Magnetic correlation in the square-lattice spin system \((\text{CuBr})\text{Sr}_2\text{Nb}_3\text{O}_{10}\): A neutron diffraction study

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Magnetic correlation in the quantum \(S = 1/2\) square-lattice system \((\text{CuBr})\text{Sr}_2\text{Nb}_3\text{O}_{10}\) has been studied by neutron diffraction. A novel commensurate in-plane, helical antiferromagnetic (AFM) ordering, characterized by the propagation vector \(k = (0 3/8 1/2)\), has been confirmed from the appearance of magnetic Bragg peaks below \(T_N \approx 7.5\) K. The ordered moment at 2 K is found to be \(0.79(7) \mu_B\text{Cu}^{2+}\)-ion. The observed helical AFM structure differs from the ground state predicted theoretically from the \(J_1-J_2\) model as well as from experimentally reported states for other quantum \(S = 1/2\) square-lattice systems. However, the observed helical magnetic structure can be described in a \(J_1-J_2-J_3\) model. Under a 4.5 T magnetic field, the spin-order changes drastically and is characterized by the propagation vector \(k_3 = (0 1/3 0.446)\) and a probable \(k_2 = (0 0 0)\) vector.

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I. INTRODUCTION

Low-dimensional magnetic systems have been of great interest in recent years due to their unconventional, novel, and complex magnetic properties.$^{1,2}$ Different topologies of spin arrangements such as quasi-one-dimensional spin chains, triangular, kagome, and square lattices can be found. The spin-1/2 Heisenberg square-lattice systems where magnetic moments on a square lattice are subjected to the nearest-neighbor interaction \(J_1\) along the side of the square and the next-nearest-neighbor interaction \(J_2\) along the diagonal of the square have received considerable attention. In the literature a large number of theoretical studies on systems with antiferromagnetic (AFM) \(J_1\) and \(J_2\) exist$^{3-14}$ Here the \(J_1-J_2\) model$^{1-14}$ reveals several interesting magnetic ground states involving quantum phase transitions, such as (i) for \(\alpha = |J_2/\ J_1| \lesssim 0.4\), a Néel AFM state \([Q = (\pi \pi)]\), (ii) for \(\alpha \sim 0.4-0.6\), a quantum spin-liquid state, and (iii) for \(\alpha \approx 0.6\), an ordered collinear AFM state \([Q = (0 0)\) or \((0 \pi)]\), i.e., AFM coupling of ferromagnetic (FM) chains in a given plane (by disorder stabilization). However, for the model with FM \(J_1\) and AFM \(J_2\), so far only a few studies exist.$^{15-19}$ The FM \(J_1-J_2\) model yields a FM ground state \([Q = (0 0)\) for lower values of \(\alpha \approx 0.4\). However, the FM state breaks down at \(\alpha \sim 0.4\). For the sufficiently large \(J_2\) \((\alpha \gtrsim 0.6)\), a long-ranged collinear stripe phase, similar to the finding for the corresponding AFM \(J_1-J_2\) model, appears. A disordered state is predicted over the intermediate regime of \(\alpha\). The precise nature of the disordered state is qualitatively different for the FM \(J_1\) from AFM \(J_1\). While the model with the AFM \(J_1\) has a spin-liquid ground state for a narrow range of \(\alpha$, the intermediate state of the model with the FM \(J_1\) is either a spin nematic$^{15}$ or presumably does not exist at all.$^{16}$ Extensive experimental investigations, carried out on a number of vanadium-based square-lattice compounds \(\text{Li}_2\text{VOSiO}_4\) and \(\text{Li}_2\text{VOGeO}_4\), reveal AFM \(J_1\) and \(J_2$.$^{17-20}$ The AFM \(J_1\) and \(J_2\) have also been found for other systems, such as the two-dimensional (2D) square-lattice antiferromagnet \(\text{Cu}(\text{pz})_2\text{ClO}_3\) \((\text{pz}\) denotes pyrazine),$^{21}$ \(\text{VOMo}_4$, $^{22}$ and the layered perovskite \(\text{PbV}_2\) \(^{23,24}$ The square-lattice layered vanadium phosphate \(\text{AA}'\text{VO(Po)}_2\) with \(\text{AA}' = \text{Zn}\) also reveals AFM \(J_1\) and \(J_2$.$^{23,26}$ On the other hand, the other layered vanadium phosphates \(\text{AA}'\text{VO(Po)}_2\) with \(\text{AA}' = \text{Pb}_2$, $^{27}$ \(\text{BaZn}$,$^{28}$ \(\text{SrZn}$,$^{29}$ and \(\text{BaCd}$,$^{30}$ (with square-lattice spin arrangements) show the FM \(J_1\) and AFM \(J_2\). A recent investigation shows that \(\text{PhZnV(O)}_2\) also belongs to the square-lattice compound with FM \(J_1\) and AFM \(J_2$.$^{21}$ A preliminary magnetization and specific-heat study$^{32}$ has suggested that the triple-layered perovskite \((\text{CuBr})\text{Sr}_2\text{Nb}_3\text{O}_{10}\) is a possible new addition to the list with the FM \(J_1\) and AFM \(J_2\).

\((\text{CuBr})\text{Sr}_2\text{Nb}_3\text{O}_{10}\) belongs to the Dion-Jacobson series of layered oxides with the general formula \((\text{CuX})\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}\)$,$^{1}$ where \(X = \text{Br}^-$, \(\text{Cl}^-$\) ions, \(A = \text{La}^{3+}, \text{Ca}^{2+}, \text{Na}^+$ ions, and \(B = \text{Nb}^5+, \text{Ta}^{5+}, \text{and Ti}^{4+}$ ions.$^{32-36}$ This system shows a layered-type crystal structure (tetragonal symmetry, space group \(P4/mmm\)) with \(a = 3.91069(4)$ and \(c = 16.0207(3)$ A. CuBr square planes are widely separated by nonmagnetic slabs of \([\text{Sr}_2\text{Nb}_3\text{O}_{10}]^-$ along the crystallographic c axis. The \(S = 1/2\) Cu ions are octahedrally coordinated by two apical oxygen atoms and by four bromine atoms. Magnetization \((M)$ and specific-heat studies$^{32,33}$ suggested that this compound...
is a geometrically frustrated quantum spin system in which the square-lattice arrangement of the Cu ions causes spin frustration due to the competing AFM and FM interactions. Two successive phase transitions at $T_{c1} \sim 9.3$ and $T_{c2} \sim 7.5$ K were observed in the specific-heat study and were found to merge under an applied magnetic field ($H$) of 3 T. The magnetic specific heat $C_m$ has a $T^2$ dependence below 5 K ($<T_{c2}$), which is a characteristic feature of 2D AFM spin correlations. A $1/3$ plateau of the saturated magnetization was observed in the $M$ vs $H$ curves as a metamagnetic transition at low temperatures. The gradual deviation of magnetic susceptibility from Curie-Weiss behavior below 100 K suggested a short-range spin-spin correlation within the CuBr plane is already well developed at high temperatures.

Promoted by these interesting magnetization and specific-heat results, we have performed neutron diffraction experiments using a powder sample of (CuBr)Sr$_2$Nb$_3$O$_{10}$ to gain a microscopic understanding of the nature of magnetic ground state of this interesting square-lattice spin system. An in-plane (in the $ab$ plane) helical AFM structure has been discovered from the appearance of additional magnetic Bragg peaks, indexed with the propagation vector $k = (0/3/8 1/2)$, in contrast to the theoretically predicted and experimentally reported magnetic ground states for other $S = 1/2$ square-lattice systems. A different magnetic order, characterized by the propagation vector $k_1 = (0/1/3 0.446)$ and a probable $k_2 = (0/3/0)$ vector, has been observed under a 4.5 T magnetic field. The observed magnetic structures show that (CuBr)Sr$_2$Nb$_3$O$_{10}$ belongs to a new class of the spin-1/2 square-lattice system.

II. EXPERIMENTAL

The polycrystalline sample of (CuBr)Sr$_2$Nb$_3$O$_{10}$ was prepared by a two-step process involving the solid-state synthesis to yield RhSr$_2$Nb$_3$O$_{10}$ followed by a low-temperature ion-exchange reaction by CuBr$_2$ as described elsewhere. High-intensity neutron diffraction patterns were recorded at 2, 5, 8, 12, and 26 K using the D20 powder neutron diffractometer, at the Institute Laue Langevin, Grenoble, France, with a wavelength of $\lambda = 2.418$ Å. For these measurements, the sample was placed in a vanadium can, and an orange cryostat was used for low-temperature measurements. Additional data were taken between 2 and 12 K under an applied magnetic field of up to 4.5 T using a cryomagnet. The diffraction data were analyzed by the Rietveld method using the FULLPROF program. The representation theory analysis was performed using the BASIREPS software for the determination of magnetic structure.

III. RESULTS AND DISCUSSION

The neutron diffraction pattern of (CuBr)Sr$_2$Nb$_3$O$_{10}$ at 26 K (paramagnetic state) is shown in Fig. 1. The Rietveld analysis of the pattern confirms the tetragonal crystal structure shown in Fig. 2 with space group $P4_m/mmm$. The refined values of the lattice constants $a = 3.888(1)$ Å and $c = 15.947(1)$ Å are in good agreement with the values reported earlier from an x-ray diffraction study. The values of other crystal structure parameters, such as fractional atomic coordinates, bond lengths, and bond angles, are also in a good agreement with the previously reported values from an x-ray diffraction study and are not reported here. No structural change has been observed down to the lowest measured temperature 2 K. It may be mentioned that Tassel et al. and independently Tsirlin et al. reported the existence of a very small orthorhombic distortion in the similar compound (CuCl)LaNb$_2$O$_7$, which belongs to the Dion-Jacobson series with $n = 2$. Due to the limited resolution available at D20, we cannot exclude the existence of such a distortion in (CuBr)Sr$_2$Nb$_3$O$_{10}$. The magnetic diffraction patterns at 8, 5, and 2 K, after subtraction of the 26 K nuclear data, are shown in Fig. 3. At 2 and 5 K, the appearance of additional weak magnetic Bragg peaks confirms a long-range AFM ordering in this compound. At 8 K, no magnetic peaks are observed, in agreement with the earlier dc magnetization study in which $M$ vs $T$ curves showed a single magnetic transition at $\sim 7.5$ K ($T_N$). However, two successive magnetic phase transitions at 9.3 ($T_{c1}$) and 7.5 ($T_{c2}$) K were observed in the specific-heat curve. The observed magnetic ordering in the present neutron diffraction study thus can be assigned to the “second” magnetic transition temperature $T_{c2} = 7.5$ K. In the present neutron diffraction study, no signature of static spin-spin correlation has been found at 8 K, i.e., ($T_{c2} < T < T_{c1}$), which is consistent with the $\mu$SR results, showing the fluctuating nature of spin-spin correlations over the intermediate temperature range ($7.5$ K $\leq T < 9.3$ K).

All of the magnetic peaks observed at 2 and 5 K, are indexed with the propagation vector $k = (0/3/8 1/2)$. The magnetic structure has been analyzed using irreducible representational theory as described by Bertaut. For the propagation vector $k = (0/3/8 1/2)$, the irreducible representations of the propagation vector group $G_k$ are given in Table I. In the space group $P4_1/mmm$ with the propagation vector $k = (0/3/8 1/2)$, there are three possible irreducible representations. The magnetic reducible representation $\Gamma$ for $Ib$ site (Cu site) can be decomposed as a direct sum of irreducible representations as

$$\Gamma_{mag} = \Gamma_1 + \Gamma_2 + \Gamma_3$$

The basis vectors of the Cu position $Ib$ (0, 0, 0.5) for the representations, calculated using the projection operator technique implemented in BASIREPS, are given in Table II.
FIG. 2. (Color online) (a) The layered crystal structure of (CuBr)Sr2Nb3O10. (b) The square-lattice arrangement of Cu-ions in the ab plane. The pathways of nearest-neighbor, next-nearest-neighbor, and next-to-next-nearest-neighbor exchange interactions (J1, J2, and J3, respectively) are shown.

The best fit to the observed diffraction pattern at 2 K (giving a magnetic R factor of 3.6%) is obtained by refinement of the magnetic structure with a linear combination of the representations \(\Gamma_1\) and \(\Gamma_3\). The fitted pattern is shown in Fig. 4. The corresponding magnetic structure is a helical AFM structure as shown in Fig. 5. A helix of Cu spins is formed in the ab plane and an AFM coupling of adjacent planes is found along the c axis. The Cu\(^{2+}\) moments rotate around the c axis within the ab plane as shown in Fig. 5(a), and the helix propagates along the b axis with a rotation of 135° between successive moments. The helical chains are coupled ferromagnetically along the a axis. The ordered moment is found to be 0.79(7) \(\mu_B/\text{Cu}^{2+}\)-ion at 2 K. The observed helical AFM structure for the present square-lattice system (CuBr)Sr2Nb3O10 is in contrast to the reported collinear AFM structure for other square-lattice systems, such as layered vanadium phosphates AA‘VO(PO4)2 with AA‘ = Pb2,27 BaZn,28 SrZn,29 PbZn,16 and BaCd30 with the FM J1 and AFM J2. A helical AFM structure is also in contrast to the theoretically predicted magnetic states for the FM J1-J2 model, namely, a collinear AFM structure for values of \(\alpha (|=J_2/J_1|) > 0.6\), and a FM structure for \(\alpha < 0.4\).15-19

The role of \(\alpha\) in (CuBr)Sr2Nb3O10 as well as in other square-lattice compounds may be described as follows. The \(\alpha\) value for the present compound was found (from the earlier magnetization measurement\(^{32}\)) to be 0.59 [\(J_2/J_1 = 30.6\ K/(−51.5\ K)\)] with a FM J1. From the value of \(\alpha\), it is evident that this system is at the phase boundary between ordered collinear AFM (with a dominating AFM J2) and disordered states in the theoretical phase diagram.15-19 A collinear AFM structure \([Q = (\pi 0)\) or \((0 \pi)\)] was found for (CuBr)LaNb2O7,43 an \(n = 2\) member of the present Dion-Jacobson series \([(\text{Cu}X)_{n−1}\text{An}_{−1}\text{Bn}O_{3n}+1]\) with FM J1 and an \(\alpha\) value of \((J_2/J_1) = 41.3\ K/(−35.6\ K)) = 1.1\), which is well inside the range for a collinear AFM state \((\alpha > 0.6)\). The other reported square-lattice compounds with FM J1 having a collinear AFM structure, such as Pb2VO(PO4)2 (\(\alpha \sim 1.6\))27 and BaCdVO(PO4)2 (\(\alpha \sim 0.9\)),30 are as well far above the lower limit of \(\alpha > 0.6\). At the other extreme of \(\alpha\) values [i.e., for compounds with lower values of \(J_2/(\text{FM J1})\)], a FM state \([Q = (0 0)]\) is predicted.15-19 The FM J1-J2 model with \(\alpha\) in the range \(\sim 0.4-0.6\) predicts either a spin nematic phase15 or a sharp phase boundary between FM order and collinear stripe order at \(\alpha = 0.4\), i.e., no disorder phase exists at all.16 It is, therefore, evident that the observed magnetic ground state for

TABLE I. Irreducible representations of the group of the propagation vector \(G_k\).

<table>
<thead>
<tr>
<th>Symmetry element of (G_k)</th>
<th>1</th>
<th>2 (0, y, 0)</th>
<th>m(x, y, 0)</th>
<th>m(0, y, z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Gamma_1)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(\Gamma_2)</td>
<td>1</td>
<td>1</td>
<td>−1</td>
<td>−1</td>
</tr>
<tr>
<td>(\Gamma_3)</td>
<td>1</td>
<td>−1</td>
<td>1</td>
<td>−1</td>
</tr>
</tbody>
</table>
1 pattern shown in Fig. 3. The vertical bars show the allowed magnetic

quantum fluctuations. For a pure 2D square-lattice system, the expected ordered magnetic moment is \( \sim \mu B \) per ion.44,45

It is therefore, evident that the magnetic ground state for the present system differs from the theoretically predicted with FM \( J_1 \) and AFM \( J_2 \) systems. The observed moment of 0.79(7) \( \mu B \) at 2 K is typical for Cu\(^{2+} \) oxides, with some reduction from the ideal value of 1 \( \mu B \) due to covalency effects and quantum fluctuations. For a pure 2D system, the expected ordered magnetic moment is \( \sim 0.6 \mu B \) per ion.44,45

It is, therefore, necessary to perform further experiments, particularly, an inelastic neutron scattering on single crystals of the present compound to measure \( J_1, J_2 \), and particularly \( J_3 \).
FIG. 6. (Color online) The magnetic diffraction pattern of (CuBr)Sr2Nb3O10 measured at 2 K under a 4.5 T magnetic field, after subtraction of the 12 K nuclear profile. The peaks are indexed with a propagation vector $k_1 = (0 1/3 0.446)$ and a probable $k_2 = (0 0 0)$ vector.

are mostly composed of several magnetic satellites as shown in Fig. 6.

The observation of magnetic order with the propagation vector $k_1 = (0 1/3 0.446)$ under a 4.5 T magnetic field provides a direct microscopic confirmation of a change of the magnetic structure at the $1/3$ magnetization plateau, which had been observed in the previous magnetization study. An in-plane magnetic structure with $Q = (0 2\pi/3)$ was theoretically predicted from the quantization condition of the plateau magnetization. According to theoretical work by Oshikawa et al. for a Heisenberg spin system, the quantization condition on the magnetization at a plateau is $p(S-m) = \text{integer}$, where $p$ and $m$ are the period of the spin state and the magnetization per site, respectively. For the present compound with $S = 1/2$ Cu$^{2+}$ ions, the minimal necessary condition of the $1/3$ plateau ($m = 1/6$) gives the preference for $p = 3$. (CuBr)Sr2Nb3O10 has only one Cu$^{2+}$ ion per chemical unit cell which implies $p = 1$, so breaking of translational symmetry is needed to satisfy the quantization condition. Magnetic structures with an up-up-down arrangements of ions, the minimal necessary condition of the $1/3$ magnetization plateau, which is different compared to the zero-field case.

IV. SUMMARY AND CONCLUSIONS

In summary, a novel helical AFM structure has been found for the $S = 1/2$ square-lattice system (CuBr)Sr2Nb3O10 at temperatures below $T_N \sim 7.5$ K in its ground state. A helix of Cu spins is formed in the $ab$ plane, and such planes are coupled antiferromagnetically along the $c$ axis. The ordered moment is found to be $0.79(7) \mu_B$/Cu$^{2+}$ ion at 2 K. The observed helical AFM structure is in contrast to the experimental observations and theoretical predictions for the ground state of a $S = 1/2$ square-lattice system on the basis of the $J_1$-$J_2$ model. The observed heligic magnetic ground state indicates that the third-nearest-neighbor exchange interaction $J_3$ may play a significant role for the present system. Under a 4.5 T magnetic field, we have observed a different magnetic structure, characterized by the propagation vector $k_1 = (0 1/3 0.446)$ and a probable $k_2 = (0 0 0)$ vector, which is different compared to the zero-field case.

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