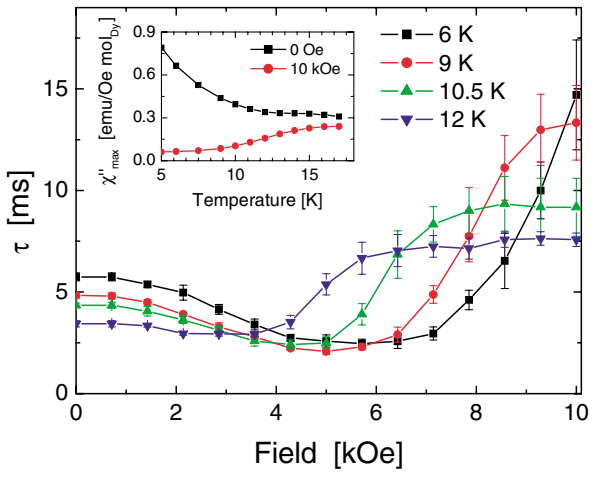

FIG. 4 (color online). The field dependence of the characteristic spin relaxation time, τ. Inset: the magnitude of the peak in $\chi''(f)$ as a function of temperature at $H = 0$ and 10 kOe.

[111] directions of the Dy spins in $Dy_2Ti_2O_7$ and that our samples are polycrystalline, the applied field has components both transverse and along the axis of almost all spins in the sample. The low field decrease in $\tau(H)$ can be partially attributed to enhanced quantum tunneling through coupling to the transverse components of $\vec{H}_{\rm applied}$ [24]. The applied field also can enhance tunneling by locally canceling the longitudinal component of $\vec{H}_{\rm dipole}$, and thus making the $\pm S_z$ states degenerate. This latter effect is evident in a numerical evaluation [25] of the quantum tunneling barrier (averaging over the directions of both $\vec{H}_{\rm dipole}$ and $\vec{H}_{\rm applied}$), which indicates that $\tau(H)$ should exhibit a minimum when the cancellation is optimized. Indeed, the field at which we observe a minimum (~ 5 kOe) corresponds approximately to an energy scale of 1.7 K—only slightly smaller than the dipolar interaction of $\sim$2.35 K [5,14]. The corresponding minimum in the data of Fig. 4 shifts to lower field at higher temperatures, as expected from the reduction of the mean dipolar field with increasing thermal fluctuations.

The increasing $\tau(H)$ at higher magnetic fields is attributable to the longitudinal component of $\vec{H}_{\rm applied}$ separating the energies of the $\pm S_z$ states. The weaker field dependence of $\tau(H)$ at the highest fields (at 12 K, for example) presumably marks the return to thermal relaxation processes when the $\pm S_z$ states are highly separated by $\vec{H}_{\rm applied}$. A difference between the physics of tunneling at low and high fields is suggested by the magnitude of the maxima in $\chi''(f)$, shown in the inset of Fig. 4, which increase monotonically with decreasing temperature in zero field (as expected from the reduced dissipation at lower temperatures), but decrease monotonically at 10 kOe. The temperature dependences suggest strong coupling of phonons to the quantum spin relaxation as has been previously observed in Mn-12 acetate [21]. The rich behavior of $\tau(H, T)$ in $Dy_2Ti_2O_7$ suggests that detailed modeling including the phonon spectrum will be necessary for a complete description of the quantum tunneling phenomena.

While a crossover between thermal and quantum spin relaxation has been observed in many systems, the case of $Dy_2Ti_2O_7$ is particularly interesting because it is a dense system in which spin-spin correlations are developing as $T \to T_{\rm ice}$. Below $T_{\rm ice}$, a maximum in $\chi'(T)$ and irreversibility in the dc magnetization [11,14] suggest that τ again increases with decreasing temperature as the spin ice correlations develop at low temperatures. We have also performed direct measurements of $\tau(T)$ for $T < T_{\rm ice}$ in a powder sample of $Dy_2Ti_2O_7$ potted in epoxy for thermal contact (Fig. 3, inset) [19]. Surprisingly, while $\tau(T)$ is almost temperature independent for $T_{\rm ice} < T < T_{\rm cross}$, it increases extremely sharply below $T_{\rm ice}$. This low temperature increase in $\tau(T)$ indicates the existence of an unusual double crossover in spin relaxation upon cooling: first changing from thermally activated to quantum tunneling at $T_{\rm cross}$, and then reverting to thermally activated as the

developing spin correlations require that groups of spins must evolve coherently. The authors are unaware of similar behavior in other systems exhibiting spin relaxation through quantum tunneling, suggesting that this phenomenon is associated with the development of correlations and the associated emergence of a collective degree of freedom [26].

Aside from the novelty of a double-crossover in the relaxation mechanism, the observation of quantum relaxation in $Dy_2Ti_2O_7$ indicates the importance of such processes in frustrated rare-earth magnets, which display a range of novel low temperature states [27]. The results imply that even such large spin systems, where the spins are typically treated classically, must be considered with the effects of quantum dynamics. As the emergence of thermal relaxation of the correlated spins at low temperatures indicates, the combination of quantum and thermally activated processes in a strongly correlated spin system can form the basis for unanticipated physical phenomena associated with the collective properties of such spin systems.

We acknowledge helpful discussions with D. Huse and R. Moessner, and support from the Army Research Office Grant No. DAAD19-01-1-0021. R. J. C. was supported in part by NSF Grant No. DMR-9725979. A. M. acknowledges support from the Packard Foundation.

*Email address: schiffer@phys.psu.edu

[1] A. P. Ramirez, in *Handbook of Magnetic Materials*, edited by K. J. H. Buschow (Elsevier, Amsterdam, 2001), Vol. 13.
[2] P. Schiffer and A. P. Ramirez, Comments Condens. Matter Phys. **18**, 21 (1996).
[3] The first excited state crystal field in $Dy_2Ti_2O_7$ has an energy scale ~200–300 K. S. Rosenkranz *et al.*, J. Appl. Phys. **87**, 5914 (2000).
[4] R. Siddharthan *et al.*, Phys. Rev. Lett. **83**, 1854 (1999); R. Siddharthan, B. S. Shastry, and A. P. Ramirez, Phys. Rev. B **63**, 184412 (2001).
[5] B. C. den Hertog and M. J. P. Gingras, Phys. Rev. Lett. **84**, 3430 (2000); R. G. Melko, B. C. den Hertog, and M. J. P. Gingras, Phys. Rev. Lett. **87**, 067203 (2001).
[6] S. T. Bramwell and M. J. P Gingras, Science **294**, 1495 (2001).
[7] M. J. Harris *et al.*, Phys. Rev. Lett. **79**, 2554 (1997).
[8] M. J. Harris *et al.*, Phys. Rev. Lett. **81**, 4496 (1998); S. T. Bramwell and M. J. Harris, J. Phys. Condens. Matter **10**, L215 (1998).
[9] A. P. Ramirez *et al.*, Nature (London) **399**, 333 (1999).
[10] J. Snyder *et al.*, Nature (London) **413**, 48 (2001); Phys. Rev. B **66**, 064432 (2002).
[11] K. Matsuhira, Y. Hinatsu, and T. Sakakibara, J. Phys. Condens. Matter **13**, L737 (2001).
[12] K. Matsuhira *et al.*, J. Phys. Condens. Matter **12**, L649 (2000).
[13] A. L. Cornelius and J. S. Gardner, Phys. Rev. B **64**, 060406 (2001).
[14] H. Fukazawa *et al.*, Phys. Rev. B **65**, 054410 (2002).
[15] G. Ehlers *et al.*, J. Phys. Condens. Matter **15**, L9 (2003).
[16] S. T. Bramwell *et al.*, Phys. Rev. Lett. **87**, 047205 (2001).
[17] We have also obtained qualitatively equivalent data on a single crystal sample.
[18] H. B. G. Casimir and F. K. du Pré, Physica (Amsterdam) **5**, 507 (1938).
[19] The spin-relaxation times for samples potted in epoxy (nonmagnetic Stycast 1266) are offset relative to those in loose powder samples, presumably resulting from the pressure induced by the differential thermal contraction of the epoxy and the $Dy_2Ti_2O_7$. J. Snyder (unpublished).
[20] N. Vernier and G. Bellessa, J. Magn. Magn. Mater. **177**, 962 (1998), and references therein.
[21] B. Barbara *et al.*, J. Magn. Magn. Mater. **200**, 167 (1999), and references therein.
[22] The applied dc field is parallel to the excitation field used for the ac magnetic susceptibility measurements.
[23] The full effects of dilution on the relaxation time are discussed elsewhere. J. Snyder, Ph.D. thesis, Pennsylvania State University, 2003; (to be published).
[24] For example, see J. Brooke, T. F. Rosenbaum, and G. Aeppli, Nature (London) **413**, 610 (2001); J. Brooke *et al.*, Science **284**, 779 (1999), and references therein.
[25] Ari Mizel (unpublished).
[26] O. Tchernyshyov, R. Moessner, and S. L. Sondhi, Phys. Rev. Lett. **88**, 067203 (2002); S.-H. Lee *et al.*, Nature (London) **418**, 856 (2002).
[27] See, for example, Y. K. Tsui *et al.*, Phys. Rev. Lett. **82**, 3532 (1999).