

## Synthesis, Structural and Magnetic Properties of the Solid Solution $(\text{CuCl}_{1-x}\text{Br}_x)\text{LaNb}_2\text{O}_7$ ( $0 \leq x \leq 1$ )

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(Received August 12, 2009; accepted October 7, 2009; published December 25, 2009)

The two-dimensional (2D) quantum spin system  $(\text{CuCl})\text{LaNb}_2\text{O}_7$  has a spin-singlet ground state with a gap of 2.3 meV, while the isostructural material  $(\text{CuBr})\text{LaNb}_2\text{O}_7$  displays a collinear antiferromagnetic order at  $T_N = 32$  K. Here, we report on the synthesis of solid solution  $(\text{CuCl}_{1-x}\text{Br}_x)\text{LaNb}_2\text{O}_7$  ( $0 \leq x \leq 1$ ), and its structural and magnetic properties investigated by magnetic susceptibility, high-field magnetization, and neutron diffraction measurements. The  $x$  dependences of cell parameters follow Vegard's law, verifying the uniform distribution of Cl and Br atoms at the halide site, although a more complex structural evolution is inferred from an opposing correlation between the intra- and interlayer cell distances (vs  $x$ ). 5%-Br substitution is found to induce an antiferromagnetic order with  $T_N = 7$  K, consistent with recent  $\mu\text{SR}$  results, and the magnetic structure is collinear, having a significantly reduced moment. Further Br substitution leads to a linear increase in  $T_N$  up to  $x = 1$ . These results indicate that  $(\text{CuCl})\text{LaNb}_2\text{O}_7$  is located in the vicinity of the quantum phase boundary.

KEYWORDS: quantum spin system, spin gap,  $(\text{CuCl})\text{LaNb}_2\text{O}_7$ ,  $(\text{CuBr})\text{LaNb}_2\text{O}_7$ , susceptibility, magnetization, neutron diffraction

DOI: [10.1143/JPSJ.79.014709](https://doi.org/10.1143/JPSJ.79.014709)

### 1. Introduction

Novel quantum phase transitions can be driven by tuning various parameters such as magnetic field and pressure, not temperature. For a quantum spin system having a spin-singlet ground state with a finite gap, the application of an external magnetic field is known to induce the Bose-Einstein condensation (BEC) of triplet magnons as observed in  $\text{TlCuCl}_3$ ,<sup>1-4</sup> or the crystallization of triplet magnons to yield magnetization plateaus as observed in  $\text{SrCu}_2(\text{BO}_3)_2$ .<sup>5</sup>

Cationic substitution is also a useful and versatile parameter for studying spin-singlet compounds, which is classified into two types. One is substitution by (non-)magnetic ions with different spin multiplicities at the magnetic site. Magnetic order is induced by the substitution of small amounts of  $\text{Zn}^{2+}$  ( $S = 0$ ) substitution for  $\text{Cu}^{2+}$  ( $S = 1/2$ ) in  $\text{CuGeO}_3$ <sup>6</sup> and  $\text{SrCu}_2\text{O}_3$ ,<sup>7</sup> and of  $\text{Mg}^{2+}$  ( $S = 0$ ) substitution for  $\text{Ni}^{2+}$  ( $S = 1$ ) in  $\text{PbNi}_2\text{V}_2\text{O}_8$ .<sup>8</sup> Of particular interest is microscopic phase segregation in a doped one-dimensional chain between spin-ordered and disordered states with a modulated staggered magnetization along the chain.<sup>9,10</sup> The other type of cation substitution is conducted for the counteractions, which leads to chemical pressure and/or bond randomness in the magnetic coupling constants. A Bose-glass state has recently been suggested in  $\text{Tl}_{1-x}\text{K}_x\text{CuCl}_3$ .<sup>11,12</sup> By contrast, anionic substitution (e.g., O-S-Se and F-Cl-Br) has been rarely studied, mainly owing to the large differences in anionic radius and electronegativity, making it difficult to prepare a homoge-

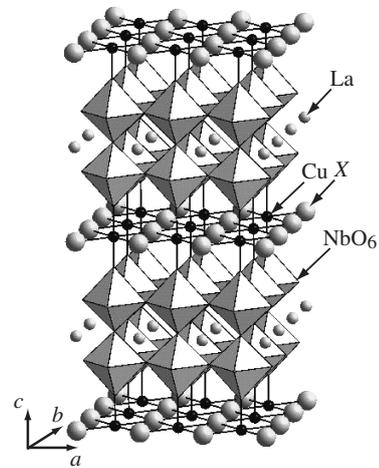


Fig. 1. Crystal structure of  $(\text{CuX})\text{LaNb}_2\text{O}_7$  ( $X = \text{Cl}, \text{Br}$ ).

neous solid solution. However, when magnetic ions are bridged by substitutable anions, we can control the superexchange coupling constants.

$(\text{CuX})\text{LaNb}_2\text{O}_7$  ( $X = \text{Cl}, \text{Br}$ ), as prepared by ion-exchange reactions, consists of  $\text{CuX}$  square-lattice layers with  $S = 1/2$  separated by nonmagnetic perovskite blocks (see Fig. 1).<sup>13</sup>  $(\text{CuCl})\text{LaNb}_2\text{O}_7$  has a spin-singlet ground state separated from the excited state by 2.3 meV,<sup>14</sup> and magnetic field induces the Bose Einstein condensation (BEC) of triplet magnons at 10.3 T.<sup>15,16</sup> In contrast, the Br counterpart undergoes a collinear antiferromagnetic (CAF) order at 32 K.<sup>17</sup>  $(\text{CuX})\text{LaNb}_2\text{O}_7$  were initially assumed as candidates of the  $J_1$ - $J_2$  model where the ferromagnetic (FM) nearest-

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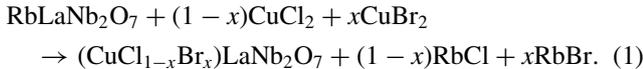
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neighbor ( $J_1$ ) and antiferromagnetic (AFM) next-nearest-neighbor ( $J_2$ ) interactions compete with each other.<sup>15,18</sup> However, nuclear magnetic resonance (NMR) and transmission electron microscopy measurements of the two compounds demonstrated the absence of the  $C_4$  symmetry at both Cu and X sites,<sup>19</sup> inconsistent with the original results of structural analysis.<sup>13</sup> Several superstructures in the CuX plane were proposed to explain the spin-singlet state for  $X = \text{Cl}$ <sup>19</sup> and the CAF state for  $X = \text{Br}$ .<sup>20</sup> However, it is not yet clear whether the proposed model can answer the questions, for example, of why the field-induced transition occurs at a much lower field than that expected from the zero-field spin gap, and of how magnetic coupling differs between  $X = \text{Cl}$  and Br.

In this study, we present the successful preparation of a whole solid solution  $(\text{CuCl}_{1-x}\text{Br}_x)\text{LaNb}_2\text{O}_7$  ( $0 \leq x \leq 1$ ) and its structural and magnetic characterizations by means of X-ray diffraction, neutron diffraction, magnetic susceptibility and high-field magnetization. The motivation of the present study is partly due to the recent observation of magnetic order by muon spin relaxation ( $\mu\text{SR}$ ) for a 5%-Br substituted sample ( $x = 0.05$ ).<sup>21</sup>

## 2. Experimental Results and Discussion

The preparation of  $(\text{CuCl}_{1-x}\text{Br}_x)\text{LaNb}_2\text{O}_7$  ( $x = 0, 0.05, 0.33, 0.50, 0.66, 1$ ) was performed by the following ion-exchange reaction:



The parent compound  $\text{RbLaNb}_2\text{O}_7$  was prepared by a high-temperature reaction using  $\text{Rb}_2\text{CO}_3$  (rare metallic, 99.9%),  $\text{La}_2\text{O}_3$  (rare metallic, 99.99%), and  $\text{Nb}_2\text{O}_5$  (rare metallic, 99.99%) following methods in the literature.<sup>22</sup> Anhydrous  $\text{CuCl}_2$  (Alfa, 99.999) and  $\text{CuBr}_2$  (Alfa, 99.999%) in stoichiometric ratio,  $x$ , were mixed with  $\text{RbLaNb}_2\text{O}_7$ , pressed into pellets inside an argon-filled glove box, sealed in evacuated ( $<10^{-3}$  Torr) Pyrex tubes, and heated at  $320^\circ\text{C}$  for 7 days. To complete the desired reaction, a two-molar excess of  $\text{CuCl}_2/\text{CuBr}_2$  relative to  $\text{RbLaNb}_2\text{O}_7$  was added. The final products were isolated by washing with warm distilled water.

X-ray powder diffraction measurements were carried out at room temperature with Cu  $K\alpha$  radiation on a M18XHF diffractometer (Mac Science). Magnetic susceptibility measurements were performed using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS) in the temperature range of 2–300 K at an applied field  $H = 0.1$  T. High-field magnetization measurements were conducted using an induction method with a multilayer pulsed magnet installed at the Institute for Solid State Physics, The University of Tokyo (ISSP). Magnetization data were collected at 1.3 K in magnetic fields up to 60 T. Powder neutron diffraction measurements were performed on the 5%-Br substituted sample using the ISSP-PONTA triple-axis spectrometer (5G) installed at JRR-3 of the Japan Atomic Energy Agency (JAEA), Tokai. A polycrystalline sample of about 10 g mass was placed in a vanadium cylinder. Neutrons with a wavelength of 2.3618 Å were obtained by the (002) reflection of pyrolytic graphite (PG), and a collimation of open-40'-sample-80'-80' was

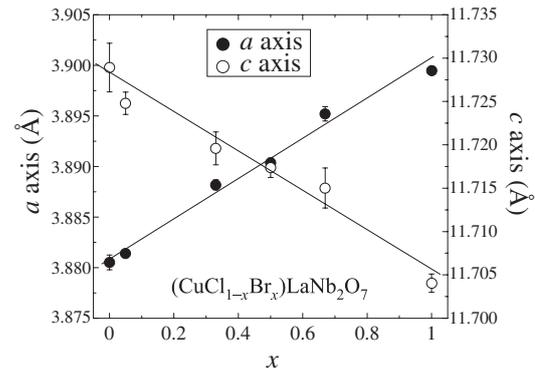


Fig. 2. Crystallographic unit-cell parameters as a function of Br concentration ( $x$ ) in  $(\text{CuCl}_{1-x}\text{Br}_x)\text{LaNb}_2\text{O}_7$ .

employed in combination with a PG filter placed before the sample to eliminate higher-order beam contamination.

Elemental analysis of the products, carried out by energy dispersive spectroscopy (EDS) on a JSM-5600 scanning electron microscope (JEOL), supported the nominal stoichiometry  $(\text{CuCl}_{1-x}\text{Br}_x)\text{LaNb}_2\text{O}_7$ . X-ray diffraction profiles of the whole solid solution  $(\text{CuCl}_{1-x}\text{Br}_x)\text{LaNb}_2\text{O}_7$  were indexed to the tetragonal symmetry as in the case of the end members ( $x = 0$  and 1).<sup>13</sup> The peak widths of the solid solution were as sharp as those of the end members, and no multiphase region was observed within the experimental resolution. The uniform distributions of the Cl and Br atoms at the X site were further supported by results of EDS on a JEM-2010F transmission electron microscopy (TEM) with an operating voltage of 200 kV at ISSP. The  $x$  dependences of the lattice parameters, as shown in Fig. 2, demonstrate that both  $a$  and  $c$  change in proportion to  $x$ , following Vegard's law, implying the successful preparations of the whole solid solution. However, Br substitution cannot be simply understood as a negative chemical pressure, since the  $a$ -axis increases and the  $c$ -axis decreases with increasing  $x$ , a finding whose explanation remains unclear at the present stage. However, this should be a common feature of this family of ion-exchanged compounds, because  $(\text{CuBr})\text{LaTa}_2\text{O}_7$  and  $(\text{CuBr})\text{La}_2(\text{Ti}_2\text{Nb})\text{O}_{10}$  also have shorter  $c$ -axes than their Cl counterparts.<sup>23</sup> The determination of the precise structure of  $(\text{CuCl}_{1-x}\text{Br}_x)\text{LaNb}_2\text{O}_7$  is required in the future. For example, a superstructure, as that found in  $(\text{CuCl})\text{LaNb}_2\text{O}_7$ ,<sup>19</sup> might also be observed in the (Cl, Br) solid solution.

Figure 3(a) shows the temperature dependence of the magnetic susceptibility  $\chi(T)$  for the solid solution in the region below 50 K. The kink at 32 K for  $x = 1$  was ascribed to the onset of the CAF order.<sup>17</sup> Likewise, kinks were found at 17, 21, and 25 K for  $x = 0.33, 0.5$ , and  $0.67$ , respectively. The linear decrease in the kink temperature [see Fig. 3(b)] strongly suggests that those kinks are due to magnetic order as well. In Fig. 4, the magnetization curves for  $x \geq 0.33$  show a linear increase over a wide field range. Although the magnetizations do not saturate up to 60 T applied in this study, one can say that the saturation field would become smaller with decreasing  $x$ , implying a weaker superexchange constant for Cu–Cl–Cu than for Cu–Br–Cu.

On the other hand, as shown Figs. 3(a) and 4, both  $\chi(T)$  and  $M(H)$  for  $x = 0.05$  are considerably different from those

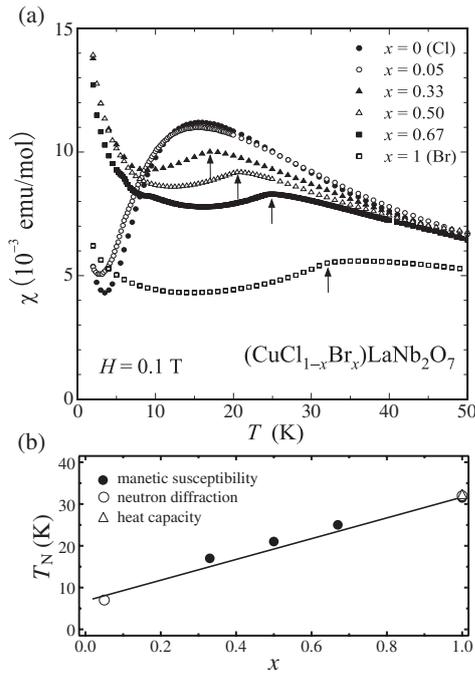


Fig. 3. (a) Magnetic susceptibilities of  $(\text{CuCl}_{1-x}\text{Br}_x)\text{LaNb}_2\text{O}_7$  measured at  $H = 0.1$  T. Arrows indicate the kink temperatures. (b)  $x$  dependence of  $T_N(x)$ , determined by magnetic susceptibility (solid circles), neutron diffraction (open circles) and heat capacity (triangle) measurements.<sup>17)</sup>

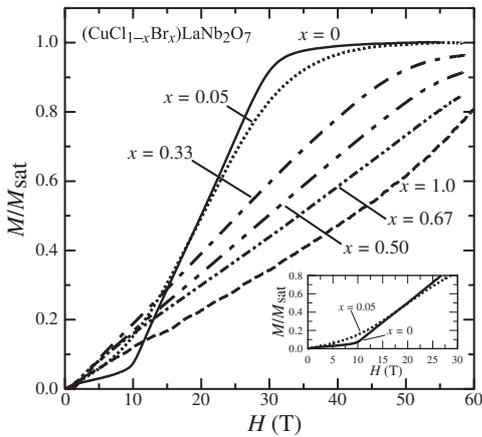


Fig. 4. Magnetization curves for  $(\text{CuCl}_{1-x}\text{Br}_x)\text{LaNb}_2\text{O}_7$  measured at  $1.3$  K. The inset shows the magnetizations for  $x = 0$  and  $0.05$  below  $H = 30$  T.

for  $x \geq 0.33$ . However, their behaviors are similar to those for  $x = 0$ .<sup>14,15)</sup> The  $\chi(T)$  for  $x = 0.05$  is characterized by a broad maximum at about 15 K and a substantial decrease in  $\chi(T)$  below this temperature, and the concave behavior in  $M(H)$  at around 10 T (see the inset of Fig. 4) is reminiscent of the transition from the spin-singlet state to the field-induced antiferromagnetic state. However, recent  $\mu\text{SR}$  experiments revealed the presence of a magnetic order in this material.<sup>21)</sup> In fact, a very careful look at the  $\chi(T)$  data revealed a tiny kink at around 7 K, suggesting the breakdown of the spin gap. Accordingly, in order to obtain insight into the ground state of  $x = 0.05$ , we performed neutron powder diffraction measurements. Figure 5(a) shows the intensity difference,  $I(3.5\text{ K}) - I(18\text{ K})$ , in the  $2\theta$  range from 16 to  $20^\circ$ . We observed a relatively weak magnetic peak corresponding

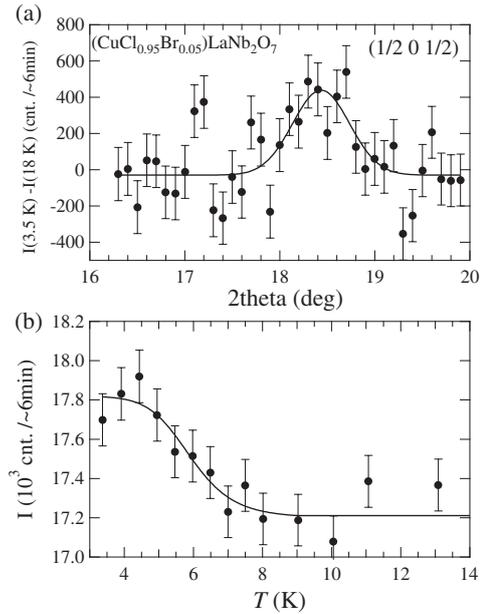


Fig. 5. (a) Difference plot of neutron scattering intensity for the  $x = 0.05$  sample,  $I(3.5\text{ K}) - I(18\text{ K})$ , corresponding to the  $(1/2, 0, 1/2)$  magnetic reflection. The solid curve is a single-component Gaussian fit. (b) Temperature dependence of the  $(1/2, 0, 1/2)$  intensity. The solid line is a guide to the eyes.

to the  $(1/2, 0, 1/2)$  reflection, the peak width of which was resolution limited. Hence, it is natural to assume that this material has the same CAF order as  $(\text{CuBr})\text{LaNb}_2\text{O}_7$  ( $x = 1$ ).<sup>17)</sup> From the temperature dependence of this magnetic reflection [Fig. 5(b)], we estimated  $T_N$  as 7 K, which again agrees with the  $\mu\text{SR}$  result. From the data at 3.5 K, the magnitude of the magnetic moment in the ordered state was roughly estimated as  $0.2(1)\mu_B$ , where the crystal structure of  $(\text{CuCl})\text{LaNb}_2\text{O}_7$  determined by X-ray diffraction analysis at room temperature<sup>13)</sup> and the magnetic structure with the moments aligned parallel to the  $b$ -axis as found in  $(\text{CuBr})\text{LaNb}_2\text{O}_7$ <sup>17)</sup> were assumed. The estimated ordered moment is significantly smaller than  $0.6\mu_B$  for  $x = 1$ . It is also evidenced from the  $\mu\text{SR}$  measurements<sup>21)</sup> that the magnetic moment for  $x = 0.05$  is considerably smaller than that for  $0.33 \leq x \leq 1$ . The observations of long-range magnetic order induced by substituting only 5% Br and the significantly reduced magnetic moment for  $x = 0.05$  indicate that  $(\text{CuCl})\text{LaNb}_2\text{O}_7$  is located in the vicinity of the quantum phase boundary adjacent to the ordered state.

Contrasting behavior has been observed in the Nb-site substituted system  $(\text{CuCl})\text{La}(\text{Nb}_{1-y}\text{Ta}_y)_2\text{O}_7$ ,<sup>21,24)</sup> in which the spin-singlet state is robust against cationic substitution. Substantial substitution on the order of  $y \sim 0.4$  is needed to induce CAF magnetic order, but with the coexistence of the ordered and disordered phases extending up to  $y = 1$ . Note that the effect of chemical disorder in the magnetic layer  $\text{CuX}$  is larger than that in the nonmagnetic layer  $\text{LaB}^{5+}_2\text{O}_7$  [ $B^{5+}$ :  $\text{Nb}^{5+}$  or  $\text{Ta}^{5+}$  ( $d^0$ )]. So far, there have been many theoretical works on the rapid breaking of spin-singlet dimers upon the addition of vacancies in a variety of spin-gapped models, a procedure which is considered relevant to creating free spins. Some theories showed that staggered spin-spin correlations are enhanced in the vicinity of spin vacancies,<sup>25–29)</sup> which accounts for the emergence of the

ordered phase in the cationic-substituted 1D magnetic materials  $\text{CuGeO}_3$  and  $\text{SrCu}_2\text{O}_3$ .<sup>9,10</sup> In the 2D orthogonal dimer  $\text{SrCu}_2(\text{BO}_3)_2$ , staggered magnetization develops around the triplet excitation in the  $1/8$  plateau phase.<sup>5</sup> Thus, in spin-singlet compounds, independent of their dimensionality, any local perturbations such as defects or chemical randomness can potentially induce staggered magnetizations, leading to a magnetically ordered state. By analogy, the creation of magnetic order by a small amount of Br substitution in  $(\text{CuCl})\text{LaNb}_2\text{O}_7$  may be associated with staggered correlations induced around Br ions. A rapid depolarization of the  $\mu\text{SR}$  signal observed in the 5%-Br system<sup>21</sup> may be related to the spatial variation of staggered ordered moment size. The  $\mu\text{SR}$  spectra of  $\text{CuGeO}_3$  doped with Zn and Si exhibit fast relaxation owing to this effect.<sup>9</sup> Further experiments are necessary to clarify the local state.

### 3. Conclusion

We succeeded in synthesizing the solid solution system  $(\text{CuCl}_{1-x}\text{Br}_x)\text{LaNb}_2\text{O}_7$  ( $0 \leq x \leq 1$ ) and investigated its magnetic properties by means of susceptibility, magnetization, and powder neutron diffraction measurements. The experimental results reveal that the switching of the spin-singlet state in  $(\text{CuCl})\text{LaNb}_2\text{O}_7$  to a collinear-type magnetic ordered state occurs by as little as 5% substitution of Br, which is in stark contrast to the Ta-for-Nb substitution systems. It is likely that the chemical disorder in the magnetic layer  $\text{CuX}$  has a stronger effect on the magnetic properties than that in the nonmagnetic layer  $\text{LaB}_2\text{O}_7$ .

The chemistry of the present material can yield a large family of materials represented as  $(\text{MX})\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}$  ( $M$ : divalent transition-metal,  $A$ : alkali, alkali-earth, and rare-earth metals,  $n$ : integer),<sup>23</sup> and these materials provide a variety of magnetic states, depending on the tunable parameters. For example, it was shown that substituting the  $A$ -site in  $(\text{CuBr})\text{A}_2\text{Nb}_3\text{O}_{10}$  controls the width of the  $1/3$  magnetization plateau.<sup>30</sup> Here, we note that ion-exchange reactions for yielding  $(\text{MX})\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}$  rely on the stability of the byproduct alkali halides, in the present case  $\text{RbCl}$  and  $\text{RbBr}$ , relative to transition-metal halides, so anionic substitution should be generally applied to the entire  $(\text{MX})\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}$  systems. It would be interesting to see, e.g., how anionic substitution for  $(\text{CuBr})\text{Sr}_2\text{Nb}_3\text{O}_{10}$  affects the  $1/3$  plateau phase.

### Acknowledgements

This work was supported by a Grant-in-Aid for Science Research on Priority Areas “Novel States of Matter Induced by Frustration” (No. 19052004) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, the Japan–U.S. Cooperative Science Program from the Japan Society for the Promotion of Science and NSF (No. 14508500001), and by the Global COE program International Center for Integrated Research and Advanced Education in Materials Science, Kyoto University, Japan. This work was also supported by Murata Science Foundation (No. A71115). The work at Columbia University was supported by US NSF grants DMR-05-02706 and DMR-08-06846. One of the authors (Y.T.) was supported by the Japan Society for the Promotion of Science for Young Scientists.

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