Quantum spin liquid and electric quadrupolar states of single crystal Tb\textsubscript{2+x}Ti\textsubscript{2-x}O\textsubscript{7+y}

M Wakita, T Taniguchi, H Edamoto, H Takatsu and H Kadowaki
Department of Physics, Tokyo Metropolitan University, Hachioji-shi, Tokyo 192-0397, Japan

Abstract. The ground states of the frustrated pyrochlore oxide Tb\textsubscript{2+x}Ti\textsubscript{2-x}O\textsubscript{7+y}, sensitively depending on the small off-stoichiometry parameter \(x\), have been studied by specific heat measurements using well characterized samples. Single crystal Tb\textsubscript{2+x}Ti\textsubscript{2-x}O\textsubscript{7+y} boules grown by the standard floating zone technique are shown to exhibit concentration \((x)\) gradient. This off-stoichiometry parameter is determined by precisely measuring the lattice constant of small samples cut from a crystal boule. Specific heat shows that the phase boundary of the electric quadrupolar state has a dome structure in the \(x-T\) phase diagram with the highest \(T_c \approx 0.5\) K at about \(x = 0.01\). This phase diagram suggests that the putative U(1) quantum spin-liquid state of Tb\textsubscript{2+x}Ti\textsubscript{2-x}O\textsubscript{7+y} exists in the range \(x < x_c \approx 0.0025\), which is separated from the quadrupolar state via a first-order phase-transition line \(x = x_c\).

1. Introduction
Magnetic systems with geometric frustration 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 fascinating many investigators in recent years are quantum spin liquid (QSL) states [5, 6], where conventional long-range orders (LRO) are suppressed to very low temperatures.

Among frustrated magnetic pyrochlore oxides [4], Tb\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} (TTO) has attracted much attention because it does not show any conventional LRO down to 50 mK [7], suggesting that it is a candidate for a QSL state. Although many experimental studies of TTO have been performed to date, the problem why TTO does not show any magnetic LRO remains very difficult [8, 9]. This is partly because TTO shows strong sample dependence [10], extremely strong for single crystals. And accordingly, simple interpretation of experimental data is precluded.

Recently, we investigated polycrystalline samples of off-stoichiometric Tb\textsubscript{2+x}Ti\textsubscript{2-x}O\textsubscript{7+y}, and showed that a very small change of \(x\) induces a quantum phase transition between a spin liquid state \((x < -0.0025 = x_c)\) and a LRO state with a hidden order parameter \((x_c < x)\) [11]. The \(x-T\) phase diagram of Tb\textsubscript{2+x}Ti\textsubscript{2-x}O\textsubscript{7+y} suggested in Ref. [11] has a dome-shape LRO phase boundary. More recently, we study the hidden LRO using an \(x\)-controlled single crystal, which shows a very sharp peak in specific heat at \(T_c = 0.53\) K \((x \approx 0.005)\) [12]. By using semi-quantitative analyses, we propose [12–14] that the LRO of Tb\textsubscript{2+x}Ti\textsubscript{2-x}O\textsubscript{7+y} is an electric multipolar (or quadrupolar) state. This LRO state was theoretically predicted [15] using electronic superexchange interactions for non-Kramers ions, including Tb\textsuperscript{3+}, which have both magnetic dipole and electric quadrupole (16-pole, and 64-pole) moments. In addition, quite intriguingly, the estimated parameter set [12] of the effective pseudospin-1/2 Hamiltonian is...
located very close to a theoretical phase boundary between the electric quadrupolar and U(1) quantum spin-liquid states [15, 16], which could naturally explain the spin liquid state of TTO.

The purpose of this investigation is to extend our study of polycrystalline Tb$_{2+x}$Ti$_{2-x}$O$_{7+y}$ [11] to single crystals in the hope that the above scenario for the TTO problem is reinforced. We grow single crystals of Tb$_{2+x}$Ti$_{2-x}$O$_{7+y}$ by the standard floating zone (FZ) technique [17] and have found that very precise measurements of the lattice constant are useful to characterize the single crystals. Specific heat of these samples with different off-stoichiometry parameters ($x$) have been measured down to 0.1 K to obtain an $x$-$T$ phase diagram.

2. Experimental methods and results

Polycrystalline samples of Tb$_{2+x}$Ti$_{2-x}$O$_{7+y}$ were prepared by the standard solid-state reaction as described in Ref. [11]. The two starting materials, Tb$_4$O$_7$ and TiO$_2$, were heated in air at 1350 °C for several days with periodic grindings to ensure a complete reaction. The value of $x$ was adjusted by changing the mass ratio of the two materials, and is nominal with an offset about ±0.002. The resulting Tb$_{2+x}$Ti$_{2-x}$O$_{7+y}$ powder samples were used for single crystal growth by the standard FZ technique [17]. Crystal growth was carried out in an Ar gas flow atmosphere using a double ellipsoidal image furnace (NEC SC-N35HD).

X-ray powder-diffraction experiments were carried out using a RIGAKU-SmartLab diffractometer equipped with a Cu K$_{\alpha 1}$ monochromator. To precisely measure the lattice constant we performed $\theta$-2$\theta$ scans on powder mixtures of polycrystalline or crushed-crystalline Tb$_{2+x}$Ti$_{2-x}$O$_{7+y}$ and Si [11, 18]. Absolute values of lattice constants are normalized by using the certified lattice parameter for a temperature of 22.5 °C of the SRM-640d Si powder, $a = 5.43123$ Å [19], being further corrected for the temperature dependence [20].

Temperature dependence of the lattice constant $a(T, x)$ of Tb$_{2+x}$Ti$_{2-x}$O$_{7+y}$ was measured using a polycrystalline sample with $x = -0.0075$, and the result is shown in Fig. 1(a). The $x$ dependence of $a(T = 26.0^\circ C, x)$ of polycrystalline samples is plotted in Fig. 1(b), where we converted the published lattice constants (Fig. 1 in Ref. [11]) to those at 26.0 °C [18].

Figure 2 shows a single crystal Tb$_{2+x}$Ti$_{2-x}$O$_{7+y}$ boule that was grown from a feed rod of $x = -0.005$ powder and was post-annealed for about 7 days at 1000 °C in air. Lattice constants

![Figure 1](image.png)

**Figure 1.** Lattice constant $a(T, x)$ of polycrystalline Tb$_{2+x}$Ti$_{2-x}$O$_{7+y}$ samples. (a) Temperature dependence of $a(T, x = -0.0075)$. (b) Off-stoichiometry parameter dependence of $a(T = 26.0^\circ C, x) = 0.124418x + 10.15280$ from Ref. [18].
Figure 2. Single crystal Tb$_{2+x}$Ti$_{2-x}$O$_{7+y}$ boule grown by the FZ method, where the missing part ($40 < L < 48$ mm) was cut before taking this photograph. The numbers represent distances $L$ along the growth direction, where small crystals are cut at these $L$ values. Lattice constant and specific heat of these crystals are shown in Figs. 3 and 4.

![Figure 2](image.png)

Figure 3. Lattice constants of small Tb$_{2+x}$Ti$_{2-x}$O$_{7+y}$ crystals cut from the boule shown in Fig. 2. These lattice constants are converted to $x$ using the polycrystalline curve, i.e., $a(T = 26.0^\circ C, x)$ of Fig. 1(b) and are shown on the right vertical axis.

![Figure 3](image.png)

of small crystals cut from this boule were measured at 26.0 °C and are plotted as a function of the distance along the growth direction $L$ shown in Fig. 3. We assume that $a(T = 26.0^\circ C, x)$ of polycrystalline samples (Fig. 1(b)) and its linear extension to the range $x > 0.01$ can be used to estimate the off-stoichiometry parameter ($x$) of the small crystals. These $x$ values are shown on the right vertical axis of Fig. 3. One can see that the boule has a systematic $x$ gradient. During the crystal growth the off-stoichiometry parameter starts from $x \approx 0.04$ ($L = 1 - 5$ mm), then decreases linearly as a function of $L$, and finally varies more slowly ($L > 40$ mm).

To characterize crystal samples we also measured specific heat $C_P(T)$ at low temperatures using a $^3$He or an adiabatic demagnetization refrigerator. In Fig. 4(a) we show specific heat as a function of temperature for the several crystals cut from the boule (Fig. 2) and a few from another boule. Based on these $C_P(T)$ data we draw a tentative $x$-$T$ phase diagram for the single crystals in Fig. 4(b). We note that these $C_P(T)$ data and the $x$-$T$ phase diagram for the single crystals are quite consistent with those of polycrystalline Tb$_{2+x}$Ti$_{2-x}$O$_{7+y}$ [11]. This indicates that our trial method of estimating small $x$ ($|x| < 0.01$) for single crystals using the precise measurement of the lattice constant is probably reliable.

The $x$-$T$ phase diagram (Fig. 4(b)) implies that one has to take a special care of very small change of the off-stoichiometry existing even in a single crystal boule to investigate
Figure 4. (a) Temperature dependence of specific heat of several single crystals. The \( x \) values are estimated by the method shown in Fig. 3. (b) \( x-T \) phase diagram determined from the specific heat measurements of single crystals. Temperature ranges of the specific heat measurements are shown by vertical blue dashed lines.

\( \text{Tb}_{2+x}\text{Ti}_{2-x}\text{O}_{7+y} \) (or nominal \( \text{Tb}_2\text{Ti}_2\text{O}_7 \)). Previous experimental investigations using small TTO crystals will have to be reinterpreted as investigations on different \( \text{Tb}_{2+x}\text{Ti}_{2-x}\text{O}_{7+y} \) crystals. In particular, previous experiments using large crystals, especially inelastic neutron scattering for example Refs. [21–24], require special caution in their interpretation, because the crystals may not be sufficiently homogeneous.

3. Discussion and summary

The \( x-T \) phase diagram shows that around \( x = x_c \simeq -0.0025 \) the transition temperature \( T_c \) of the quadrupolar state [12] disappears abruptly in a small \( x \) range. This suggests that the neighboring putative QSL state is separated by a first-order phase transition line \( x = x_c \) [11, 12]. It is interesting that this type of first-order phase transition between U(1) QSL and quadrupolar states is predicted by a gauge mean-field theory [16], presumably relevant to TTO [12]. One may naturally expect that \( \text{Tb}_{2+x}\text{Ti}_{2-x}\text{O}_{7+y} \) with \( x = x_c \) is on the theoretical border of U(1) QSL and quadrupolar states [16], and that the spin liquid state of \( \text{Tb}_{2+x}\text{Ti}_{2-x}\text{O}_{7+y} \) with \( x < x_c \) is U(1) QSL of Ref. [16]. This is a very intriguing hypothesis for further studies.

On the other hand, in a larger \( x \) range of \( x > 0.01 \) the transition temperature of the quadrupolar state seems to decrease gradually and the specific heat peak gradually becomes smaller as \( x \) is increased. These suggest that an effect of randomness controls the system. A possible scenario of the randomness effect may be as follows. Most of excess Tb atoms reside on the \( \text{Ti}^{4+} \) site and become \( \text{Tb}^{4+} \) ions. These magnetic \( \text{Tb}^{4+} \) ions behave as magnetic impurities in the system, where local magnetic short-range order is restored around each \( \text{Tb}^{4+} \) ion. The quadrupolar state is completely suppressed in \( x > 0.04 \).

In summary, we have investigated single-crystalline samples of the frustrated pyrochlore oxide \( \text{Tb}_{2+x}\text{Ti}_{2-x}\text{O}_{7+y} \) by growing single crystals using the standard floating zone technique and by characterizing them using X-ray diffraction techniques and specific heat measurements down to 0.1 K. We show that a precise determination of the lattice constant is useful for estimating the small off-stoichiometry parameter \( x \). Small crystals cut from single crystal rods, exhibiting \( x \) gradient, show three different low temperature behaviors: a paramagnetic QSL \( (x < x_c) \), a long range quadrupolar, and possibly a randomness dominating state. The phase boundary of the quadrupolar state shows a dome structure in the \( x-T \) phase diagram with the highest \( T_c \simeq 0.5 \).
K at $x = 0.01$ and suggests existence of a first-order phase-transition line separating the QSL and quadrupolar states.

Acknowledgments
We thank S. Onoda and Y. Kato for useful discussions. This work was supported by JSPS KAKENHI grant numbers 25400345 and 26400336.

References
[1] Lacroix C, Mendels P and Mila F (eds) 2011 *Introduction to Frustrated Magnetism* (Berlin, Heidelberg: Springer)
[2] Wannier G H 1950 *Phys. Rev.* **79** 357
[3] Syözi I 1951 *Proc. Theor. Phys.* 306
[4] Gardner J S, Gingras M J P and Greedan J E 2010 *Rev. Mod. Phys.* **82** 53
[5] Lee P A 2008 *Science* **321** 1306
[6] Balents L 2010 *Nature* **464** 199
[7] Gardner J S, Dunsiger S R, Gaulin B D, Gingras M J P, Greedan J E, Kiefe R F, Lumsden M D, MacFarlane W A, Raju N P, Sonier J E, Swainson I and Tun Z 1999 *Phys. Rev. Lett.* **82** 1012
[8] Gingras M J P and McClarty P A 2014 *Rep. Prog. Phys.* **77** 056501
[9] Petit S, Guitteny S, Robert J, Bonville P, Decorse C, Ollivier J, Mutka H and Mirebeau I 2015 *EPJ Web of Conferences* **83** 03012
[10] Takatsu H, Kadowaki H, Sato T J, Lynn J W, Tabata Y, Yamazaki T and Matsuhira K 2012 *J. Phys. Condens. Matter* **24** 052201
[11] Taniguchi T, Kadowaki H, Takatsu H, Fäk B, Ollivier J, Yamazaki T, Sato T J, Yoshizawa H, Shimura Y, Sakakibara T, Hong T, Goto K, Yaraskavitch L R and Kycia J B 2013 *Phys. Rev. B* **87** 060408
[12] Takatsu H, Kittaka S, Kasahara A, Kono Y, Sakakibara T, Kato Y, Onoda S, Fäk B, Ollivier J, Lynn J W, Taniguchi T, Wakita M and Kadowaki H arXiv:1506.04545
[13] Kadowaki H, Takatsu H, Taniguchi T, Fäk B and Ollivier J 2015 *Spin* **5** 1540003
[14] Takatsu H, Taniguchi T, Kittaka S, Sakakibara T and Kadowaki H 2016 *J. Phys.: Conf. Ser.* **683** 012022
[15] Onoda S and Tanaka Y 2011 *Phys. Rev. B* **83** 094411
[16] Lee S, Onoda S and Balents L 2012 *Phys. Rev. B* **86** 104412
[17] Gardner J, Gaulin B and Paul D 1998 *J. Crystal Growth* **191** 740
[18] Taniguchi T, Kadowaki H, Takatsu H, Fäk B, Ollivier J, Yamazaki T, Sato T J, Yoshizawa H, Shimura Y, Sakakibara T, Hong T, Goto K, Yaraskavitch L R and Kycia J B 2015 *Phys. Rev. B* **92** 019903
[19] Kaiser D L and Watters R L 2010 NIST Certificate of SRM 640d, https://www-s.nist.gov/armors/view_cert.cfm?srn=640d
[20] Izumi F and Nakai I (eds) 2009 *Funmatsu Xsen kaiseki no jissai* 2nd ed (Tokyo: Asakurashoten)
[21] Yasui Y, Kanada M, Ito M, Harashina H, Sato M, Okumura H, Kakurai K and Kadowaki H 2002 *J. Phys. Soc. Jpn.* **71** 599
[22] Fennell T, Kenzelmann M, Roessler B, Mutka H, Ollivier J, Ruminy M, Stuur U, Zaharko O, Bovo L, Cervellino A, Haas M K and Cava R J 2014 *Phys. Rev. Lett.* **112** 017203
[23] Guitteny S, Robert J, Bonville P, Ollivier J, Decorse C, Steffens P, Boehm M, Mutka H, Mirebeau I and Petit S 2013 *Phys. Rev. Lett.* **111** 087201
[24] Fritsch K, Ross K A, Qiu Y, Copley J R D, Guidi T, Bewley R I, Dabkowska H A and Gaulin B D 2013 *Phys. Rev. B* **87** 094410