

**Magnetic ground state of the pyrochlore oxide  $Y_2Nb_2O_7$** 

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We report dc magnetization and specific heat of a series of insulating pyrochlore oxides  $Y_2Nb_{2-x}Ti_xO_7$ . Although the end member  $Y_2Nb_2O_7$  contains magnetic tetravalent Nb ions ( $4d^1$ ,  $S=1/2$ ), it does not exhibit any sign of magnetic ordering at least between 0.35 and 800 K. In addition, it exhibits Curie-Weiss behavior originating from spins  $S=1/2$  on less than 0.3% of the Nb sites; the remaining spins of Nb ions apparently disappear. With the substitution of *nonmagnetic* Ti ions, this magnetic component increases only up to 4.7% of the  $B$  sites, with Nb and Ti combined. These results are ascribable to a strongly correlated spinless state, which is a specific character derived from a band structure of  $d$ -electron pyrochlore oxides.

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**I. INTRODUCTION**

Since Anderson showed the possibility of the quantum spin liquid (QSL) state for the Heisenberg antiferromagnetic (AF) spins on the two-dimensional triangular lattice,<sup>1</sup> many efforts have been made in search of such a magnetic ground state.<sup>2</sup> However, it is difficult to realize an ideal triangular-lattice or *kagomé*-lattice material with geometrical frustration, because three-dimensional (3D) intercoupling is crucial for the determination of the ground state in real materials. In contrast, there are a number of candidate materials with the 3D lattice with geometrical frustration for which the correspondence between the models and actual materials can be excellent; one such example is a pyrochlore lattice, in which each tetrahedron shares its corners with those of the surrounding tetrahedra and forms a 3D network.

The magnetically disordered QSL state is, indeed, theoretically predicted for the Heisenberg pyrochlore antiferromagnet (HPAF).<sup>3-7</sup> Because of the geometrical frustration of the pyrochlore lattice, there can be macroscopically degenerate sets of spin singlets, which are formed in the presence of the nearest-neighbor AF interaction. This QSL state is different from a better known localized dimer state, since a spin in a QSL state can change its singlet partner from one of six nearest-neighbor spins at any instance, thus involving the entire system.

There are a number of useful compounds containing pyrochlore lattice, since, for example, many of the pyrochlore oxides  $A_2B_2O_7$  and the spinel oxides  $AB_2O_4$  allow many possible sets of elements ( $A, B$ ). Therefore, one may be able to choose a set of elements ( $A, B$ ) which provides a stable pyrochlore lattice down to low temperature and is composed of a nonmagnetic element for  $A$  and an element with AF  $S=1/2$  spins for  $B$ .

It has been considered that lightly diluted  $YMn_2$  with Sc also exhibits the QSL behavior, since magnetic Mn ions resides in the pyrochlore lattice.<sup>8,9</sup> However, this compound itself is a metal; a direct correspondence with the models is difficult to make.

Recently physical properties of  $Y_2Ir_2O_7$  down to low temperatures have been investigated<sup>10-12</sup> with an expectation that  $5d^5$  electrons of Ir ions in the  $t_{2g}$  orbitals give rise to a HPAF and form the QSL state. Instead, it exhibits spin-glass ordering below 170 K. The pyrochlore oxide  $Lu_2V_2O_7$  ( $V^{4+}$ :  $3d^1$ ) is a well-known Mott insulator with  $S=1/2$ .<sup>13</sup> However, it exhibits *ferromagnetic* ordering below about 70 K.

Quite recently it is reported that a spin singlet ground state is realized in  $Tl_2Ru_2O_7$  ( $Ru^{4+}$ :  $4d^4$ ,  $S=1$ )<sup>14</sup> and in spinel oxide  $MgTi_2O_4$  ( $Ti^{3+}$ :  $3d^1$ ,  $S=1/2$ ).<sup>15</sup> Not a QSL state but a localized dimer state is expected to be the most probable ground state because this singlet formation occurs simultaneously with a structural phase transition, which leads to a Peierls-like transition.

These facts urge us to search for other pyrochlore or spinel compounds which possess quantum spins on the pyrochlore lattice. In this paper, we report dc magnetization and specific heat of a new series of insulating pyrochlore niobates  $Y_2Nb_{2-x}Ti_xO_7$ , in which Nb ions are expected to be tetravalent ( $4d^1$ ,  $S=1/2$ ). Thus, one may expect the end member  $Y_2Nb_2O_7$  to be HPAF.<sup>16</sup> To the best of our knowledge, except for the lattice parameter the physical properties of  $Y_2Nb_2O_7$  have not been reported,<sup>17</sup> although magnetization and resistivity of other related pyrochlore niobates have been reported.<sup>18-20</sup> We found unexpectedly that the  $S=1/2$  spins apparently disappear in this pyrochlore. We discuss the possible magnetic ground state of  $Y_2Nb_2O_7$ .

**II. EXPERIMENTS**

Polycrystalline samples of  $Y_2Nb_{2-x}Ti_xO_7$  ( $0.0 \leq x \leq 2.0$ ) were synthesized using an infrared image furnace (NEC Machinery, model SC-E15HD) in pure-Ar reduced atmosphere. For  $Y_2Ti_2O_7$ , we also grew crystals in pure oxygen atmosphere. The detailed procedure of the synthesis will be described elsewhere.<sup>21</sup>

In Fig. 1, we compare the x-ray diffraction pattern of  $Y_2Nb_2O_7$  along with the diffraction pattern of oxygen-

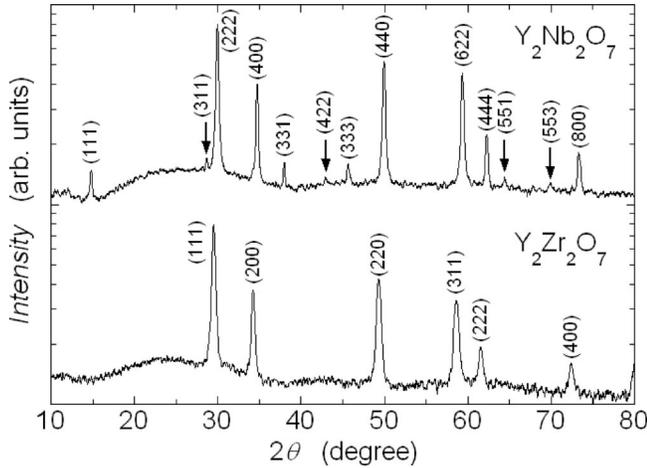


FIG. 1. X-ray diffraction pattern of pyrochlore  $\text{Y}_2\text{Nb}_2\text{O}_7$  and oxygen-deficient fluorite  $\text{Y}_2\text{Zr}_2\text{O}_7$ . Cu- $K\alpha$  radiation was used and the intensity is plotted on a logarithmic scale.

deficient fluorite oxide  $\text{Y}_2\text{Zr}_2\text{O}_7$ .<sup>21–23</sup> For  $\text{Y}_2\text{Nb}_2\text{O}_7$  it is clear that the peaks correspond to a pyrochlore structure and are distinct from those of an oxygen-deficient fluorite structure. The important difference is the presence of additional diffraction peaks in the pyrochlore spectra, for example, a peak around  $15^\circ$  and a peak around  $38^\circ$ . For an oxygen-deficient fluorite structure with nearly half the unit cell size, there should be no peaks around such angles as pointed out in the previous report.<sup>17</sup> Therefore, we conclude that  $\text{Y}_2\text{Nb}_2\text{O}_7$  is not in a fluorite structure but in a pyrochlore structure. In fact, all the diffraction peaks can be indexed according to those of a pyrochlore structure (see Fig. 1). We note that the samples with  $x$  less than unity tends to contain nonmagnetic  $\text{YNbO}_4$  ( $\text{Nb}^{5+}$ ,  $S=0$ ) as a second phase, but in some cases also superconductor  $\text{NbO}$  ( $\text{Nb}^{2+}$ ,  $T_{\text{SC}} = 1.4$  K) at the same time.

Nearly linear decrease of the lattice parameters with  $x$  was found from  $a = 10.33(1)$  Å ( $\text{Y}_2\text{Nb}_2\text{O}_7$ ) to  $a = 10.09(1)$  Å ( $\text{Y}_2\text{Ti}_2\text{O}_7$ ). Our observation for the formation of the pyrochlore  $\text{Y}_2\text{Nb}_2\text{O}_7$  is consistent with the previous report<sup>17</sup> in which continuous variation of the lattice parameter within the pyrochlore structure is observed between the composition  $\text{Y}_2\text{Nb}_2\text{O}_7$  and  $\text{Y}_3\text{NbO}_7$  [=  $\text{Y}_2(\text{YNb})\text{O}_7$ ]; the lattice parameter of our crystals corresponds to the composition  $\text{Y}_2(\text{Y}_{0.35}\text{Nb}_{1.65})\text{O}_7$  reported in Ref. 17. We have examined the oxidation state of Nb ion in  $\text{Y}_2\text{Nb}_2\text{O}_7$  by thermogravimetric analysis and have found that the effective valency is less than 4.3, which was consistent with the results of EPMA (electron-probe microanalysis).<sup>21</sup> We note that all the materials exhibit insulating behavior with the activation energy of 0.1–0.2 eV, determined from the resistivity.

We measured dc magnetization between 1.8 and 350 K for fields up to 7 T with a superconducting quantum interference device magnetometer (Quantum Design, model MPMS<sub>XL</sub>).<sup>24</sup> We used an additional oven to measure the magnetization between 300 and 800 K. We measured specific heat by a thermal relaxation method between 0.35 and 25 K for fields up to 5 T with a commercial calorimeter (Quantum Design, model PPMS<sub>6000</sub>).

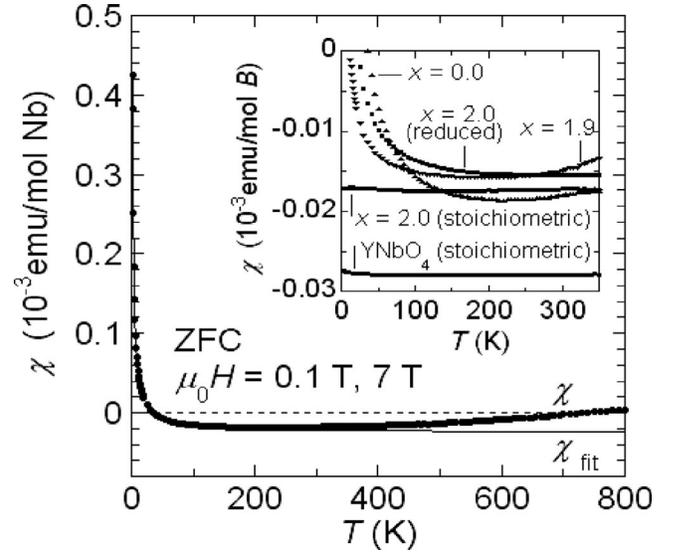


FIG. 2. Magnetic susceptibility  $\chi(T)$  of  $\text{Y}_2\text{Nb}_2\text{O}_7$ . The solid line represents the Curie-Weiss fitting using the data between 1.8 and 50 K. In the inset,  $\chi(T)$ 's of  $\text{Y}_2\text{Nb}_{2-x}\text{Ti}_x\text{O}_7$  and  $\text{YNbO}_4$  are shown. The unit of the  $\chi(T)$ 's in the inset is given per one molar elements in the B sites (Nb and Ti combined).

### III. RESULTS AND DISCUSSION

Let us first summarize the physical properties of  $\text{Y}_2\text{Nb}_2\text{O}_7$ . In Fig. 2, we show magnetic susceptibility  $\chi(T)$  obtained at 0.1 T in the zero-field-cooled (ZFC) sequence. Above 350 K we show the magnetization measured at 7 T.<sup>25</sup> We did not observe magnetic hysteresis in the data obtained between the ZFC and the field-cooled (FC) sequences. We note that the recent  $^{55}\text{Nb}$  nuclear-magnetic-resonance (NMR) measurement also indicates the absence of magnetic ordering at 4.2 K.<sup>26</sup> Nevertheless,  $\text{Y}_2\text{Nb}_2\text{O}_7$  exhibits Curie-Weiss behavior, as well as a gradual increase of the magnetization with increasing temperature above about 250 K. We performed the Curie-Weiss fitting between 1.8 and 50 K,

$$\chi_{\text{fit}}(T) = \chi_0 + \frac{C}{T - \theta_{\text{CW}}}. \quad (1)$$

Here,  $\chi_0$ ,  $C$ , and  $\theta_{\text{CW}}$  are the paramagnetic component arising from inner shell diamagnetization and van Vleck paramagnetism, Curie constant, and Curie-Weiss temperature, respectively. The obtained  $C$  is only 0.23(1)% of the Curie constant expected for one  $S = 1/2$  spin per Nb site. The obtained  $\theta_{\text{CW}}$  is  $-0.12(5)$  K, which is quite small for an insulating  $d$ -electron system and implies the presence of nearly isolated spins.

As seen in the inset of Fig. 2, the  $\chi(T)$  of  $\text{Y}_2\text{Nb}_{0.1}\text{Ti}_{1.9}\text{O}_7$  ( $x = 1.9$ ) exhibits similar temperature dependence to that of  $\text{Y}_2\text{Nb}_2\text{O}_7$  ( $x = 0.0$ ), while that of stoichiometric  $\text{Y}_2\text{Ti}_2\text{O}_7$  ( $x = 2.0$ ) and  $\text{YNbO}_4$  exhibits nearly temperature-independent behavior. The oxygen-reduced  $\text{Y}_2\text{Ti}_2\text{O}_7$  ( $x = 2.0$ ) exhibits only Curie-Weiss behavior originating from the electronic spin of trivalent Ti ion *without* the increase of  $\chi(T)$  at high temperature. We have observed this increase of  $\chi(T)$  for all the samples except for  $x = 2$ . This

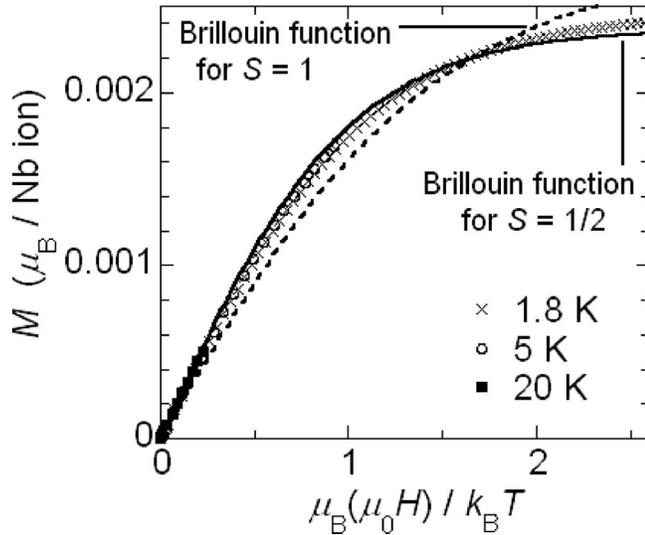


FIG. 3. Magnetization curves of  $Y_2Nb_2O_7$ . Horizontal axis is scaled by a nondimensional variable  $h = \mu_B(\mu_0 H)/k_B T$ . Solid line represents the Brillouin function for  $S=1/2$  multiplied by 0.00237. Dotted line represents the Brillouin function for  $S=1$  multiplied by 0.00280.

suggests that the increase of  $\chi(T)$  above about 200 K in  $Y_2Nb_2O_7$  and  $Y_2Nb_{0.1}Ti_{1.9}O_7$  is due to *magnetic* Nb ions, namely, tetravalent Nb ions. Thus, we expect that tetravalent Nb ions are more stable compared with trivalent Ti ions in this system, although we cannot completely rule out the existence of small amount trivalent Ti ions. The origin of the increase of  $\chi(T)$  is ascribable to the contribution from a thermally excited magnetic state, as we discuss below.

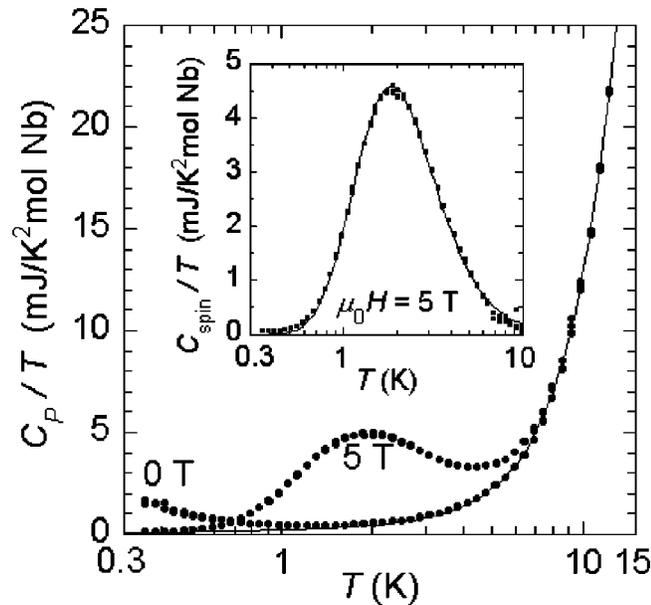


FIG. 4. Specific heat divided by temperature  $[C_p(T,H)/T]$  of  $Y_2Nb_2O_7$  at 0 and 5 T. Solid line represents the fourth-order fitting ( $C_{fit}/T$ ) for the data at 0 T between 6 and 25 K. In the inset, the electronic specific heat at 5 T is shown. Solid line is the Schottky-specific-heat fitting multiplied by 0.0027.

In Fig. 3, we plot magnetization curves for  $Y_2Nb_2O_7$ . Horizontal axis is scaled by a nondimensional variable  $h = \mu_B(\mu_0 H)/k_B T$ , where  $\mu_B$ ,  $\mu_0$ , and  $k_B$  are the Bohr magneton, the vacuum permeability, and the Boltzmann constant. Solid line represents the Brillouin function for  $S=1/2$  multiplied by 0.00237:  $M(h) = 0.00237 \tanh(h) \mu_B / \text{Nb ion}$ . Although a slight difference between the observed  $M(h)$  and the Brillouin function exists,<sup>27</sup> these magnetization curves are ascribable to 0.24(2)% of free  $S=1/2$  spin per Nb site.<sup>28</sup> This value is consistent with the fraction derived from the Curie-Weiss fitting.

In Fig. 4, the specific heat divided by temperature  $C_p(T,H)/T$  of  $Y_2Nb_2O_7$  at 0 and 5 T is shown. Neither data exhibits a clear sign of a phase transition. In order to estimate the lattice contribution in the specific heat, we performed the fourth-order fitting ( $C_{fit}/T = c_0 + c_1 T + c_2 T^2 + c_3 T^3 + c_4 T^4$ ) for the data at 0 T between 6 and 25 K (a solid line in Fig. 4). The obtained  $c_0$  and  $c_1$  are 0.0193 mJ/K<sup>2</sup>molNb and  $-0.0119$  mJ/K<sup>3</sup>molNb, respectively. The contributions from  $c_0$  and  $c_1$  are less than about 0.2% of total specific heat at all the temperatures of this investigation, and are negligible. This result supports that  $Y_2Nb_2O_7$  is indeed an insulator.

In the inset of Fig. 4, the electronic specific heat at 5 T,  $C_{spin}/T = C_p(T,5T)/T - C_{fit}/T$ , is shown. We performed the Schottky fitting by assuming that the observed peak in  $C_{spin}/T$  originates from free  $S=1/2$  spins

$$\frac{C}{T} = \frac{zR}{T} \left( \frac{2\Delta E}{k_B T} \right)^2 \frac{\exp^{2\Delta E/k_B T}}{(1 + \exp^{2\Delta E/k_B T})^2}. \quad (2)$$

Here,  $z$ ,  $R$ , and  $2\Delta E$  are constants corresponding to the fraction of free  $S=1/2$  spin per Nb site, the gas constant, and the characteristic temperature of the Schottky specific heat, respectively. Solid line in the inset of Fig. 4 represents the above fitting curve. We obtained  $z=0.0027(1)$  and  $\Delta E = 3.02(5)$  K. This fraction  $z$  is again consistent with the two values independently deduced from the susceptibility and magnetization data. Moreover, the  $\Delta E$  is consistent with the Zeeman energy of a free  $S=1/2$  spin at 5 T,  $E_{Zeeman} = gS\mu_B(\mu_0 H) = 3.36$  K, if we use Landé's  $g$  factor equal to 2. The above result conversely implies that the increase of  $C/T$  at low temperature in the zero-field data is due to the electronic specific heat of 0.27% of free  $S=1/2$  spin. The obtained  $\Delta E(H=0)$  is quite small, 0.06(1) K.

The above three independent analyses strongly indicate that the *observable*  $S=1/2$  spin exists on less than 0.3% of the Nb sites in  $Y_2Nb_2O_7$  and does not undergo any magnetic phase transition; the rest of the Nb spins apparently disappears. This leads us to conclude that either a spinless state ( $S_{band}=0$ ) due to the specific band structure (discussed below) or spin-singlet ( $S_{total}=0$ ) state is realized in this material. In the latter case, however, it may not be easy to explain how the spin-singlet formation occurs at a temperature greater than 800 K since this temperature is rather high for the energy scale of spin interaction of a  $d$ -electron system. The observed minor  $S=1/2$  spins ( $<0.3\%$ ) are attributable to the localized free spins at grain boundaries or around

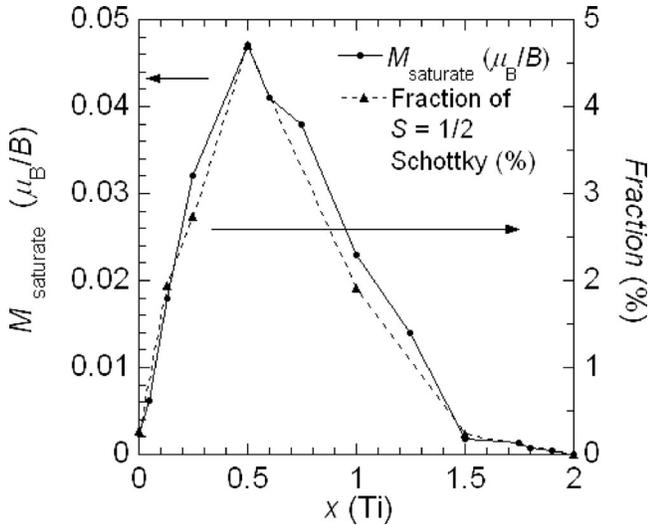


FIG. 5. Titanium substitution dependence of the saturated magnetic moment of  $Y_2Nb_{2-x}Ti_xO_7$  at 1.8 K and the fraction of the electronic Schottky specific heat for  $S=1/2$  spins.

defects. Similar suppression of apparent spins is reported by Istomin *et al.* in other pyrochlore niobates  $CaLnNb_2O_7$  ( $Ln=Sm, Lu$ ), in which the average valency of Nb ions is 4.5.<sup>20</sup> We also note that results similar to those in  $Y_2Nb_2O_7$  are obtained in the rutile  $NbO_2$  ( $Nb^{4+}$ :  $S=1/2$ ),<sup>29</sup> in which Peierls transition might be attributable to the disappearance of the major  $S=1/2$  spins.<sup>30</sup>

In order to investigate the origin of the smallness of the amount of the observed  $S=1/2$  spins in  $Y_2Nb_2O_7$ , we prepared  $Y_2Nb_{2-x}Ti_xO_7$  with an expectation that nonmagnetic tetravalent Ti ions breaks the intercoupling between the Nb ions.  $Y_2Nb_{2-x}Ti_xO_7$  ( $0 < x < 2.0$ ) exhibits physical properties similar to those of  $Y_2Nb_2O_7$ . We emphasize that no sign of magnetic ordering was observed between 0.35 and 800 K for all the samples. In Fig. 5, we summarize the saturated moment per B site, with Nb and Ti combined, deduced from the magnetization curve at 1.8 K, along with the fraction of the free  $S=1/2$  spin per B site deduced from the specific heat. As clearly seen, these two results nearly coincide, since the saturated moment of  $S=1/2$  spins would give  $M=1 \mu_B/B$  ion. We note that the fraction obtained from the Curie constant (data not shown) also coincides with these results. The prominent feature of the results is the appearance of spins with increasing  $x$  up to  $x=0.5$ . Nevertheless, the observed saturated moment at  $x=0.5$  is only 4.7(1)% of free  $S=1/2$  spin per B site.

From the above experimental results, we may conclude that  $Y_2Nb_2O_7$  has a spinless ground state. In order to explain this state, we should consider a band structure based on a unit cell of single tetrahedron containing four electrons of four Nb ions. For the  $s$  electron system, for example, the energy levels consist of the ground-state singlet, the first-excited singlet and the second-excited doublet.<sup>31</sup> The latter singlet and the doublets are degenerate at the  $\Gamma$  point. Con-

sequently, in the half-filled case (four  $s$  electrons per tetrahedron), strong electronic correlation among the electrons would open a Coulomb gap between the singlet and the doublet and would make the system spinless state ( $S_{\text{band}}=0$ : the ground-state singlet and the first-excited singlet are filled with four electrons). For a band structure of pyrochlore oxide  $Y_2Nb_2O_7$ , the ground state arising from hybridized  $t_{2g}$  orbitals originating from four Nb sites is expected to be in most cases a doublet by the molecular orbital method. [It is a singlet for  $Lu_2V_2O_7$  (Ref. 32) and in most cases for spinel oxides (Ref. 15).] This is also supported by the band structure for  $Y_2Ti_2O_7$  calculated by local-density approximation (LDA), in which  $3d-t_{2g}$  hybridized bands correspond to the electronic state at the Fermi level of  $Y_2Nb_2O_7$ .<sup>33</sup> The lowest twofold-degenerate  $3d-t_{2g}$  band at  $\Gamma$  point corresponds to the ground-state doublet, which was discussed above, for  $Y_2Nb_2O_7$ . Hence, considering the correlations among the  $4d$  electrons of Nb, we may expect  $Y_2Nb_2O_7$  to be in a spinless state ( $S_{\text{band}}=0$ : the ground state doublet is occupied by four electrons) with a Coulomb gap between the ground-state doublet and the first-excited state. Without sufficient electron correlation the first excited state is partially occupied because of the band overlap and the system would have exhibited metallic behavior. The experimental results suggest that this band structure is robust in the presence of nonmagnetic impurity since the system remains insulating even for  $0.0 < x < 2.0$ . The clarification of the  $x$  dependence of emerging magnetic moment requires further theoretical study.

#### IV. SUMMARY

In summary, we report  $M$  and  $C_p$  of a series of insulating pyrochlore niobates  $Y_2Nb_{2-x}Ti_xO_7$ . Although the end member  $Y_2Nb_2O_7$  contains magnetic tetravalent Nb ions ( $4d^1$ ) on the pyrochlore lattice, it does not exhibit any sign of magnetic ordering at least between 0.35 and 800 K. Less than 0.3% amount of spin  $S=1/2$  is observed; the remaining spins of Nb ions apparently disappear. In addition, this magnetic component increases only up to 4.7% of B sites with the substitution of the nonmagnetic Ti ions. These indicate that the ground state of  $Y_2Nb_2O_7$  is ascribable to a strongly correlated spinless state. In order to seek the realization of the QSL state in real materials, one should take into account such a specific band structure of the pyrochlore oxides.

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- <sup>21</sup>H. Fukazawa, R. Higashinaka, O. Sakai, and Y. Maeno (unpublished).
- <sup>22</sup>With the help of S. Shamoto (private communication) it was shown by a Rietveld analysis [(RIETAN-2000), F. Izumi and T. Ikeda, *Mater. Sci. Forum* **321-324**, 198 (2000)] of our x-ray diffraction data that the oxygen occupation and the oxygen position of the end member  $Y_2Nb_2O_7$  are those for a pyrochlore structure but not for an oxygen-deficient fluorite structure.
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- <sup>24</sup>We performed background subtraction for all the data by using the following formula:  $M_1 - M_{BGM} = m_1 \times (M_2 - M_1) / (m_2 - m_1)$ . Here,  $M_{BGM}$ ,  $M_1$  and  $M_2$  are the background magnetization, the magnetization with mass  $m_1$ , and the magnetization with mass  $m_2$  ( $\neq m_1$ ), respectively.
- <sup>25</sup>Because of the limitation of the sample space in an oven of the magnetometer, it was necessary to reduce the sample weight. Thus, the high-temperature data was obtained under a high field of 7 T. We confirmed that the data between 300 and 350 K at 7 T with the oven quantitatively agree with those at 0.1 T without the oven.
- <sup>26</sup>K. Ishida and Y. Kitaoka (private communication).
- <sup>27</sup>This difference may be attributable to the uncertainty in the demagnetization effect.
- <sup>28</sup>As clearly seen in Fig. 3, the Brillouin function for  $S$  larger than  $1/2$  worsens the fits.
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