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.

Magnetic systems with geometric frustration, a prototype of which is an antiferromagnetically coupled Ising spins on a triangle, have been intensively studied experimentally and theoretically for decades. Spin systems on networks of triangles or tetrahedra, such as triangular, kagomé, and pyrochlore lattices, play major roles in these studies. Subjects that have fascinated many investigators in recent years are classical and quantum spin-liquid states, where conventional long-range order (LRO) is suppressed to very low temperatures. Quantum spin-liquid states in particular have been challenging both theoretically and experimentally since the proposal of the resonating valence bond state. The spin ice materials R$_2$Ti$_2$O$_7$ (R = Dy, Ho) are the well-known classical examples, while other experimental candidates found recently have been studied.

Among frustrated pyrochlore oxides, Tb$_3$Ti$_2$O$_7$ has attracted much attention because it does not show any conventional LRO down to 50 mK and remains in a dynamic spin-liquid state. Theoretical considerations of the crystal-field (CF) states of Tb$^{3+}$ and exchange and dipolar interactions of the system showed that it should undergo a transition into a magnetic LRO state at about 1.8 K within a random phase approximation. The puzzling origin of the spin-liquid state of Tb$_2$Ti$_2$O$_7$ is a subject of hot debate. An interesting scenario for the spin-liquid state is the theoretical proposal of a quantum spin-ice state. More recently, another scenario for 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.

Several experimental puzzles of Tb$_2$Ti$_2$O$_7$ 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. In contrast, experimental results on polycrystalline samples are more consistent. Among the experimental results reported to date, an important clue to solve the puzzles of Tb$_2$Ti$_2$O$_7$ seems to be a change of state at about 0.4 K suggested by specific heat, inelastic neutron scattering, and neutron spin echo measurements on polycrystalline samples. At this temperature, a few single-crystalline samples show a peak in the specific heat suggesting a phase transition, 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. The two-singlet spin-liquid scenario of Refs. and is based on the assumption of a tetragonal lattice distortion in Tb$_2$Ti$_2$O$_7$ and the closely related ordered spin-ice compound Tb$_2$Sn$_2$O$_7$, but the accompanying lattice distortion might be too difficult to observe directly. 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.

In the present work, we investigate the hypothesis that the non-stoichiometry $x$ 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 $x < x_c$. 

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Polycrystalline samples of $\text{Tb}_{2+x}\text{Ti}_{2-x}\text{O}_{7+y}$ with $-0.015 < x < 0.01$ were prepared by standard solid-state reaction. The value of $x$ was adjusted by changing the mass ratio of the two starting materials, $\text{Tb}_4\text{O}_7$ and $\text{TiO}_2$, 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 $\pm 0.002$. The value of $y$ is determined by the oxidizing conditions. X-ray powder-diffraction experiments were carried out using a RIGAKU-SmartLab powder diffractometer equipped with a Cu Kα monochromator. The absence of impurity peaks in the powder diffraction patterns shows that the samples are single phase with the pyrochlore structure.

To measure the $x$ dependence of the lattice constant $a$ at 25 °C, we performed $\theta-2\theta$ scans on powder mixtures of $\text{Tb}_{2+x}\text{Ti}_{2-x}\text{O}_{7+y}$ and Si. Figure 1 shows that the lattice constant $a$, consistent with the previous work for $x = 0$, has a smooth variation with $x$, which ensures a continuous change of the stoichiometry of $\text{Tb}_{2+x}\text{Ti}_{2-x}\text{O}_{7+y}$ 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 quasi-adiabatic relaxation method on a dilution refrigerator. DC magnetization measurements were carried out by a capacitive Faraday magnetometer in a $^3\text{He}$ 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 $^3\text{He}$ (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. Earlier work have shown qualitatively similar results, as well as the present measurements below 0.6 K of a sample prepared in the same manner as in Ref. 23, are plotted for comparison. The inset shows a phase diagram expected from the specific heat, susceptibility, and neutron scattering.
tent $T$ dependence from any of the polycrystalline samples. The sharp peak at $0.37$ K may result from a portion of the sample having a non-stoichiometry parameter around $x = -0.005$, 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 poly-crystalline samples have significant, but presently not well understood, differences in quality.

In order 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 $x = -0.005$ and 0.000. The susceptibilities for $x = 0.005$ and 0.000 show only slight anomalies around the clear ordering with a moment of 5.9 $\mu_B$ distinctly separates Tb$_2$Ti$_2$O$_7$ from the ordered spin-ice compound Tb$_2$Sn$_2$O$_7$, 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, with an energy resolution of $\Delta E = 0.012$ meV (FWHM), which is 5 times better than that in our previous study. Figure 4 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 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. 4 for comparison. Its spectral shape can be approximately expressed by a Lorentzian squared $\text{Im} \times (\sqrt{2} - 1) E^2 + \Gamma^2 \right)^{-2}$ with $\Gamma = 0.1$ meV (FWHM) 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 CTA 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 $(\frac{11}{22})$. 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$_2$Ti$_2$O$_7$ showed magnetic short-range order around the same $Q = (\frac{11}{22})$. A roughly estimated ordered moment for the $x = 0.005$ sample is 0.08 $\mu_B$ at 1 K, where we assume the phase factor $e^{iQ\cdot r} = 1$ in the magnetic structure factor.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3}
\caption{(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.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig4}
\caption{(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.}
\end{figure}
ordered moment is much smaller than the magnetic moment $\sim 5 \mu_B$ of the ground doublets, which implies that most of the spin fluctuations persist below $T_c$. In contrast, the entropy change around $T_c = 0.5$ K is $S(T = 0.55) - S(T = 0.38) \approx 0.25R\ln(2)$ (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 $\text{Tb}_2\text{Ti}_2\text{O}_7$ 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 $x = 0.005$ sample shows that a gap opens in the magnetic excitation spectrum below $T_c$.

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1. C. Lacroix, P. Mendels, and F. Mila, eds., Introduction to Frustrated Magnetism (Springer, 2011).
2. G. H. Wannier, Phys. Rev. 79, 357 (1950).
3. I. Sy"ozi, Prog. Theor. Phys. 6, 306 (1951).
4. J. S. Gardner, M. J. P. Gingras, and J. E. Greedan, Rev. Mod. Phys. 82, 53 (2010).
5. S. T. Bramwell and M. J. P. Gingras, Science 294, 1495 (2001).
6. P. A. Lee, Science 321, 1306 (2008).
7. L. Balents, Nature 464, 199 (2010).
8. S. Yan, D. A. Huse, and S. R. White, Science 332, 1173 (2011).
9. P. W. Anderson, Mater. Res. Bull. 8, 153 (1973).
10. J. S. Helton, K. Matan, M. P. Shores, E. A. Nytko, B. M. Bartlett, Y. Yoshida, Y. Takano, A. Suslov, Y. Qiu, J.-H. Chung, D. G. Nocera, and Y. S. Lee, Phys. Rev. Lett. 98, 107204 (2007).
11. T. Itou, A. Oyamada, S. Maegawa, M. Tamura, and...
R. Kato, Phys. Rev. B 77, 104413 (2008).
B. Fäk, E. Kermarrec, L. Messio, B. Bernu, C. Lhuillier, F. Bert, P. Mendels, B. Koteswararao, F. Bouquet, J. Ollivier, A. D. Hillier, A. Amato, R. H. Colman, and A. S. Wills, Phys. Rev. Lett. 109, 037208 (2012).
K. A. Ross, L. Savary, B. D. Gaulin, and L. Balents, Phys. Rev. X 1, 021002 (2011).
J. F. Bonville, I. Mirebeau, A. Forget, D. Colson, V. Glazkov, J. P. Sanchez, O. Isnard, and E. Suard, Phys. Rev. Lett. 94, 246402 (2005).
T. A. Lummen, I. P. Handayani, M. C. Donker, S. Vanishri, D. Aoki, B. Fäk, L. P. Regnault, C. Buisson, A. P. Ramirez, A. Hayashi, R. J. Cava, and S. Rosenkranz, Phys. Rev. Lett. 105, 047201 (2012).
J. A. Quilliam, C. G. A. Mugford, A. Gomez, S. W. Kycia, J. P. C. Ruff, B. D. Gaulin, J. P. Castellan, K. C. Rule, J. P. Clancy, J. Rodriguez, and H. A. Dubikowska, Phys. Rev. Lett. 99, 237202 (2007).
Y. Nakamichi, T. Kumagai, M. Yoshizawa, K. Matsuhira, S. Takagi, and Z. Hiroi, Phys. Rev. B 83, 184434 (2011).
K. Goto, H. Takatsu, T. Taniguchi, and H. Kadowaki, J. Phys. Soc. Jpn. 81, 015001 (2012).
S. Onoda, S. Takagi, Y. Nakanishi, T. Kumagai, M. Yoshizawa, K. Matsuhira, S. Takagi, and Z. Hiroi, Phys. Rev. B 83, 184434 (2011).
S.-W. Han, J. S. Gardner, and C. H. Booth, Phys. Rev. B 69, 024416 (2004).
J. A. Quilliam, C. G. A. Mugford, A. Gomez, S. W. Kycia, and J. B. Kycia, Phys. Rev. Lett. 98, 037203 (2012).
R. Siddharthan, B. S. Shastry, A. P. Ramirez, A. Hayashi, R. J. Cava, and S. Rosenkranz, Phys. Rev. Lett. 83, 1854 (1999).
A. Cornelius, B. Light, R. S. Kumar, M. Eichenfield, T. Dutton, R. Pepin, and J. Gardner, Physica B: Condensed Matter 359-361, 1243 (2005).
J. M. Roper, B. Fäk, M. B. Stone, P. R. Hammar, D. H. Reich, and B. D. Gaulin, Phys. Rev. B 68, 174407 (2003).
I. Mirebeau, A. Apetrei, J. Rodríguez-Carvajal, S. Petit, P. Bonville, J. Robert, Phys. Rev. B 85, 054428 (2012).
I. Mirebeau, A. Petre, J. Rodríguez-Carvajal, P. Bonville, A. Forget, D. Colson, V. Glazkov, J. P. Sanchez, O. Isnard, and E. Suard, Phys. Rev. Lett. 94, 246402 (2005).
T. J. Sato, J. W. Lynn, S. Petit, P. Bonville, I. Mirebeau, H. Mutka, and J. Robert, Phys. Rev. B 85, 054428 (2012).
M. Revell et al., Nature Physics 9, 34 (2013) show an x-dependent effect for Dy2(Ti2−xYbx)O7−x/2. In addition to disorders due to x considered in these papers, chemical pressure effects could be at play, because the off-stoichiometric x = 0.005 sample shows the largest peak of Cp(T) (Fig. 2).
L. G. Mamsurova, K. S. Pigal’skii, and K. K. Pukhov, JETP Lett. 43, 755 (1986).
S. Petit, P. Bonville, I. Mirebeau, H. Mutka, and J. Robert, Phys. Rev. B 85, 054428 (2012).
J. A. Quilliam, C. G. A. Mugford, A. Gomez, S. W. Kycia, J. P. C. Ruff, B. D. Gaulin, J. P. Castellan, K. C. Rule, J. P. Clancy, J. Rodriguez, and H. A. Dubikowska, Phys. Rev. Lett. 99, 237202 (2007).
Y. Nakamichi, T. Kumagai, M. Yoshizawa, K. Matsuhira, S. Takagi, and Z. Hiroi, Phys. Rev. B 83, 184434 (2011).
K. Goto, H. Takatsu, T. Taniguchi, and H. Kadowaki, J. Phys. Soc. Jpn. 81, 015001 (2012).
S. Onoda, S. Takagi, Y. Nakanishi, T. Kumagai, M. Yoshizawa, K. Matsuhira, S. Takagi, and Z. Hiroi, Phys. Rev. B 83, 184434 (2011).
S.-W. Han, J. S. Gardner, and C. H. Booth, Phys. Rev. B 69, 024416 (2004).
J. A. Quilliam, C. G. A. Mugford, A. Gomez, S. W. Kycia, and J. B. Kycia, Phys. Rev. Lett. 98, 037203 (2007).
R. Siddharthan, B. S. Shastry, A. P. Ramirez, A. Hayashi, R. J. Cava, and S. Rosenkranz, Phys. Rev. Lett. 83, 1854 (1999).
A. Cornelius, B. Light, R. S. Kumar, M. Eichenfield, T. Dutton, R. Pepin, and J. Gardner, Physica B: Condensed Matter 359-361, 1243 (2005).
X. Ke, D. V. West, R. J. Cava, and P. Schiffer, Phys. Rev. B 80, 144426 (2009).
I. Mirebeau, P. Bonville, and M. Hennion, Phys. Rev. B 76, 184436 (2007).
J. Ollivier and H. Mutka, J. Phys. Soc. Jpn. 80, SB003 (2011).
J. Jensen and A. R. Mackintosh, Rare Earth Magnetism (Clarendon Press, 1991).
G. A. Gehring and K. A. Gehring, Rep. Prog. Phys. 38, 1 (1975).