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# Anomalous Magnetization of Two-Dimensional $S = 1/2$ Frustrated Square-Lattice Antiferromagnet $(CuCl)LaNb_2O_7$

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High-field magnetization measurements have been performed up to 56 T for a two-dimensional $S = 1/2$ frustrated square-lattice antiferromagnet $(CuCl)LaNb_2O_7$, a recently discovered spin gap system ($\Delta/k_B = 26.7$ K). It is found that the spin gap closes at a surprisingly low field $H_{c1} = 10.3$ T compared with that expected from the zero-field spin gap ($\Delta/g\mu_B = 18.4$ T). For $H > H_{c1}$, the magnetization exhibits a linear increase without any trace of anomalies such as fractional plateaus until it saturates at $H_{c2} = 30.1$ T. This means that the gapless phase, where the field-induced magnetic ordering is expected to occur at low temperatures, is stable over a wide field region. These results suggest strong correlations of triplet excitations in the layer and the proximity of the spin-liquid phase to the magnetically ordered phase.

KEYWORDS: magnetization, spin liquid, square lattice, $J_1$–$J_2$ model, ion-exchange reaction, bound state, $(CuCl)LaNb_2O_7$
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A soft chemical approach carried out under relatively mild conditions allows access to metastable phases with novel physical and chemical features, providing a diverse range of applications that include catalysis,[1)] ionic conduction[2)] and exotic superconductivity.[3)] A number of chemical reactions involving inorganic solids such as dehydration, oxidation, reduction, and ion exchange are known to proceed *topochemically* to yield well-defined products that bear a definite structural relationship with the mother compounds. In particular, layered perovskites, intergrowths of perovskite and other structures, have been the target of many low-temperature topochemical manipulations.[4)] The $A$-site ordered compounds $A'[A_{n-1}B_nO_{3n+1}]$ ($A'$ = alkali metals, H, Ag, Tl, etc.; $A$ = Ca, Sr, Ba, La; $B$ = Ti, Nb, Ta), termed the Dion-Jacobson series, have one interlayer cation per formula unit.[5,6)] Most of the studies on these compounds have focused on the $A'$-site ion-exchange between monovalent single ions. It has been realized, however, that insertion of metal-anion arrays within perovskite hosts to yield, *e.g.*, $(CuCl)LaNb_2O_7$ and $(CuCl)Sr_2Nb_3O_{10}$, is also possible.[7–10)]

It has been recently demonstrated that the two-dimensional (2D) $S = 1/2$ frustrated square-lattice system $(CuCl)LaNb_2O_7$, corresponding to $A' = [CuCl]$, $A = La$, $B = Nb$ and $n = 2$, achieves a spin-liquid state with a finite gap of $\Delta/k_B = 26.7$ K to the lowlying excited triplet state.[11)] The lattice is of tetragonal symmetry ($P4/mmm$) with room-temperature cell constants $a = 3.879$ Å and $c = 11.728$ Å.[7)] As shown in Fig. 1, the structure consists of copper-chlorine planes that are widely separated from each other by double perovskite slabs. The magnetism of this compound is due to $S = 1/2$ $Cu^{2+}$ ions, which are arranged in the square lattice.

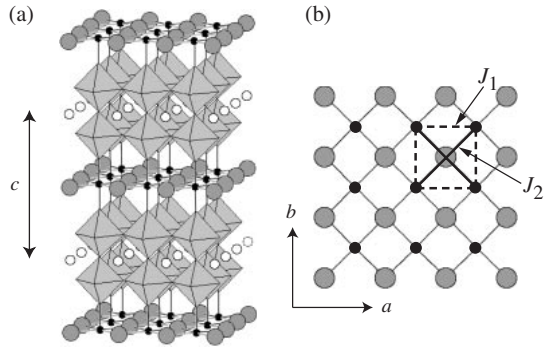


Fig. 1. (a) Schematic representation of structure of $(CuCl)LaNb_2O_7$. The closed spheres are coppers, the gray spheres are chlorines, the open spheres are lanthanums, and the octahedra are $NbO_6$ octahedra.[7)] (b) Copper–chlorine layer viewed along $c$-axis. The bold broken and solid lines represent, respectively, the $J_1$ and $J_2$ bonds.

The copper ion is octahedrally coordinated, bridging between apical oxygen atoms from the perovskite layer and surrounded by four chlorines in the CuCl plane. The $CuO_2Cl_4$ octahedra share corners with the $NbO_6$ octahedra of the perovskite slabs, while they share edges with other $CuO_2Cl_4$ octahedra in the $ab$ plane.

Our dc magnetic susceptibility measurement clearly indicates a thermally activated behavior at low temperatures.[11)] The analysis of the data suggests competing interactions between the ferromagnetic first-nearest-neighbor $J_1$ ($< 0$) and the antiferromagnetic second-nearest-neighbor $J_2$ ($> 0$). Inelastic neutron scattering (INS) measurements directly probed the one-triplet excitation at 2.3 meV (corresponding to $\Delta$) as well as the multitriplet excitation at 5.0 meV. Most likely as a result of the strong geometrical frustration, we observed a nearly flat dispersion of the lowlying mode and an oscillatory $Q$-dependence of its

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intensity, indicating an extremely localized nature of the excited triplets. Accordingly, $(CuCl)LaNb_2O_7$ markedly resembles the Shastry–Sutherland system $SrCu_2(BO_3)_2$.[12–14] It is known in $SrCu_2(BO_3)_2$ that fractional magnetization plateaus exist at 1/8, 1/4, and 1/3 of the saturation magneization,[12,15] and anisotropic interactions cause singlet–triplet mixing and eliminate phase transition at the expected critical field $H_c$ for gap closing.[16]

Such novel phenomena in the presence of a magnetic field might also be observed in $(CuCl)LaNb_2O_7$. This letter deals with a high-field magnetization investigation of the $(CuCl)LaNb_2O_7$ powder sample. Among our motivations are (i) to observe the field-induced transition from the disordered to the ordered phase, (ii) to evidence the point that the spin-singlet dimers are not magnetically isolated, but strongly interacting with each other, (iii) to unambiguously evaluate exchange constants, which was difficult from the dc susceptibility measurement alone, (iv) to reveal the effect of multitriplet bound states under a magnetic field and (v) to check whether or not fractional magnetization plateaus appear.

The ion-exchange reaction for the synthesis of $(CuCl)LaNb_2O_7$ is expressed as

$$RbLaNb_2O_7 + CuCl_2 \rightarrow (CuCl)LaNb_2O_7 + RbCl. \quad (1)$$

$RbLaNb_2O_7$ was prepared by a high-temperature ceramic method from $Rb_2CO_3$ (99.99%), $La_2O_3$ (99.99%), and $Nb_2O_5$ (99.999%). Stoichiometric quantities of $La_2O_3$ and $Nb_2O_5$ with a 25% molar excess of $Rb_2CO_3$ were weighed and ground thoroughly inside an Ar-filled glove box (UNIlab2000, MBRAUN), annealed overnight at 850°C followed by an additional thermal treatment at 1050°C for 24 h. The excess of $RbCO_3$ was added to balance that lost due to volatilization. To prepare $(CuCl)LaNb_2O_7$, $RbLaNb_2O_7$ was mixed with a two-fold molar excess of ultradry $CuCl_2$ (99.99%) and then pressed into pellets inside the glove box. Reactions were carried out in sealed, evacuated ($< 10^{-3}$ Torr) Pyrex tubes at 320°C for one week. The final product was washed with water to eliminate the excess copper chloride and alkali-metal byproduct, and dried at 120°C. The high-field magnetization measurements were conducted using a pulse magnet installed at the High Magnetic Field Laboratory, KYOKUGEN, Osaka University. A powder sample of 100 mg was made to fill a cylindrical Teflon tube with a diameter of 2.4 mm that was then closed by two quartz plates at the top and the bottom. The sample holder attached at one end of a quartz rod was inserted into the $^4$He cryostat combined with the pulse magnet.

Figure 2 shows the magnetizations $M$ and the differential magnetizations $dM/dH$ at 1.3 K (blue) and 4.2 K (green) plotted against magnetic field $H$, where within the experimental accuracy, no hysteresis was observed upon increasing and decreasing the external field. Field-induced phase transitions are observed at $H_{c1} = 10.3$ T and $H_{c2} = 30.1$ T, as indicated by the arrows in Fig. 2. Here, the critical fields are determined as the inflection point in the differential magnetization curve at 1.3 K. Reflecting the spin-singlet ground state with a finite spin gap,[11] the initial magnetization slope is very small. The slow increase in the magnetization for $H < H_{c1}$ is attributable to a small amount

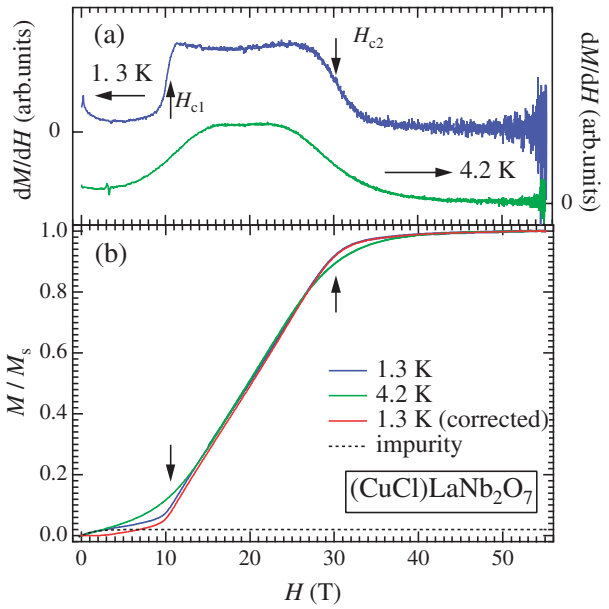


Fig. 2. (a) Differential magnetization curves $dM/dH$ measured at $T = 1.3$ and 4.2 K. Arrows point to the transition fields. (b) Magnetization curves $M$ measured at $T = 1.3$ K (blue) and $T = 4.2$ K (green). The broken line represents the impurity term, given by the Brillouin function for 2.0% of noninteracting $S = 1/2$ ions and $T = 1.3$ K. After subtracting the impurity term from the 1.3 K data, the (corrected) intrinsic magnetization (red) is obtained.

of impurities or lattice defects as also seen in the dc magnetic susceptibility for $T < 5$ K.[11] Assuming 2.0% of noninteracting magnetic ions of $S = 1/2$, the intrinsic magnetization curve for $(CuCl)LaNb_2O_7$ is obtained (see the red line in Fig. 2). A slight increase in the magnetization observed above around 4 T might be spurious due to inappropriate estimation of the impurity/defect term. However, we cannot totally exclude the possibility that such a behavior is an intrinsic property of $(CuCl)LaNb_2O_7$. The magnetization curve has several remarkable features. First of all, the value of the lower critical field $H_{c1}$ is not what is expected from $\Delta$. Since the onset of magnetization is triggered by the softening (or the Zeeman splitting) of the gapped triplet magnon, the lower critical field $H_{c1}$ should coincide with $\Delta/g\mu_B$. However, the obtained value of $H_{c1}$ ($= 10.3$ T) is by far much smaller than that expected from the known zero-field gap ($\Delta/g\mu_B = 18.4$ T), where we assume $g = 2.17$ estimated from ESR experiments.[17]

Above $H_{c1}$, the magnetization grows progressively and almost linearly with increasing magnetic field until it reaches the saturation magnetization $M_s$ at around $H_{c2}$. No indication of fractional plateaus is seen, in contrast to that observed in $SrCu_2(BO_3)_2$[12,15] and $[Ni_2(medpt)_2(\mu\text{-ox})(\mu\text{-}N_3)]ClO_4 0.5H_2O$.[18] The ground state in this field region is gapless. Accordingly, long-range magnetic ordering, described by the Bose–Einstein condensation (BEC) of magnetic excitations, is expected to take place at low temperatures.[19] Here, the transverse spin components perpendicular to the applied field are responsible for the field-induced magnetic ordering. The second important point to be stressed is that the gapless phase is stable over a wide field range, i.e., $H_{c2} - H_{c1} = 19.8$ T. This fact suggests the existence of sizable and repulsive interactions among magnetic excitations, because

otherwise the magnetization would abruptly jump to saturate at $H_{c1}$ ($= H_{c2}$). The existence of sizable interactions and the extremely localized nature of the triplet excitations observed in the INS experiments[11] appear to contradict each other. However, these facts remind us of what was observed in $SrCu_2(BO_3)_2$, where the lowest dimer-triplet excitation has a tiny bandwidth[13] despite a fairly large coupling between dimers. Our observation may indicate the existence of fairly strong geometrically frustrated interactions among $S = 1/2$ spins which, for some reasons, suppress the particle propagation. We may expect that a system with a small kinetic energy (or tiny magnon bandwidth) and large repulsive interactions has several intermediate plateaus in its magnetization curve, since magnetization plateaus can be attributed to a kind of crystalline states. However, this is not the case for the present system. This point will be discussed later.

To estimate the values of exchange interactions, we take the $S = 1/2$ $J_1$–$J_2$ model as the simplest theoretical model, which is suggested by the crystal structure. Knowledge of the Weiss constant $\theta_s = J_1 + J_2$ and the saturation field $H_{c2}$ enables us to determine the values of $J_1$ and $J_2$. The saturation field of the $J_1$–$J_2$ model is obtained by calculating the energy of one-magnon excitation in the fully polarized state, provided that we have no multimagnon bound states. In the cases of relevance,[20] it is given either by $H_{c2} = 2(J_1 + 2J_2)/(g\mu_B)$ [collinear anitiferromagnetic (CAF) phase[21] $J_2 > |J_1|/2$] or by $H_{c2} = 4J_1/(g\mu_B)$ [Néel antiferromagnetic (NAF) phase $J_2 < J_1/2$]. The observed values of $\theta_s$ and $H_{c2}$ yield the following sets: $J_1 = -2.74\,\mathrm{K}$, $J_2 = 12.34\,\mathrm{K}$ for CAF and $J_1 = 10.97\,\mathrm{K}$, $J_2 = -1.37\,\mathrm{K}$ for NAF. Unfortunately, these sets fail to explain the existence of a finite spin gap since the $J_1$–$J_2$ model with $J_1$ and $J_2$ given by the above parameters is believed to be in an ordered phase.[21] (We also checked that the high-temperature part of the susceptibility data yielded a similar result.) From this, we may conclude that a simple analysis based on a pure $J_1$–$J_2$ model does not work.

To highlight the peculiarity of the observed magnetization curve, the experimental data at 1.3 K is compared with the magnetization curve of a simple phenomenological model. Let us consider a spin cluster which has a singlet and a triplet separated by a finite spin gap $\Delta$, where the triplet is regarded as an excited magnetic particle. If we consider a 2-spin cluster and set $\Delta = J$ ($=$ coupling between two $S = 1/2$ spins), this is simply the isolated dimer model. The $M$–$H$ curve of the isolated dimer model is given by[22]

$$M_d(H) = \frac{Ng\mu_B \sinh(g\mu_B H/k_B T)}{1 + \exp(\Delta/k_B T) + 2\cosh(g\mu_B H/k_B T)}, \quad (2)$$

where $N$ denotes the number of $S = 1/2$ ions. The calculated magnetization for $\Delta/k_B = 26.7\,\mathrm{K}$ and $T = 1.3\,\mathrm{K}$, shown by the dotted line in Fig. 3, exhibits a considerable deviation from the experimental one.

In order to reproduce the obtained magnetization curve having a gentle slope in the gapless region, a fairly large kinetic energy (or the interdimer coupling $J'$ in the dimer model) should be taken into account. Keeping only two states $|S, S^z\rangle = |0, 0\rangle$ and $|1, 1\rangle$ of each cluster excitation, the system reduces to that of pseudospin-1/2 and we can apply the theory of Tachiki and Yamada[23] to obtain the magnetization curve. The lower and upper critical fields at $T = 0$

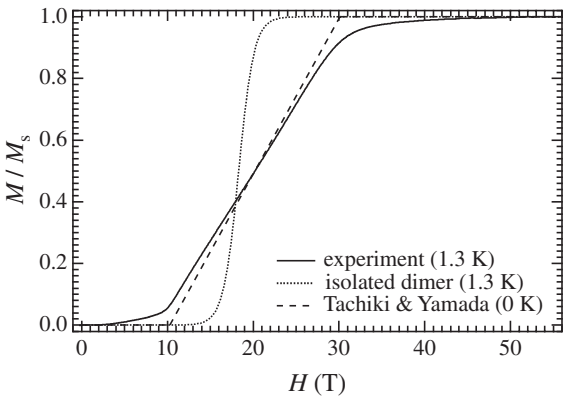


Fig. 3. The solid line is the corrected experimental magnetization at $T = 1.3\,\mathrm{K}$. The dotted and broken lines are, respectively, the theoretical magnetizations based on the isolated dimer model with $\Delta/k_B = 26.7\,\mathrm{K}$, $T = 1.3\,\mathrm{K}$, and $g = 2.17$, and on the Tachiki–Yamada model at 0 K.[23]

depend on the sign of $J'$. One obtains $H_{c1} = (J + \alpha)/g\mu_B$ and $H_{c2} = J/g\mu_B$ when $J' < 0$, while $H_{c1} = (J - \alpha)/g\mu_B$ and $H_{c2} = (J + 2\alpha)/g\mu_B$ is obtained when $J' > 0$, where $\alpha$ denotes $zJ'/2$ with $z$ being the number of interacting neighbors. Supposing $z = 4$ for simplicity, comparison with our experimental data led to two sets of coupling constants: $J/g\mu_B = 30.1\,\mathrm{T}$ and $J'/g\mu_B = -9.9\,\mathrm{T}$ for $J' < 0$, or $J/g\mu_B = 16.9\,\mathrm{T}$ and $J'/g\mu_B = 3.3\,\mathrm{T}$ for $J' > 0$. Despite the *apparent* agreement between the Tachiki–Yamada theory and our experiment, the theory fails to explain the zero-field gap of 2.3 meV observed by INS.[11] This is not surprising since such simple models of gapped magnons always predict $\Delta = g\mu_B H_{c1}$.

Therefore, the discrepancy in the present compound suggests the necessity to go beyond this simple assumption and consider a contribution from other states seriously. One possibility is that the branch at 2.3 meV observed in INS is not the lowest one, which might have been missed in INS for some reasons (*e.g.*, by selection rules). In this case, however, the experimental magnetic susceptibility cannot be reproduced. Another possibility, which is more plausible, is that there exists a bound state with a higher spin (*e.g.*, $S = 2$ quintet); the bound quintet mode, given sufficient binding energy, is able to touch the spin-singlet ground state faster than the one-triplet mode does. A relevant behavior can be seen in the field-frequency diagram of the ESR spectra of $SrCu_2(BO_3)_2$;[24] a simple linear extrapolation of the bound quintet mode to zero energy gives a critical field smaller than that of the one-triplet mode. In this case, however, a Dzyaloshinsky–Moriya interaction and a staggered $g$ tensor cause singlet–triplet mixing and make the spin gap remain open until the system enters the 1/8 plateau phase.[16] For this reason, $(CuCl)LaNb_2O_7$ possibly provides the first experimental example of magnetic ordering driven by a bound state. It is noted that INS detects in principle the transition involving $S - S' = \pm 1$ and 0. Thus, the bound quintet state from the singlet ground state is not observable by INS. In order to check the validity of this scenario, other spectroscopic measurements such as ESR and Raman scattering are highly desired. We should address the fact that the quintet level ($\Delta_2/k_B = 29.9\,\mathrm{K}$), derived from the critical field $H_{c1}$, is slightly above the triplet level so that the fitting of the

magnetic susceptibility may not be very successful. However, such an analysis involves a difficulty because of the nonnegligible contribution from impurities/defects and averaged anisotropic factors due to the use of a polycrystalline sample.[11] Therefore, for the unambiguous analysis of the magnetic susceptibility it is important to obtain single crystals of high purity.

As an alternative scenario, it is considered that the spin–liquid phase in $(CuCl)LaNb_2O_7$ may be located in the vicinity of the ordered phase. The spin–liquid state would then be easily and markedly changed by external parameters such as magnetic field. Here, the geometrical spin frustration may have a crucial role to play. As suggested in ref. 11, the flat dispersion of the triplet excitation in the absence of a magnetic field should not be as a result of the spatial isolation of spin clusters, but of the strong spin frustration brought about by the geometry. Thus, the triplet excitations must be *potentially* correlated strongly to each other. In other words, without the geometrical spin frustration, the triplet excitations in $(CuCl)LaNb_2O_7$ would have a dispersion whose bandwidth is comparable to the magnitude of exchange interactions.

Finally, let us make a brief comment on the absence of intermediate plateaus in the magnetization, which is distinct from the case of $SrCu_2(BO_3)_2$, where 1/8, 1/4, and 1/3 plateaus exist. From the arguments discussed above, $(CuCl)LaNb_2O_7$ is expected to have strong interactions and a small kinetic energy, which usually favor formation of plateaus. We consider that correlated hopping processes proposed[25] to explain the unusual magnetic properties of $SrCu_2(BO_3)_2$ may give some hints to understand this point.

To conclude, we measured the high-field magnetization of the 2D $S = 1/2$ frustrated square-lattice antiferromagnet $(CuCl)LaNb_2O_7$. A field-induced magnetic phase transition from the gapfull to the gapless phases has been observed. The lower critical field is significantly smaller than that expected from the zero-field spin gap and the Zeeman splitting of the triplet state. To explain this anomaly, the crucial role of the bound states and the quantum criticality are suggested. Since we are in possession of the series of $(CuX)A_{n-1}B_nO_{3n+1}$ ($n = 2, 3$; $X =$ Cl, Br),[7–10] the study of this family will not only help to understand the magnetism of the title compound but also offer a wide variety of new phenomena occurring in the $S = 1/2$ square lattice.

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