Journal of the Physical Society of Japan
Vol. 76, No. 9, September, 2007, 093706

Bose–Einstein Condensation of Quasi-Two-Dimensional Frustrated Quantum Magnet $(CuCl)LaNb_2O_7$

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(Received June 15, 2007; accepted July 25, 2007; published September 10, 2007)

A quasi-two-dimensional $S = 1/2$ Heisenberg square-lattice antiferromagnet $(CuCl)LaNb_2O_7$ is studied by specific heat and magnetic susceptibility measurements in external fields up to 14 T. The experimental results in low fields verify the absence of the order–disorder transition, as reported previously. By further application of magnetic fields, we obtain direct evidence for the phase transition, which can be interpreted as the Bose–Einstein condensation (BEC) of magnons. However, the critical field of 10 T significantly deviates from that estimated from the zero-field gap, indicating that, unlike known experimental examples, the one-magnon mode is *not* a primary source to drive the BEC.

KEYWORDS: $(CuCl)LaNb_2O_7$, spin gap, square lattice, ion exchange, frustration, Bose–Einstein condensation
DOI: 10.1143/JPSJ.76.093706

Field-induced transitions (FITs) occur in Heisenberg antiferromagnetic spin systems, which, for various reasons, have a collective singlet ground state separated by an energy gap Δ from the first excited one-magnon (triplet) states. The application of magnetic fields decreases the separation between the ground state and the lowest branch ($M_z = 1$) of the triplet states and finally leads to a quantum phase transition at the critical field H_c (corresponding to $\Delta = g\mu_B H_c$). The ordered phase is described as a Bose–Einstein condensation (BEC) of hard-core bosons for which magnetic fields act as the chemical potential.[1)] This concept is exclusively applicable to all known compounds including $TlCuCl_3$,[1)] $KCuCl_3$,[2)] $Pb_2V_3O_9$,[3)] $PbNi_2V_2O_8$,[4)] $BaCuSi_2O_6$,[5)] and $NiCl_2$–$4SC(NH_2)_2$.[6)] Theoretically, a new route to the BEC has recently been proposed in the square-lattice frustrated model with modulating coupling constants, for which the two-magnon bound states condense above a certain magnetic field.[7)]

Chimie douce, solid-state reactions at relatively low temperatures, i.e., away from the thermodynamic equilibrium, offer a rational design of the magnetic lattices in nonmolecular solids.[8)] Recently, various exotic quantum magnetic phenomena have emerged from a new class of $S = 1/2$ layered transition-metal oxyhalides $(CuX)[A_{n-1}B_nO_{3n+1}]$ (where $X = Cl^-$, Br^-; $A = La^{3+}$, Ca^{2+}, Na^+, …; $B = Nb^{5+}$, Ta^{5+}, Ti^{4+}, …; $n = 2, 3$), obtained by low-temperature ion-exchange reactions.[9–12)] They range from collective singletground states in $(CuCl)LaNb_2O_7$,[13,14)] a collinear order at 32 K with a reduced magnetic moment in $(CuBr)LaNb_2O_7$,[15)] to successive phase transitions and 1/3 magnetization plateaus in $(CuBr)Sr_2Nb_3O_{10}$.[16)] Common to this family, the CuX layer with an $S = 1/2$ square lattice is isolated by nonmagnetic perovskite slabs, making it a quasi-two-dimensional magnet. Within the layer, the halogen atom locates itself at the center of a copper square, so that the competition between first-nearest-neighbor (1NN) and second-nearest-neighbor (2NN) exchange couplings, denoted hereafter as J_1 and J_2, respectively, is expected. This situation differs markedly from the case of perovskite oxides ABO_3 with magnetic B sites that typically experience less frustration because the intervening superexchange anions are located at the edges of the square (or cube), resulting in dominating J_1 bonds.

From our previous studies, it is now apparent that $(CuCl)LaNb_2O_7$ has a spin-singlet ground state with an energy gap, but there remain questions to be answered. Of particular interest is the unusual behavior under magnetic fields. Whereas the magnetic susceptibility at 0.1 T and inelastic neutron scattering (INS) experiments at 0 T have consistently yielded the zero-field gap $\Delta/k_B = 26.7$ K (corresponding to $H_c = 18.4$ T),[13)] the magnetization measurements at 1.3 K using pulsed fields have revealed the onset of magnetization at as low as 10.3 T.[14)] However, a problem is that the magnetization increases slowly even in a field region below 10.3 T, most likely due to defects and/or unidentified magnetic impurities; the Curietail is also detected in the magnetic susceptibility. Therefore, it is unfortunately uncertain whether the anomaly at 10.3 T can be truly attributed to the FIT or not. It may be a more complicated crossover behavior or just an extrinsic effect caused by the impurities. In the present study, we have performed measurements of the temperature variations of specific heat and magnetization at static magnetic fields up to 14 T. Our data not only indicate the absence of order–disorder transitions in the presence of a finite energy gap for low fields but also provide evidence that $(CuCl)LaNb_2O_7$ undergoes the FIT described by the magnon BEC, which is probably of a new type.

The $(CuCl)LaNb_2O_7$ sample was synthesized via an ion-exchange route, as described in detail in ref. 13. To avoid the complexity arising from the dependence of the sample on the magnetic properties, the same sample used in previous measurements[13,14)] was employed. Specific heat measurements were performed by the heatrelaxation method for $T > 2$ K and in magnetic fields up to $H = 14$ T in a QD-PPMS system. Further, 4.43 mg of $(CuCl)LaNb_2O_7$ powder was mixed with 2.34 mg of fine gold powder in order

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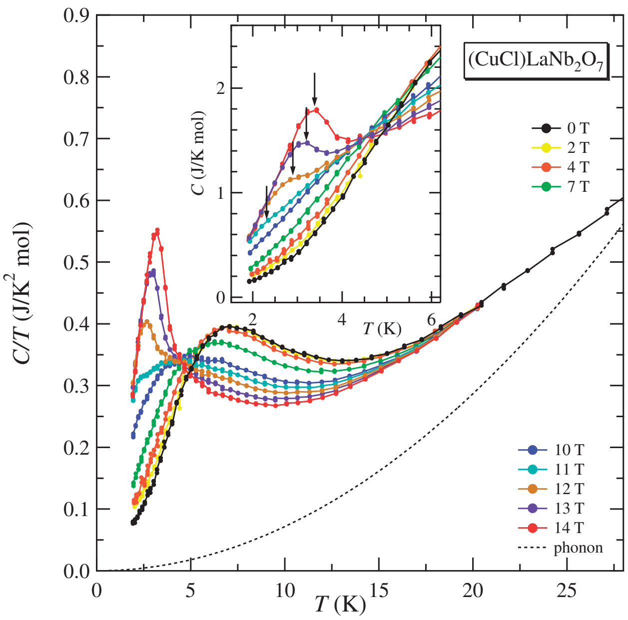

Fig. 1. Specific heat divided by temperature (C/T) for $(CuCl)LaNb_2O_7$ collected with fields of $H = 0, 2, 4, 7, 10, 11, 12, 13$, and 14 T. The dotted curve represents the phonon contribution assumed as $C_L \sim \beta T^3$ [$\beta = 0.717\,\text{mJ/(K}^4\cdot\text{mol)}$]. The inset shows the C vs T plots in the low-temperature region, where arrows denote the transition temperatures.

to improve thermal contact and pressed into a pellet. The pellet was attached to an alumina platform with a small amount of Apiezon N grease. The heat capacity was obtained by fitting a heat relaxation curve recorded after a heat pulse caused a temperature increase of approximately 2%. The heat capacity of the alumina platform and mixed gold powder was measured in separate runs without the sample and was subtracted from the data. The temperature dependence of magnetization was measured between 2 and 20 K in fixed fields up to $H = 14$ T using the QD-PPMS system.

The total specific heat divided by the temperature (C/T) measured in the absence of a magnetic field is plotted by black circles in Fig. 1. The data display no trace of anomalies associated with the phase transitions. Instead, we observe the Schottky anomaly, i.e., a round maximum centered at around $T_{max} \sim 7$ K. This is a typical behavior of spin-singlet compounds with a finite gap to the lowest excited state and is consistent with the magnetic susceptibility and neutron scattering experiments.[13] It is not straightforward to extract a magnetic contribution C_M from the measured data because a nonmagnetic isomorph is not presently available from which the lattice contribution $C_L \sim \beta T^3$ in a low-temperature regime could be estimated. Therefore, a rough estimation is made and the result is indicated by the dotted line in Fig. 1, where β is assumed as $0.717\,\text{mJ/(K}^4\cdot\text{mol)}$. The magnetic contribution is subsequently determined by subtracting the C_L term from C. By integrating C_M/T between 2 and 30 K, we obtain 1.1 J/(mol K). This value is approximately 13% smaller than the total magnetic entropy ($R \ln 2$) for 1 mol of $S = 1/2$ spins, but is acceptable considering the crude assumption of the lattice contribution.

For a spin-gap compound in which the spin-singlet ground state is separated simply from the first excited one-magnon

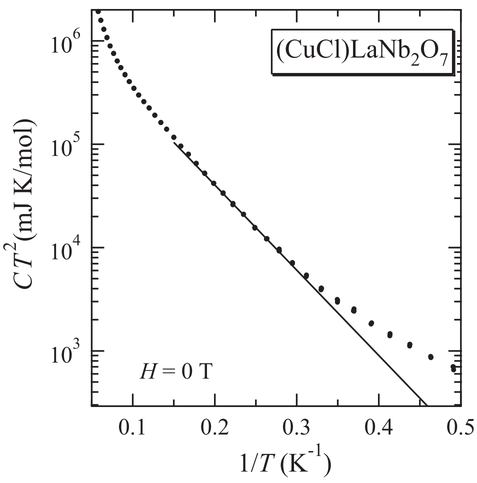

Fig. 2. Logarithmic plot of CT^2 as a function of $1/T$ for $H = 0$ T. The solid line represents the fit to eq. 1.

states by a gap Δ, the specific heat in the low-temperature limit is, in general, given by the following expression:[17]

$$C \propto T^{-2} \exp\left(-\frac{\Delta}{k_B T}\right). \tag{1}$$

Thus, CT^2 is plotted against $1/T$ on the logarithmic scale, as shown in Fig. 2. The fit with $\Delta/k_B = 19$ K is also shown. This value is slightly smaller than that estimated by the magnetic susceptibility and neutron scattering experiment, $\Delta/k_B = 26.5$ K. Alternatively, it is also possible to estimate the gap using the relation $k_B T_{max}/\Delta \sim 0.28$ in the isolated dimer limit.[17] Thus, the obtained value $\Delta/k_B = 25$ K is closer to the values determined by magnetic susceptibility and neutron scattering studies. Similar values of the gap have been recently obtained by NMR.[18] It is noteworthy that a deviation from the temperature-activated behavior appears below 3 K (Fig. 2), thereby leading to the ambiguity in the evaluation of the gap size because eq. (1) is more valid at lower temperatures. In fact, such a deviation is sometimes observed for spin-gapped materials[19,20] and is ascribed to the phonon contribution or extrinsic effect involving defects and unidentified impurities. Recent NMR experiments also show a deviation from the temperature activation curve at low temperatures, which are assigned as the extrinsic artifact factors from some nonmagnetic impurities.

As soon as the magnetic fields are applied (up to 7 T), the broad maximum of C/T shifts gradually to a lower temperature, indicating not only the absence of order-disorder transitions but also a reduction in the energy gap $\Delta(H)$ with the field. A deviation from the temperature activation behavior is again appreciable below 3 K (not shown). The concave temperature dependence of the specific heat at low temperatures below 7 T reflects the spin-singlet nature of the ground state. However, it changes to a linear behavior at 10 T. Finally, we observe the most spectacular feature of the present study: a cusp-like peak in $C(T)$ at and above 11 T, which is the first evidence of a field-induced phase transition in this compound. The transition temperature T_N at 11 T is 2.3 K, as indicated by the arrow in the inset of Fig. 1. When the magnetic field is further increased, the peak associated with the phase transition develops and shifts systematically to higher temperatures, and T_N becomes 3.3 K at 14 T. The

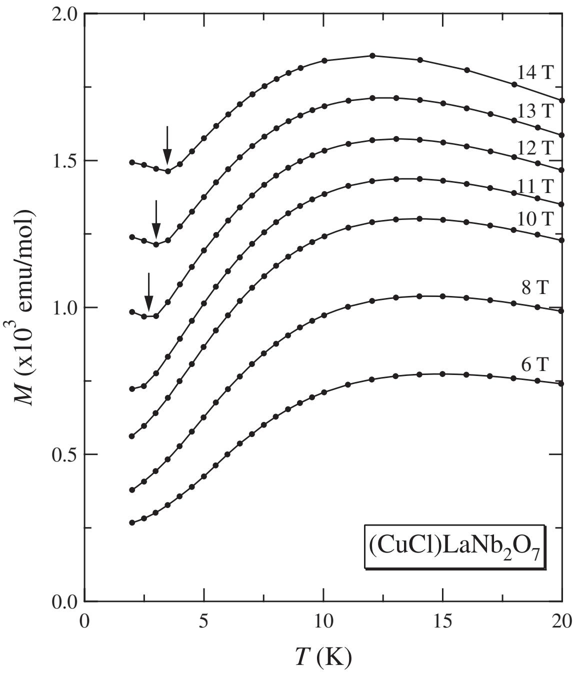

Fig. 3. Low-temperature magnetizations of (CuCl)LaNb$_2$O$_7$ measured at various external magnetic fields up to 14 T.

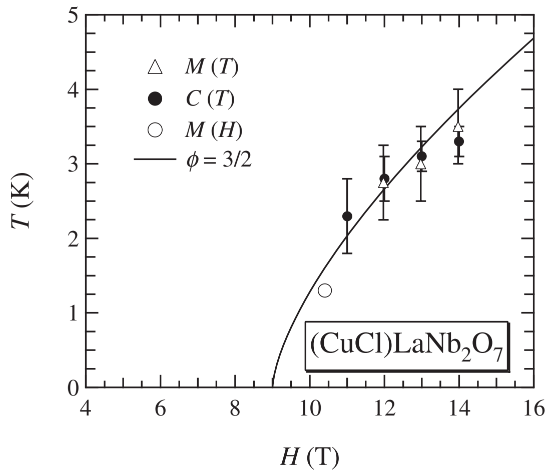

Fig. 4. Phase boundary in (CuCl)LaNb$_2$O$_7$ determined from the results of $M(T)$ (triangles), $C(T)$ (solid circles). The open circle represents the critical field determined by the magnetization curve at 1.3 K.[14] The solid line represents a theoretical curve described in the text.

FITs observed here are nearly consistent with the abrupt increase in the magnetization at 10.3 T.[14] Therefore, it is natural to consider that the FIT should be of magnetic origin associated with the BEC of magnons.

In order to validate this picture, the temperature dependence of magnetization was measured at various constant magnetic fields shown in Fig. 3. While the $M(T)$ curves at 6, 8, and 10 T are featureless, those above 10 T signal magnetic phase transitions as cusp-like anomalies. In Fig. 4, the field dependence of T_N is summarized in a temperature vs magnetic field phase diagram. It is seen that T_N's determined by $C(T)$ and $M(T)$ are in good agreement with each other. Furthermore, both the increase in magnetization for decreasing temperature below T_N and the growth of the peak of the specific heat around T_N with increasing magnetic field can be attributed to the increased magnon density on the basis of the BEC scenario. From these results, we conclude that (CuCl)LaNb$_2$O$_7$ is a new experimental correspondence of the BEC of magnons.

Figure 4 shows a theoretical curve of the Hartree–Fock approximation that gives the power law behavior $[H_c(T) - H_c(0)] \propto T^{\phi}$ with the critical exponent $\phi = 3/2$. Here, we assume $H_c(0) = 9.0$ T. The result *appears* to follow the theory. We notice, however, that the fitted results largely depend on the choice of $H_c(0)$. Accurate determination of ϕ is also hampered by rather broadened anomalies at T_N, probably due to the use of the polycrystalline specimen. Thus, quantitative discussions on the criticality require future experimental investigation with single crystals and at lower temperatures.

The most remarkable implication of our findings is that (CuCl)LaNb$_2$O$_7$ undergoes the magnon BEC at a surprisingly small magnetic field around 10 T, far below the critical field estimated from the zero-field gap. This markedly contrasts with other known experimental examples, in which the occurrence of the BEC is directly linked to the level crossing between the spin-singlet ground state and the low-lying excited one-magnon state.[1–6] That is, for (CuCl)LaNb$_2$O$_7$, the one-magnon states are at least not directly responsible for the BEC. One possibility is that two-magnon bound states reach the ground state at 10 T and drive the transition into a gapless spin-liquid state without transverse magnetic moment (spin-nematic state), as proposed theoretically for a quadrumerized two-dimensional square-lattice antiferromagnet by Ueda and Totsuka.[7] Here, a key requirement for the spin-nematic order is the competition between ferromagnetic and antiferromagnetic interactions. Because the Weiss temperature (-9.6 K) has a much smaller magnitude than the temperature at maximum susceptibility (16.5 K), (CuCl)LaNb$_2$O$_7$ meets this requirement and thus may be the first experimental correspondence of this model. Historically, the BEC scenario of the two-magnon bound states was for the first time considered for the Shastry–Sutherland model with antiferromagnetic intra- and interdimer interactions.[21] However, unfortunately, the additional Dzyaloshinsky–Moriya interaction in the experimental counterpart SrCu$_2$(BO$_3$)$_2$ causes bending of these modes in the energy vs field diagram and eventually drives the spin-singlet phase to the 1/8 plateau phase.[22] In the case of (CuCl)LaNb$_2$O$_7$, the magnon binding may be more favored because of the presence of ferromagnetic interactions. Whether this scenario or some other explains the BEC in this compound is an interesting issue that will be analyzed in the future.

In conclusion, we have measured the temperature variations of the specific heat and magnetization for (CuCl)LaNb$_2$O$_7$. The results provide evidence that the BEC occurs at as low as 10 T. On the basis of a comparison with previous zero- and low-field experiments, we strongly believe that the one-magnons do not play the main role in the field-induced transition, thus providing a new mechanism that leads to the BEC. It seems that frustrated quantum spin systems with antiferromagnetic and ferromagnetic interactions have hardly received adequate attention, with only limited theoretical studies.[7,23] Therefore, the present compound together with its family[15,16] would provide suitable opportunities to investigate novel quantum phenomena including the BEC for systems with mixed interactions.

The authors thank Y. Baba, N. Oba, H. Ueda, and K. Totsuka for fruitful discussions. This study has been supported by Grants-in-Aid for Young Scientists (A) (No. 17684018) and Science Research on Priority Area (Nos. 19052004 and 16076210) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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