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FAST TRACK COMMUNICATION

Quantum spin fluctuations in the spin-liquid state of $Tb_2Ti_2O_7$

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Abstract
Neutron scattering experiments on a polycrystalline sample of the frustrated pyrochlore magnet $Tb_2Ti_2O_7$, which does not show any magnetic order down to 50 mK, have revealed that it shows condensation behavior below 0.4 K from a thermally fluctuating paramagnetic state to a spin-liquid ground state with quantum spin fluctuations. Energy spectra change from quasielastic scattering to a continuum with a double-peak structure at energies of 0 and 0.8 K in the spin-liquid state. Specific heat shows an anomaly at the crossover temperature.

(Some figures may appear in colour only in the online journal)

1. Introduction

Magnetic systems with geometric frustration, a prototype of which is antiferromagnetically coupled Ising spins on a triangle, have been intensively studied experimentally and theoretically for decades [1, 2]. Spin systems on networks of triangles or tetrahedra, such as triangular [3], kagomé [4], spinel [5], and pyrochlore [1] lattices, play major roles in these studies. Their rich variety of phenomena includes zero temperature entropy in Ising antiferromagnets [3, 5] and in ferromagnetically coupled spin ice [6], multiferroics induced by non-collinear magnetic structures [7], heavy fermion behavior [8], and unconventional anomalous Hall effect [9, 10].

Subjects that have fascinated many investigators in recent years are classical and quantum spin-liquid states [11–14], where conventional long range order (LRO) is suppressed to very low temperatures. Quantum spin liquids in particular have been challenging both theoretically and experimentally since the proposal of the resonating valence-bond state [11]. A prototype spin-liquid, or cooperative paramagnet, is the Heisenberg antiferromagnetic model on the pyrochlore lattice coupled by nearest-neighbor exchange interaction, which is shown to remain disordered at all temperatures [12]. The spin-ice materials, $R_2T_2O_7$ (R = Dy, Ho; T = Ti, Sn), are the best understood classical examples [15], while other experimental candidates found recently are awaiting further studies [13, 14].

Among magnetic pyrochlore oxides [1], $Tb_2Ti_2O_7$ has attracted much attention because it does not show any magnetic LRO down to 50 mK and remains dynamic with short range correlations [16, 17]. Theoretical considerations of the crystal-field (CF) states of Tb^{3+} and exchange and dipolar interactions of the system [18–20] showed that it should undergo a transition into a magnetic LRO state at about $T \sim 1.8$ K within a random phase approximation [20]. The dynamical ground state is a candidate for a quantum spin-liquid, but its puzzling origin has been in debate [1].

Recently, an interesting scenario to explain this spin-liquid state was theoretically proposed [21]; $Tb_2Ti_2O_7$ is a quantum-mechanical version of the classical spin ice [6], where additional spin-flip terms to the otherwise classical

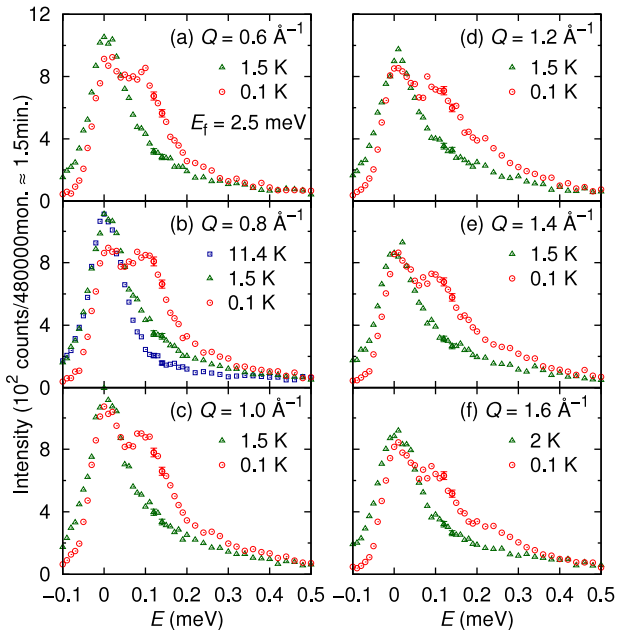

Figure 1. Constant-Q scans taken at $Q = 0.6$, 0.8, 1.0, 1.2, 1.4, 1.6 Å^{-1} in the energy range -0.1 meV $\leq E \leq 0.5$ meV measured at temperatures above and below 0.4 K.

Ising-spin Hamiltonian lift the macroscopic degeneracy of the classical '2-in, 2-out' ground states [21]. More recently a single-site mechanism was proposed [22] to account for the absence of LRO, in which the CF ground doublet becomes two singlets owing to a conjectured tetragonal distortion [23, 24], although this interpretation is not without difficulties [25].

In addition to the theoretical puzzle about the ground state, some experimental results of $Tb_2Ti_2O_7$ contradict each other [16, 17, 26, 27]. It was concluded that the majority of the spins is dynamic down to 50 mK in [17]. On the other hand, in [26, 27] it was reported that about 50% of the spins are static at 0.4 K and that there is an unknown phase transition at 0.37 K. This discrepancy is probably caused by a certain uncontrollable parameter of crystalline samples. In fact, a recent study of specific heat showed a sample dependence for single crystals [24, 28]. However, by restricting oneself to experimental data of polycrystalline samples, results are more consistent. Muon spin relaxation (μSR) [16], neutron spin echo (NSE) [17], and susceptibility [29] experiments showed no conventional phase transition and LRO. Only a small number ($\sim$10%) of spins become quasi-static at 0.1–0.3 K [17, 29]. High-resolution neutron powder-diffraction experiments [30] showed that the crystal structure of $Tb_2Ti_2O_7$ is consistent with the pyrochlore structure without disorder, Tb/Ti site interchange or oxygen deficiency.

In this work, we hypothesize that polycrystalline samples show the genuine characteristics of the spin-liquid state of $Tb_2Ti_2O_7$, and reinvestigate the low-temperature spin fluctuations of a polycrystalline sample by inelastic neutron scattering. From the NSE experiment [17], we expect that important spin fluctuations of the spin-liquid state should appear in the energy range $E > 0.05$ meV, i.e. NSE time

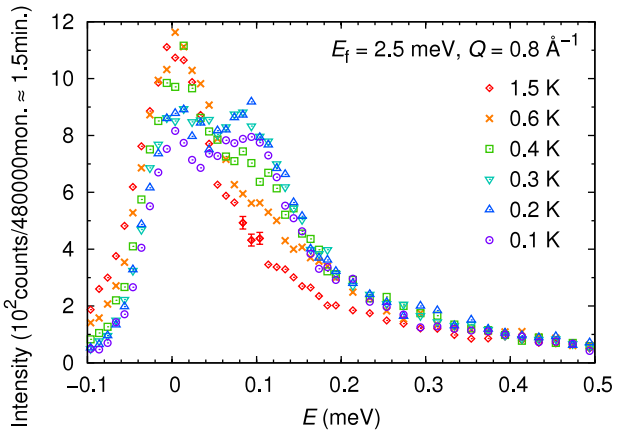

Figure 2. Constant-Q scans at $Q = 0.8$ Å^{-1} in an energy range -0.1 meV $\leq E \leq 0.5$ meV measured at several temperatures down to 0.1 K.

<0.01 ns (figure 3 of [17]), where no experimental data have been reported. The other aim of this work is to observe a certain temperature dependence of energy spectra around $\sim$0.5 K, anticipated from the quantum spin-ice theory [21]. In fact, the NSE [17] and our unpublished neutron scattering experiment [31] did suggest such a T dependence. We have found that around 0.4 K a high-temperature quasielastic spectrum becomes a continuum with a double-peak structure at energies of 0 and 0.8 K, indicating that a crossover from the paramagnetic to spin-liquid state occurs. Specific heat shows an anomaly at the crossover temperature.

2. Experiment

Polycrystalline samples of $Tb_2Ti_2O_7$ were prepared by the standard solid-state reaction at 1350 °C from Tb_4O_7 and TiO_2 [16]. Most of the neutron scattering measurements were performed on the triple-axis spectrometer NG5 at the NIST Center for Neutron Research. A sample with a weight of 7 g was mounted in a dilution refrigerator. The spectrometer was operated using a final neutron energy of $E_f = 2.5$ meV, providing an energy resolution of 0.06 meV (full width at half maximum, FWHM) at the elastic position. Higher-order neutrons were removed by cooled Be and BeO filters. A few preliminary measurements were performed on the triple-axis spectrometer HER at the Japan Atomic Energy Agency [31]. Specific heat was measured by the heat-relaxation method on a physical-property measurement system equipped with a ^{3}He refrigerator.

3. Results and discussion

To investigate the ground state, we performed inelastic scattering experiments in a low energy range -0.1 meV $\leq E \leq 0.5$ meV at low temperatures. In figures 1 and 2 we show constant-Q scans measured at several wavevectors in a range 0.6 Å^{-1} $\leq Q \leq$ 1.6 Å^{-1}. Since the first excited CF level is about 18 K or 1.7 meV [16, 32], the E spectra of these figures are transitions among the ground doublet of the CF states

of Tb^{3+}, being in the trigonal symmetry [18]. The typical energy scale of these E spectra is of the order of 0.1 meV ~1 K. This value agrees well with the estimate of the effective Tb–Tb spin exchange interaction based on μSR [16, 18]. Thus the observed E spectra represent spin fluctuations of up and down states of the Tb^{3+} Ising-like spins [18], interacting via the inter-site couplings and virtual excitations to the excited doublet [19–21].

One can see from figure 1 that the E spectra change remarkably between $T = 1.5$ and 0.1 K from a quasielastic scattering centered at $E = 0$ to an inelastic scattering with an additional peaked structure at $E \simeq 0.1$ meV. The temperature dependence shown in figure 2 indicates that the spectral change occurs around $T = 0.4$ K. We think that this crossover has an important implication that the paramagnetic states above and below 0.4 K have very different characteristics. The E spectra (figure 2) become a low-T limit only below 0.3 K, and we may conclude that $Tb_2Ti_2O_7$ condenses into the spin-liquid ground state below this temperature. It should be noted that in the same crossover T range a significant change was observed in the NSE spectra (figure 3 of [17]). In contrast to this inelastic scattering, the energy integrated diffraction varies only slightly below 1.5 down to 0.05 K (figure 2 of [17]), i.e. spin correlations over a single tetrahedron are retained at low temperatures [16].

The E spectra in figure 1 above 0.2 meV at 0.1 K exhibit additional Q-dependent structures. This Q-dependence seems to impose a restriction on the origin of the spin-liquid ground state; it is brought about by a many-body effect [18–20]. An interesting proposal along this line is the quantum spin-ice state, where a singlet ground state is formed predominantly from the '2-in, 2-out' classical spin-ice states within a single tetrahedron [21]. The estimate of an energy band spanned by excited states is of the order 0.5 K [21]. This value approximately agrees with the fit parameter Δ of the inelastic Lorentzian function at $T \leq 0.3$ K, which is discussed later.

Quite recently another possibility of the spin-liquid state considering both single- and inter-site effects has been pointed out [22]. The authors hypothesize that the ground doublet in the cubic pyrochlore structure splits into two singlets under a small tetragonal distortion, conjectured to exist as high as 1.6 K [22]. The energy splitting of 0.19 meV between the two singlets, which is claimed [22] to be observed at 1.6 K in a neutron inelastic spectrum in [32], is not reproducible in the present data of figures 1 and 2 at 1.5 K. The energy resolution 0.16 meV (FWHM) in [32] seems too large to exclude an artifact in a resolution–convolution fitting. Thus the theoretical two-singlet scenario [22] assuming the tetragonal distortion would be seriously modified to account for the present E-spectra and T-dependence, in which the crossover around 0.4 K could perhaps be ascribed to a structural transition.

In order to parameterize the E spectra shown in figure 2 as a function of temperature, we carried out fits of the data to a scattering function

$$S(Q, E) = A\delta(E) + \frac{B}{1 - e^{-E/k_B T}} \sum_{\pm} \frac{\Gamma E}{(E \pm \Delta)^2 + \Gamma^2}, \quad (1)$$

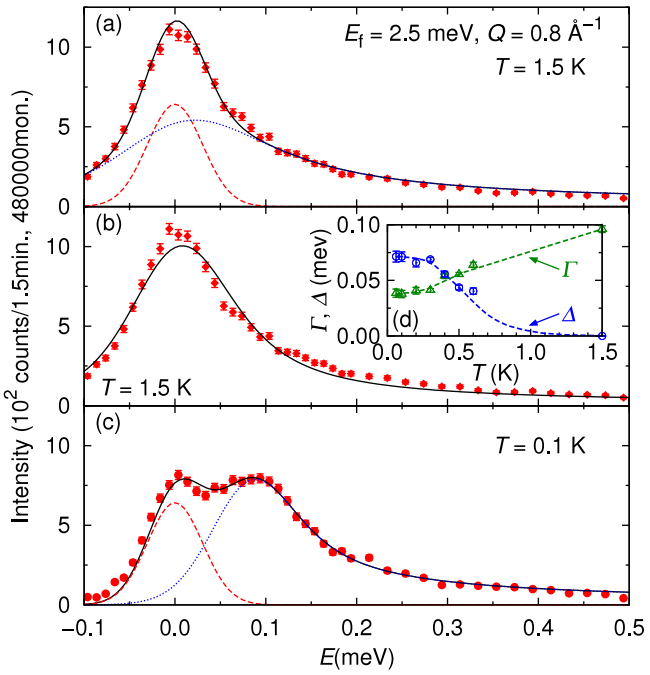

Figure 3. Results of fitting constant-Q scan data at $T = 1.5$ K ((a), (b)) and 0.1 K (c) shown in figure 2 to resolution convoluted $S(Q, E)$ of equation (1). We assume (a) $\Delta = 0$ and (b) $A = 0$ and $\Delta = 0$. Red dashed lines and blue dotted lines represent the resolution convolutions of the elastic and inelastic scattering of equation (1). The black solid lines are total fitted curves. (d) Temperature dependence of the fit parameters Γ and Δ. Lines are guides to the eye.

which is convoluted with a resolution function. The first and second terms of equation (1) represent elastic and inelastic scatterings, respectively. Typical results of the fitting are shown in figure 3. For data at 1.5 K we tried to fit the spectrum using the Lorentzian function ($\Delta = 0$) for standard quasielastic scattering with ($A \neq 0$, figure 3(a)) and without ($A = 0$, figure 3(b)) the elastic component. These fits show that the elastic component, 20–30% of the energy integrated ($E < 0.5$ meV) total intensity, cannot be neglected in this analysis. The elastic part consists of incoherent elastic scattering of Ti nuclei, multiple Bragg scattering, and magnetic scattering of Tb^{3+} spins [17]. In the present experiment, the separation of the elastic scattering from the inelastic scattering is difficult owing to the insufficient instrumental energy resolution compared to the energy scale of 0.1 meV. We could not obtain a reasonable T-dependence of the parameter A of equation (1), and assumed the same A value for all temperatures. The resulting fits are shown in figures 3(a) and (c).

The temperature dependence of the fit parameters Γ and Δ are plotted in figure 3(d). These parameters show the crossover behavior around 0.4 K. At 0.1 K the second term of equation (1) with $\Delta \sim 2\Gamma$ represents a quasi-gapped continuum with a significant spectral weight at $E = 0$. It should be noted that the very high-resolution NSE data [17] imply that ~20% of the elastic component in equation (1) contains a magnetic contribution below 0.3 K. Thus the magnetic spectrum, background subtracted equation (1), in

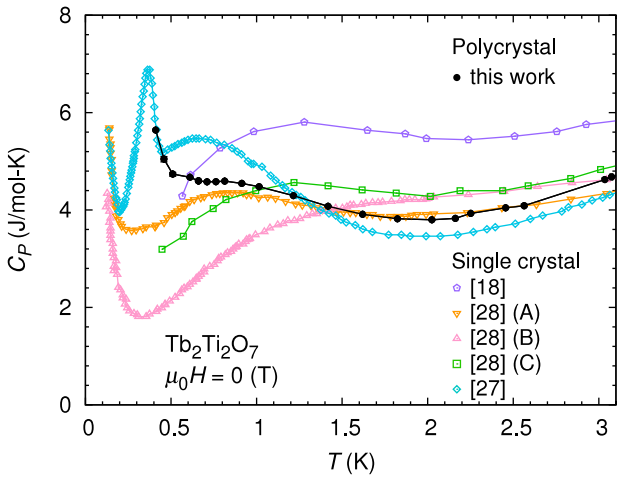

Figure 4. Temperature dependence of specific heat of polycrystalline and single-crystalline samples [18, 27, 28].

the spin-liquid state probably has a two-peak structure at $E = 0$ and 0.07 meV. This should be confirmed more directly using another spectrometer with a much higher resolution $\sim$10 μeV or better in further work.

We measured the specific heat C_P of the polycrystalline sample to check whether the crossover around 0.4 K can be observed in thermodynamic properties. The result is plotted in figure 4 together with previous measurements. C_P of the present work shows an upturn below 0.5 K, being consistent with the neutron data. We checked that the same upturn of C_P is observed by a polycrystalline sample prepared in the same way as described in [16, 17]. One can also see differences of C_P for crystalline samples [18, 24, 27, 28], demonstrating the difficulty of discussing experimental data taken on different single crystals, especially below 1 K. Control parameters of single crystals could be very small disorders, Tb/Ti site interchange, oxygen deficiency or local stress built-in during single-crystal growth carried out using image furnaces. We speculate that the large differences of C_P at low T may imply that the system is located close to a quantum critical point which is affected by these hidden material parameters. We hope that the mechanism of the spin-liquid state can be explored further in studies on well-characterized single crystals.

4. Conclusion

In summary, inelastic neutron scattering has been used to extend the work of [16, 17] and explore the spin-liquid state of polycrystalline $Tb_2Ti_2O_7$. This system condenses into a quantum spin-liquid state from the paramagnetic state via a crossover around 0.4 K, where specific heat shows an anomaly. The energy spectrum in the spin-liquid state is a continuum with a double-peak structure at energies of 0 and 0.8 K. Its wavevector dependence suggests that the spin-liquid state is brought about by many-body effects [18, 21].

Acknowledgments

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