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1/3 Magnetization Plateau in Spin-1/2 Square Lattice Antiferromagnet $(CuBr)Sr_2Nb_3O_{10}$

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A new triple-layered perovskite $(CuBr)Sr_2Nb_3O_{10}$ with the $S = 1/2$ square lattice has been prepared through a *chimie douce* route. Presence of strong spin frustration is inferred from zero-field specific heat measurements which exhibit successive phase transitions at 9.3 and 7.5 K. Application of magnetic fields merges the transition temperatures at 3 T, suggesting that the intermediate phase is of magnetic origin with fluctuating spin–spin correlation. Despite the square geometry, magnetization curves have revealed a metamagnetic transition to a novel phase characterized by a 1/3 plateau of the saturated magnetization.

KEYWORDS: $(CuBr)Sr_2Nb_3O_{10}$, square lattice, ion exchange, frustration, magnetization plateau, successive phase transitions
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Historically, the study of geometrically frustration in spin systems has been focused on the triangle-based models such as triangular, kagomé and pyrochlore lattices.[1)] This is due to the fact that they simply consist of single elements of exchange constants, i.e., nearest-neighbor (NN) interactions (J_1), and the abundance of experimental examples, allowing the verification and development of relevant theories. The opposite holds true for the square-based models that involve addition of next-nearest-neighbor (NNN) (J_2) interactions.[2)] In order to induce frustration into the latter systems, J_1 and J_2 need to be of comparable strength but nature favors the dominance of the interactions for shorter bonds, resulting in the well-known (π, π) Néel ordered state.

However, the discovery of the experimental correspondences, $Li_2VO(Si, Ge)O_4$ for the square lattice (termed as the J_1–J_2 model),[3)] CaV_4O_9 for the 1/5-depleted square lattice,[4)] and $SrCu_2(BO_3)_2$ for the Shastry-Sutherland lattice,[5)] has activated research in this area. Recently, double-layered perovskites $(CuX)LaNb_2O_7$ (X = Cl, Br), synthesized by a topotactic ion-exchange reaction,[6)] were added to the list of the J_1–J_2 model;[7–11)] For both compounds, strong competition is expected between the ferromagnetic (F) J_1 and antiferromagnetic (AF) J_2. As a result, $(CuBr)LaNb_2O_7$ establishes a $(\pi, 0)$ collinear AF order (CAF) at 32 K with a reduced moment $\sim$0.6 μ_B, while $(CuCl)LaNb_2O_7$ has the spin-singlet ground state, with a gap of 2.3 meV in the spin excitation spectrum. Here, the choice of the halogen ion seems to change the J_2/J_1 ratio and hence determines the ground state.

$(CuX)LaNb_2O_7$ belongs to the Dion-Jacobson series expressed as $(CuX)A_{n-1}B_nO_{3n+1}$, where A is La^{3+}, Ca^{2+}, Na^{+}, …, B is Nb^{5+}, Ta^{5+}, Ti^{4+}, $n = 2, 3, 4, \ldots$.[6,10,11)] The rich diversity of the family brings a crucial advantage over existing compounds, that is, a systematic control of the magnetic properties by varying parameters A, B, X, and n. Particularly interesting is tuning n, by which one can control the two-dimensionality (2D). In comparison with the $n = 2$ compounds with $a \sim 4$ Å, $c \sim 12$ Å, the c-lattice constant for the $n = 3$ compounds is expanded by $\sim$4 Å (corresponding to the one-perovskite unit), while remaining the a–lattice constant nearly unchanged [see Fig. 1(a)], offering a better 2D and enhanced quantum fluctuations. Although several $n = 3$ compounds have been prepared so far,[10,11)] only little is known about the magnetism. Here, we report the synthesis and magnetic properties of a new $n = 3$ compound $(CuBr)Sr_2Nb_3O_{10}$.

In a similar procedure as described in refs. 9 and 10, $(CuBr)Sr_2Nb_3O_{10}$ forms from the ion-exchange reaction, expressed as "$RbSr_2Nb_3O_{10} + CuBr_2 \rightarrow (CuBr)Sr_2Nb_3O_{10} + RbBr$". The product was washed with distilled water to eliminate RbBr and unreacted $CuBr_2$, which allows us to

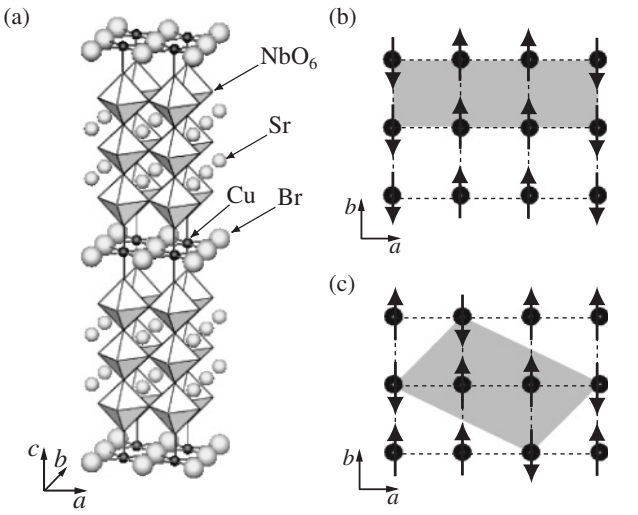

Fig. 1. (a) Structure of $(CuBr)Sr_2Nb_3O_{10}$. Small and large open circles, and solid circles denote, respectively, Sr, Br and Cu atoms, and octahedra are NbO_6. The magnetic $[CuBr]^+$ layer is sandwiched by the non-magnetic $[Sr_2Nb_3O_{10}]^-$ slabs. (b), (c) Possible magnetic structures at the 1/3 plateau, where magnetic unit cells are represented in grey.

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carry out quantitative analysis of the magnetic properties. The powder x-ray diffraction data collected on an M18XHF diffractometer (Mac Science) were readily indexed on the tetragonal symmetry. The lattice parameters $a = 3.91069(4)$ Å, $c = 16.0207(3)$ Å are similar to those of a known $(CuCl)Ca_2Nb_3O_{10}$ ($a = 3.8496$ Å, $c = 15.6593$ Å).[10] The a axis is slightly longer than that of $(CuBr)LaNb_2O_7$ ($a = 3.9025$ Å), reflecting the difference in the ionic radii of the A sites ($r_{Sr} = 1.58$ Å, $r_{La} = 1.50$ Å). No trace of impurity phase was found within the experimental resolution of the present experiment. Static magnetization measurements were performed on a powder sample with a SQUID magnetometer (Quantum Design, MPMS) over the temperature range $T = 2$–300 K at magnetic fields H up to 5 T. High-field magnetization measurements up to 30 T were made using an induction method with a multilayer pulse magnet installed at Institute for Solid State Physics (ISSP), The University of Tokyo. Specific heat capacity measurements were performed from 2 to 40 K in magnetic fields up to 9 T by the heat-relaxation method using a QD-PPMS at Institute for Chemical Research.

Figure 2(a) shows the T dependence of magnetic susceptibility χ of $(CuBr)Sr_2Nb_3O_{10}$ measured at 0.1 T. The fit to the Curie–Weiss law plus a T-independent term, $\chi(T) = C/(T-\theta) + \chi_0$, for $100 < T < 300$ K gives the Weiss temperature $\theta = 20.9(3)$ K, Curie constant $C = 0.408(1)$ emu K/(mol Cu), and $\chi_0 = -1.36(3) \times 10^{-4}$ emu/(mol Cu). The obtained value of C agrees well with that expected for 1 mol of Cu^{2+} ions, meaning completion of the ion-exchange reaction. The positive θ implies that the F J_1 has a greater magnitude than the AF J_2, in contrast to the negative θ for the $n = 2$ cases [$\theta = -5.1$ K for $(CuBr)LaNb_2O_7$ and -9.6 K for $(CuCl)LaNb_2O_7$].[7,9] The deviation from the Curie–Weiss behavior appreciable below 100 K is attributable to development of short-range magnetic ordering. Instead of a broad maximum in $\chi(T)$ typically seen for low-dimensional spin systems, however, we observed a rather smooth growth of $\chi(T)$ with reducing T which continues until it flattens out below 5 K. At this point, it is hard to judge whether or not a magnetic transition exists and if it does at which temperature it occurs, but the absence of the so-called Curie-tail originated from magnetic impurities and defects assures again a good quality of the sample. No broad maximum would be characteristic of a system where F dominates AF.

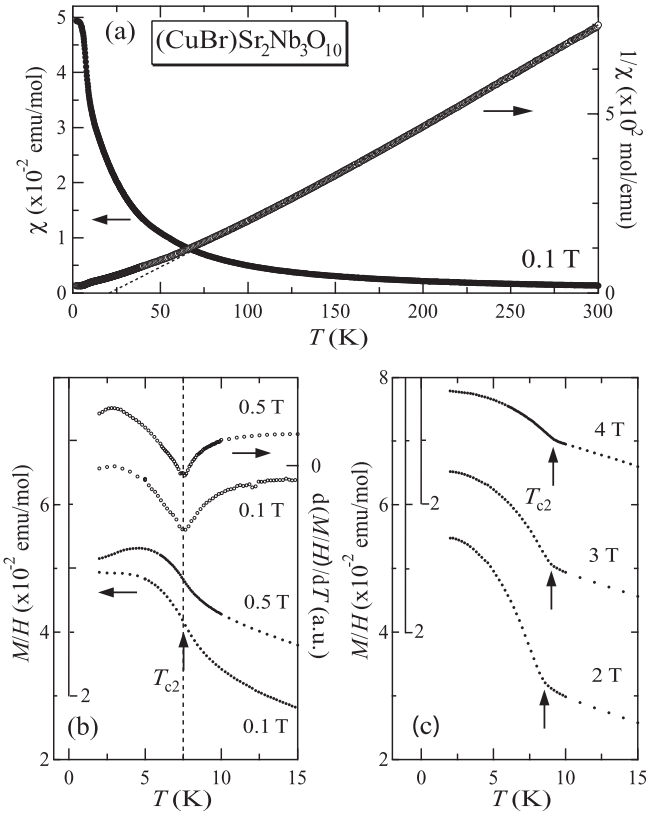

Fig. 2. (a) $\chi(T)$ and $\chi(T)^{-1}$ for $(CuBr)Sr_2Nb_3O_{10}$ measured at 0.1 T. The dotted line is the Curie–Weiss fit. (b) $M(T)/H$ and $d(M(T)/H)/dT$ at 0.1, 0.5 T. (c) $M(T)/H$ at 2, 3, 4 T.

Specific heat is a technique that can probe phase transitions with higher sensitivity. The C_p vs T plot at 0 T clearly (Fig. 3) demonstrates two peaks at 9.3 K (T_{c1}) and 7.5 K (T_{c2}), suggesting successive phase transitions. Non-discontinuous character and the absence of T hysteresis in $C_p(T)$ as well as $\chi(T)$ indicate the transitions to be of second order. Successive phase transitions are known as characteristic features of low-dimensional spin systems with geometrical frustration, as experimentally observed in triangular lattices such as $CsCoCl_3$ and $CsNiCl_3$.[12] It would be thus natural to consider that the geometrical frustration in $(CuBr)Sr_2Nb_3O_{10}$ plays a crucial role in this phenomena as well. Namely, observed transitions might be those from the paramagnetic state (P) to the intermediate magnetic state (M_1) at T_{c1} and finally to a different and probably more-ordered magnetic state (M_2) at T_{c2}. If the M_1 phase is associated with a magnetic ordering of some kind, T_{c1} and T_{c2} should be affected by the magnetic field. In fact, the application of magnetic fields decreases T_{c1} while it increases T_{c2} and finally merges two transitions together at around 3 T. Subsequently, the transition temperature T_c determined by $C_p(T)$ draws a dome shaped boundary peaking at 5 T on the T–H phase diagram, as shown in Fig. 4. It is likely that a magnetic state below the boundary is most stabilized around 5 T, as will be discussed later.

The gradual increase in $C_p(T)$ above 12 K in the P region is nearly insensitive to H. Since there exist no isomorphic compounds used as a nonmagnetic reference to derive the lattice contribution βT^3, we roughly assumed as $\beta = 0.97(2) \times 10^{-3}$ J/(K^4 mol). Subtracting βT^3 from the raw data at 0 T, one obtains magnetic specific heat C_m, and the subsequent T-integration of C_m/T gives the magnetic entropy S_m, both of which are shown in the inset of Fig. 3. The measured entropies at T_{c2} and T_{c1}, respectively, are at most 20 and 30% of the total entropy ($R \ln 2$), indicating that the present spin system is effectively correlated over much higher temperatures but nevertheless, cannot readily show a long-range order at such temperatures due to enhanced 2D (by increased n) along with competing in-plane interactions.

Stimulated by the observation of successive phase transitions in low magnetic fields, we conducted the measurements of the T dependence of magnetization at fixed magnetic fields ($H < 5$ T). As shown in the inset of Fig. 2(c), a distinct inflection appears in the M/H vs T curves at $H = 2$, 3 and 4 T. The temperature at which this inflection occurs gradually increases with H and agrees well

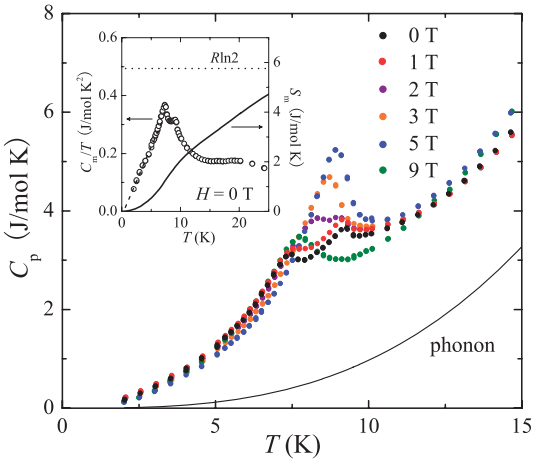

Fig. 3. C_p vs T of $(CuBr)Sr_2Nb_3O_{10}$ measured at 0, 1, 2, 3, 5, and 9 T. The solid line represents the phonon term. Inset: C_m/T (open circles) and S_m (solid line) for $H = 0$ T. The broken line is the linear fit in the low-T region.

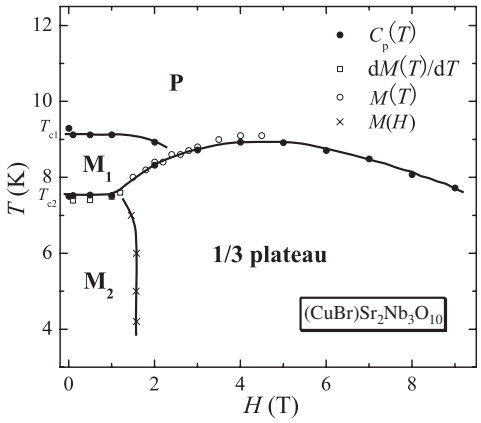

Fig. 4. The T–H phase diagram for $(CuBr)Sr_2Nb_3O_{10}$, determined by $C_p(T)$ (open circles), $dM(T)/dT$ (open squares), $M(T)$ (open circles), and $M(H)$ (crosses).

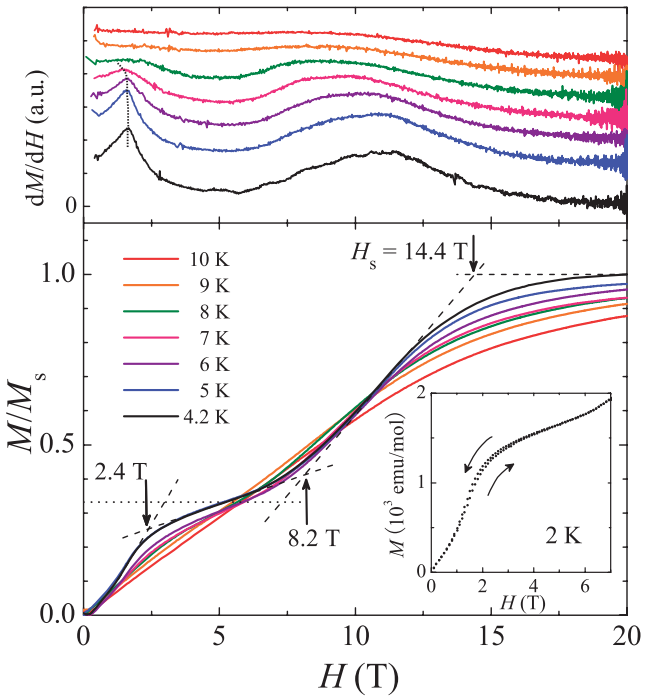

Fig. 5. Normalized (bottom) and differential (top) magnetizations for $(CuBr)Sr_2Nb_3O_{10}$ measured in pulsed fields. The static magnetization is shown in the inset, where a small hysteresis is seen. The dotted line corresponds to the 1/3 magnetization.

with T_{c2} determined by the $C_p(T)$ experiment. It is worth noting that T_{c2} at 0 T and 0.5 T coincides with the temperature at which $d(M/H)/dT$ takes a minimum value [Fig. 2(b)], so it may be the measure of T_{c2} in a low-H region below 1 T. In contrast, the T dependence of magnetization has no apparent anomaly at T_{c1} even in the presence of H. A plausible explanation is that the M_1 state may be an ordered but partially disordered state with considerable fluctuations, which smears out a long-range-order feature in $M(T)$.

Figure 5 shows the pulsed-field magnetizations divided by the saturated magnetization $M(H)/M_s$ and differential magnetizations $dM(H)/dH$. The most prominent aspect of the present paper is the appearance of a plateau corresponding to the 1/3 of the full magnetization. The plateau becomes obscured with increasing T and vanishes at 9 K, in agreement with the phase boundary determined by $C_p(T)$ and $M(T)$. Since the magnetization curves at 4.2 K and that at 1.3 K (not shown) are nearly identical, non-flat plateau is not due to thermal effects but due to the use of powder sample, the magnetization of which should be averaged by anisotropic g factors. Additionally, some anisotropic terms such as Dzyaloshinski–Moriya interaction and staggered g tensor may also play a role in making the plateau oblique as in $SrCu_2(BO_3)_2$.[13)]

The 1/3 magnetization plateau has been theoretically predicted for various triangle-based lattices,[14)] as experimentally verified by, e.g., Cs_2CuBr_4 and a copper complex.[15,16)] However, for commensurability reasons calculations of the frustrated square lattice predict plateaus such as 1/2 and 1/4.[17)] An exception is seen in $SrCu_2(BO_3)_2$ having the 1/3, 1/4, and 1/8 plateaus, for which oblique magnetic unit cells are suggested due to the orthogonal arrangement of dimers.[5)] By analogy, we may have to take deviations from the ideal square lattice into considerations, among which are the site disorder of the Br ions from the ideal 1b site as suggested in $(CuCl)LaNb_2O_7$ and the orbital order of the Cu ions, making otherwise equivalent J_1 (J_2) bonds inequivalent.

Although a clear physical picture of the 1/3 plateau in $(CuBr)Sr_2Nb_3O_{10}$ has yet to be revealed, one can derive possible magnetic structures following the theory by Oshikawa *et al.* who proposed the quantization condition on the magnetization at a plateau of Heisenberg spin system, $p(S - m) =$ integer, where p and m are the period of the spin state, the magnetization per site, respectively.[18)] For $S = 1/2$, the minimal necessary condition of the 1/3 plateau ($m = 1/6$) is $p = 3$. Since $(CuBr)Sr_2Nb_3O_{10}$ has one Cu^{2+} ion in its chemical unit cell ($p = 1$), the breaking of translational symmetry is needed to satisfy the quantization conditions. We present in Figs. 1(b) and 1(c) two possible magnetic structures of the collinear type, where the F chains align as up-up-down in the layer with a propagation vector of $k = (2\pi/3, 0)$ and $(\pi/3, 2\pi/3)$. They are analogous to

CAF in $(CuBr)LaNb_2O_7$, where the F chains align but in a sequence of up-down. It is conceived that the stability of the up-up-down configuration in the layer is rationalized by the presence of H and the dominance of F interactions deduced from positive θ. Intuitively, one may also consider the case where the F layers stack along the c axis as up-up-down, based on the competition between NN and NNN interlayer interactions, which may then be mapped on the ANNNI (axial NNN Ising) model. However, we can discard the scenario since it would be impossible to attribute the fairly large saturation field ($H_s = 14.4\,T$) and plateau width ($2.4 < H < 8.2\,T$) to the NN and NNN interlayer couplings having distances of 16 and 32 Å, respectively. In order to determine the magnetic structure, neutron diffraction and NMR under magnetic fields are necessary, which is in progress.

Finally, we will point to the nature of the M_2 phase. The abrupt increase in $M(H)$ at 1.6 T until reaching to the 1/3 plateau region is interpreted as a metamagnetic transition to the 1/3-plateau state, although T and H dependence of specific heat measurements could not detect any anomaly associated with the transition. The metamagnetic-transition field determined by the peak of dM/dH is nearly independent of T. From the absence of spontaneous magnetization and the positive value of θ, one may assume that CAF is relevant magnetic order for the M_2 phase. Then, on the basis of J_1–J_2 model, the obtained θ and H_s values yield $J_1/k_B = -51.5\,K$ and $J_2/k_B = 30.6\,K$. It is interesting to point out that the ratio $J_2/J_1 = -0.59$ locates the system to a far more frustrated region than $J_2/J_1 = -1.1$ for $(CuBr)LaNb_2O_7$ ($J_1/k_B = -35.6\,K$ and $J_2/k_B = 41.3\,K$).[19] Here, the size of A cations which modifies the in-plane constant should be effective in controlling J_1 and J_2. Vicinity to the most frustrated point $J_2/J_1 = -0.50$ might be a key for the appearance of the 1/3 plateau.

In general, the specific heat has universal behavior characterized by $C(T) \propto T^{d/\nu}$, where d and ν denote the spatial dimensionality and the exponent of magnon dispersion in the long wave limit (where $\omega \propto k^{\nu}$). For conventional spin systems ($d = 3$), the critical exponent d/ν below T_c is 1.5 and 3, for F and AF cases, respectively. As expected, a cubic exponent is observed for $(CuBr)LaNb_2O_7$ well below T_c.[9] However, what has been observed in $(CuBr)Sr_2Nb_3O_{10}$ is different from either of them; as shown in Fig. 3, C_m in the present compound has a T^2 dependence below 5 K ($<T_{c2}$), a characteristic feature for 2D AF spin waves. The measured quadratic critical exponent in $(CuBr)Sr_2Nb_3O_{10}$ implies the existence of 2D spin–spin correlation. The distinct low-energy mode that appears not for $(CuBr)LaNb_2O_7$ but for $(CuBr)Sr_2Nb_3O_{10}$ is likely to be a consequence of increased n. In 2D triangular-based compounds $SrCr_8Ga_4O_{19}$ and $NiGa_2S_4$ in which a large ground state degeneracy is suggested, the quadratic trend remains even down to dilution temperatures.[1,20] The present $C_p(T)$ experiment was performed only down to 2 K. It is interesting to check whether the quadratic feature continues at lower T which may be associated with highly disordered ground state or finally shifts to the cubic dependence. Note that the linear extrapolation curve of C_m/T runs through the origin, which may be in favor of the former scenario.

To summarize, we have demonstrated that a new compound $(CuBr)Sr_2Nb_3O_{10}$, designed using the ion-exchange reaction, has unique magnetic features such as successive phase transitions and T^2 dependence in C_m, which are not seen in $(CuCl)LaNb_2O_7$ and $(CuBr)LaNb_2O_7$. Most remarkably, we have observed the quantized plateau at 1/3 of the saturation magnetization, presumably due to enhanced 2D and competing in-plane interactions. It is surprising that choice of parameters (A, B, X, n) resulted in completely different magnetic properties. Further studies on the whole family $(CuX)A_{n-1}B_nO_{3n+1}$ will provide global understanding of the nature of the square lattice antiferromagnets.

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