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Long-range order and spin-liquid states of polycrystalline $Tb_{2+x}Ti_{2-x}O_{7+y}$

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Low-temperature states of polycrystalline samples of a frustrated pyrochlore oxide $Tb_{2+x}Ti_{2-x}O_{7+y}$ have been investigated by specific heat, magnetic susceptibility, and neutron scattering experiments. We have found that this system can be tuned by a minute change of x from a spin-liquid state ($x < x_c$) to a partly ordered state with a small antiferromagnetic ordering of the order of $0.1\mu_B$. Specific heat shows a sharp peak at a phase transition at $T_c = 0.5$ K for $x = 0.005$. Magnetic excitation spectra for this sample change from a quasielastic to a gapped type through T_c. The possibility of a Jahn-Teller transition is discussed.

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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] Spin systems on networks of triangles or tetrahedra, such as triangular,[2] kagomé,[3] and pyrochlore[4] lattices, play major roles in these studies. Subjects that have fascinated many investigators in recent years are classical and quantum spin-liquid states,[5–8] where conventional long-range order (LRO) is suppressed to very low temperatures. Quantum spin liquids[6,7] in particular have been challenging both theoretically and experimentally since the proposal of the resonating valence-bond state.[9] The spin ice materials $R_2Ti_2O_7$ (R = Dy,Ho) are the well-known classical examples,[5] while other experimental candidates found recently have been studied.[10–14]

Among frustrated pyrochlore oxides,[4] $Tb_2Ti_2O_7$ has attracted much attention because it does not show any conventional LRO down to 50 mK and remains in a dynamic spin-liquid state.[15–17] 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 1.8 K within a random-phase approximation.[20] The puzzling origin of the spin-liquid state of $Tb_2Ti_2O_7$ is a subject of hot debate.[4,21–28] An interesting scenario for the spin-liquid state is the theoretical proposal of a quantum spin-ice state.[22] More recently, another scenario of a two-singlet spin-liquid state was proposed to explain why inelastic neutron spectra in a low-energy range are observed despite the fact that Tb^{3+} is a non-Kramers ion.[23,24]

Several experimental puzzles of $Tb_2Ti_2O_7$ originate from the difficulty of controlling the quality of single-crystalline samples, resulting in strongly sample-dependent specific-heat anomalies at temperatures below 2 K.[18,26,29–33] In contrast, experimental results on polycrystalline samples are more consistent.[15,16,26] Among the experimental results reported to date, an important clue to solve the puzzles of $Tb_2Ti_2O_7$ seems to be a change of state at about 0.4 K suggested by specific heat,[26] inelastic neutron scattering,[26] and neutron spin echo[16] measurements on polycrystalline samples. At this temperature, a few single-crystalline samples show a peak in the specific heat suggesting a phase transition,[29,30] an issue that has not been pursued seriously. The possibility of a cooperative Jahn-Teller phase transition well below 1 K was inferred many years ago from the observation of an anomalous temperature dependence of the elastic constants above 1 K.[34] The two-singlet spin-liquid scenario of Refs. 23,24, and 35 is based on the assumption of a tetragonal lattice distortion in $Tb_2Ti_2O_7$ and the closely related ordered spin-ice compound $Tb_2Sn_2O_7$,[36] but the accompanying lattice distortion might be too difficult to observe directly.[25,37–40] A theoretical study on pyrochlore magnets with non-Kramers magnetic ground doublets, applicable to Pr^{3+}, Tb^{3+}, etc., pointed out the possibilities of quadrupole orderings as well as quantum spin ice.[41,42]

In the present work, we investigate the hypothesis that the nonstoichiometry x of $Tb_{2+x}Ti_{2-x}O_{7+y}$ is a tuning parameter for a quantum critical point separating a LRO state from a spin-liquid state. We have therefore performed specific heat, magnetization, and neutron scattering experiments on polycrystalline samples of $Tb_{2+x}Ti_{2-x}O_{7+y}$ with different values of x. We find that a minute change of x brings about a systematic change of the specific heat. The ground state goes from LRO with an unknown order parameter for $x > x_c$ to a spin liquid for $x < x_c$.

Polycrystalline samples of $Tb_{2+x}Ti_{2-x}O_{7+y}$ with $-0.015 < x < 0.01$ were prepared by a standard solid-state reaction.[15] The value of x was adjusted by changing the mass ratio of the two starting materials, Tb_4O_7 and TiO_2, which were heated in air at 1350 °C for several days with periodic grindings to ensure a complete reaction. It was ground into powder and annealed in air at 800 °C for one day. The values of x used in this paper are nominal, and have an offset of about ± 0.002. The value of y is determined by the oxidizing conditions. X-ray powder-diffraction experiments were carried out using

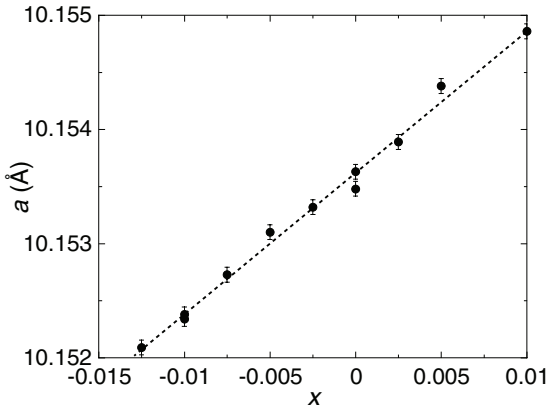

FIG. 1. Lattice constants of polycrystalline $Tb_{2+x}Ti_{2-x}O_{7+y}$ at 25 °C. The dashed line is a guide to the eye.

a RIGAKU-SmartLab powder diffractometer equipped with a Cu $K\alpha 1$ monochromator. The absence of impurity peaks in the powder diffraction patterns shows that the samples are single phase with the pyrochlore structure.[43] To measure the x dependence of the lattice constant a at 25 °C, we performed θ-2θ scans on powder mixtures of $Tb_{2+x}Ti_{2-x}O_{7+y}$ and Si. Figure 1 shows that the lattice constant a, consistent with the previous work for $x = 0$,[43] has a smooth variation with x, which ensures a continuous change of the stoichiometry of $Tb_{2+x}Ti_{2-x}O_{7+y}$ for small x.

Specific heat above 0.4 K was measured on a physical-property measurement system. Measurements below 0.4 K were carried out using the quasiadiabatic relaxation method on a dilution refrigerator.[44] dc magnetization measurements were carried out by a capacitive Faraday magnetometer in a ^{3}He refrigerator. Neutron powder diffraction measurements were performed on the triple-axis spectrometer CTAX at ORNL. Inelastic neutron scattering measurements were carried out on the time-of-flight spectrometer IN5 operated with $\lambda = 5$ and 10 Å at ILL. For these neutron scattering experiments, samples of $x = 0.005$ and -0.005 with weights of 5 and 9 g were mounted in a ^{3}He (CTAX) and a dilution refrigerator (IN5), respectively.

In Fig. 2, we show the specific heat C_P of the polycrystalline samples as a function of temperature together with a few previous measurements.[26,29,45] Earlier work have shown qualitatively similar results.[46,47] The $C_P(T)$ data show a systematic change by varying x. A sample with $x = 0.005$ shows a clear peak indicating a second-order phase transition at $T_c = 0.5$ K. Samples with $x = 0.0025$ and 0.000 show smaller peaks at 0.43 and 0.4 K, respectively. We note that C_P of the present sample with $x = 0.000$ agrees approximately with our previous measurements,[26] the temperature range of which was extended down to 0.2 K in the present work on a sample (nominal $x' = 0$) prepared from a different commercial source of Tb_4O_7. Our previous interpretation[26] of the upturn below 0.5 K as a crossover behavior is incorrect due to the insufficient temperature range. The previous C_P data[45] (Fig. 2) on a polycrystalline sample with their nominal $x'' = 0$ correspond to our $x = -0.0125$, implying that fine tuning of x requires careful sample preparation. In the inset of Fig. 2, we show a cumulative phase diagram constructed from $C_P(T,x)$

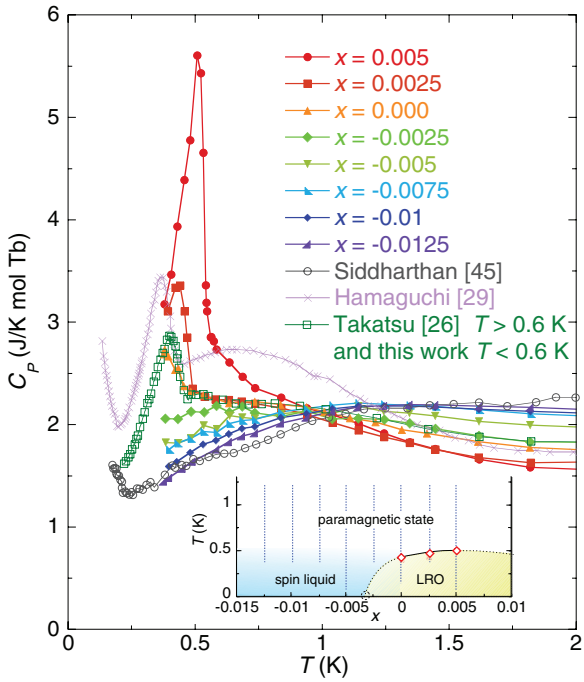

FIG. 2. (Color online) Temperature dependence of the specific heat of polycrystalline $Tb_{2+x}Ti_{2-x}O_{7+y}$. Previous measurements of poly- and single-crystalline samples,[26,29,45] as well as the present measurements below 0.6 K of a sample prepared in the same manner as in Ref. 26, are plotted for comparison. The inset shows a phase diagram expected from the specific heat, susceptibility, and neutron scattering.

in conjunction with the susceptibility and neutron scattering experiments discussed below.

A peak of $C_P(T)$ in $Tb_2Ti_2O_7$ was first reported for a single-crystalline sample at 0.37 K.[29] These $C_P(T)$ data,[29] reproduced in Fig. 2, show a significantly different T dependence from any of the polycrystalline samples. The sharp peak at 0.37 K may result from a portion of the sample having a nonstoichiometry parameter around $x = -0.001$, corresponding to a peak slightly lower in temperature than our $x = 0.000$. However, a hump in $C_P(T)$ around 0.75 K for the single crystal does not appear for the polycrystalline samples. We believe that these single- and polycrystalline samples have significant, but presently not well understood, differences in quality.

To check whether T_c is an antiferromagnetic transition, as suggested in Ref. 29, we performed magnetization and neutron powder-diffraction experiments. In Fig. 3, we show the magnetic susceptibility as a function of temperature for three polycrystalline samples with $x = \pm 0.005$ and 0.000. The susceptibilities for $x = 0.005$ and 0.000 show only slight anomalies around the clear peaks of $C_P(T)$ at $T_c = 0.5$ and 0.4 K, respectively. These weak anomalies resemble certain transitions related to magnetic degrees of freedom.

In Fig. 4, we show neutron powder-diffraction patterns for the $x = 0.005$ sample below and above T_c. The pattern below T_c shows neither any clear antiferromagnetic reflections nor any clear changes due to a structural transition. Rough estimates of the upper limits of the antiferromagnetic ordered moment and the structural change are about $0.1\mu_B$ and

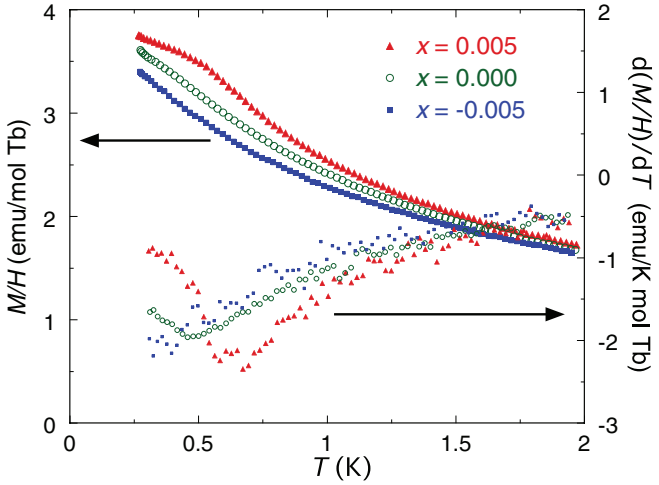

FIG. 3. (Color online) Temperature dependence of the magnetic susceptibility ($H = 0.05$ T) and its derivative with respect to T of polycrystalline $Tb_{2+x}Ti_{2-x}O_{7+y}$ with $x = -0.005$, 0.000, and 0.005.

$\Delta a/a < 0.01$ assuming a cubic to tetragonal distortion. The intensity of the sloping paramagnetic scattering, a background for Bragg peaks, decreases slightly as temperature is lowered from 1.2 to 0.28 K. This is brought about by a change in the magnetic excitations. The lack of obvious antiferromagnetism distinctly separates $Tb_2Ti_2O_7$ from the ordered spin-ice compound $Tb_2Sn_2O_7$,[36,48] in which antiferromagnetic ordering with a moment of $5.9\mu_B$ was observed well below $T_c = 0.87$ K.

To study the spectral change of the magnetic excitations through T_c, we performed inelastic neutron scattering measurements using the spectrometer IN5 (Ref. 49) with an energy resolution of $\Delta E = 0.012$ meV (full width at half-maximum), which is five times better than that in our previous study.[26] Figure 5 shows the temperature dependence of an energy spectrum for the $x = 0.005$ sample at $Q = 0.6$ Å^{-1}. It is evident that the spectrum changes from a continuum ($T > T_c$) to a peaked structure at 0.1 meV ($T < T_c$). The

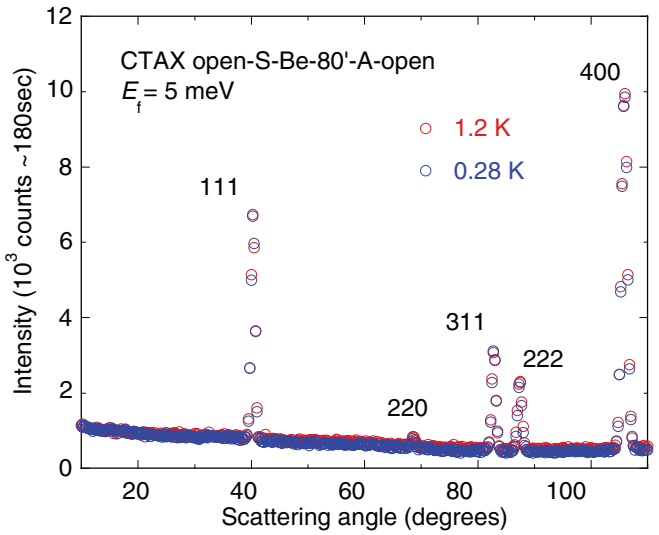

FIG. 4. (Color online) Neutron powder-diffraction pattern of polycrystalline $Tb_{2+x}Ti_{2-x}O_{7+y}$ with $x = 0.005$ taken above and below $T_c = 0.5$ K.

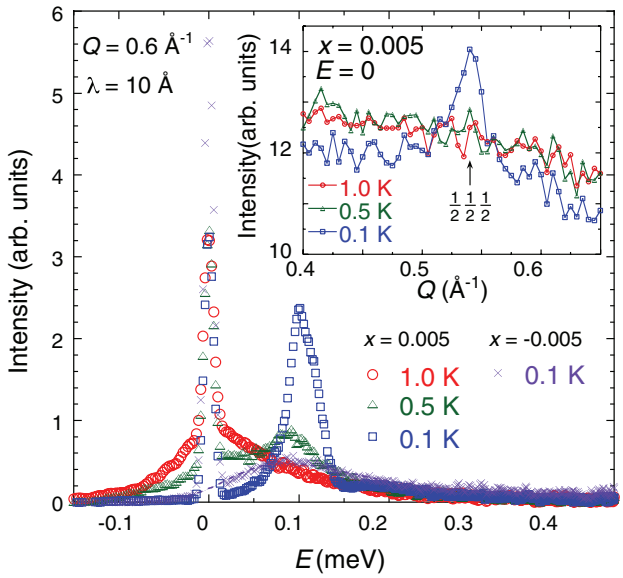

FIG. 5. (Color online) Energy spectra of inelastic neutron scattering for polycrystalline $Tb_{2+x}Ti_{2-x}O_{7+y}$ with $x = 0.005$ and -0.005. The inset shows the Q dependence of the elastic scattering for the $x = 0.005$ sample around $Q = |(\frac{1}{2}\frac{1}{2}\frac{1}{2})|$ above and below T_c. The dashed line is the fit curve.

excitation peak at $T \ll T_c$ is weakly Q-dependent, which may possibly be interpreted as a splitting of the CF ground-state doublet. An energy spectrum of the $x = -0.005$ sample is also shown in Fig. 5 for comparison. Its spectral shape can be approximately expressed by a Lorentzian squared $\mathrm{Im}\chi(E,Q)/E \propto [(\sqrt{2}-1)E^2 + \Gamma^2]^{-2}$ with $\Gamma = 0.1$ meV (half-width at half-maximum) in $-0.05 < E < 0.3$ meV, revealing quantum spin fluctuations with the same energy scale of 0.1 meV as that of the $x = 0.005$ sample.

The high sensitivity of IN5 enabled us to observe a small Bragg peak for the $x = 0.005$ sample, being undetectable in the CTAX data (Fig. 4). In the inset of Fig. 5, the intensity of the elastic scattering for $|E| < 0.005$ meV is plotted as a function of Q. Below T_c, a clear Bragg peak at $Q = 0.54$ Å^{-1} is observed, which can be indexed as $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. The Q width of this peak is somewhat larger than the instrumental Q resolution, and corresponds to a correlation length of the order of 100 Å. Although this peak could be of a nuclear (structural) origin, it is more likely an antiferromagnetic (AFM) reflection. In fact, two recent neutron scattering experiments carried out on single-crystalline samples of $Tb_2Ti_2O_7$ showed magnetic short-range order around the same $\boldsymbol{Q} = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$.[24,28] A roughly estimated ordered moment for the $x = 0.005$ sample is $0.08\mu_B$ at 0.1 K, where we assume the phase factor $e^{i\boldsymbol{Q}\cdot\boldsymbol{r}} = 1$ in the magnetic structure factor. This ordered moment is much smaller than the magnetic moment $\sim 5\mu_B$ of the ground doublets,[18,48] which implies that most of the spin fluctuations persist below T_c. In contrast, the entropy change around $T_c = 0.5$ K is $S(T = 0.55) - S(T = 0.38) \simeq 0.25R \ln 2$ (Fig. 2), which is significant. These probably indicate that there is a major order parameter, which is unknown at present.

The present results have provided an answer to the problem of the previously reported transition or crossover at about 0.4 K for the poly- and single-crystalline $Tb_2Ti_2O_7$,[16,26,29]

and they pose another question: what is the major order parameter associated with T_c? In the following, we speculatively discuss a few possibilities. A cooperative Jahn-Teller transition due to a magnetoelastic coupling[50,51] was suggested a long time ago,[34] although direct experimental evidence has not been found. Precursor effects of a Jahn-Teller transition were reported using x-ray diffraction on a single-crystalline sample.[38] According to Refs. 23,24, and 35, a splitting of the CF ground-state doublet into two singlets can be interpreted as simplest evidence of a Jahn-Teller distortion breaking the local trigonal D_{3d} symmetry of the Tb site. Along these lines, the weakly Q-dependent excitation peak at 0.1 meV (Fig. 5) can be interpreted as the splitting, and the transition is due to a Jahn-Teller effect accompanying a small AFM ordering.[51] A recent theory,[41,42] exploited to explain quantum fluctuations of pyrochlore magnets with non-Kramers Pr^{3+}, Tb^{3+}, etc., showed possibilities of quadrupole orderings due to an electronic coupling, which are located close to the quantum spin ice state.[22] One of these quadrupole orderings[41,42] may be the order parameter. A resulting structural distortion coupled to the quadrupole ordering could be too small to be observed. Although the major order parameter is unknown at present, the long-standing puzzle of the spin-liquid state of $Tb_2Ti_2O_7$ seems to be reformulated to a novel problem of frustration having spin and other degrees of freedom. Experimentally, single-crystalline samples with tunable x or y are indispensable for further studies.

In summary, we have investigated the low-temperature states of polycrystalline $Tb_{2+x}Ti_{2-x}O_{7+y}$ samples by specific heat, magnetic susceptibility, and neutron scattering experiments. We have found that this system can be tuned by a minute change of x from a LRO ground state with an unknown major order parameter accompanying a minor AFM ordering for $x > x_c$ to a liquid-type ground state with quantum spin fluctuations for $x < x_c$. Specific heat shows a sharp peak at a second-order phase transition T_c for $x > x_c$. Inelastic neutron scattering of an $x = 0.005$ ($>x_c$) sample shows that a gap opens in the magnetic excitation spectrum below T_c.

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