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Citation for published version:
https://doi.org/10.1103/PhysRevB.88.104401

Digital Object Identifier (DOI):
10.1103/PhysRevB.88.104401

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Publisher's PDF, also known as Version of record

Published In:
Physical Review B

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Field-induced evolution of magnetic ordering in the quantum spin system (CuBr)Sr₂Nb₃O₁₀ with a 1/3 magnetization plateau

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(Received 15 May 2013; published 3 September 2013)

The field-induced evolution of the magnetic ordering in (CuBr)Sr₂Nb₃O₁₀ with a 1/3 magnetization plateau has been investigated by neutron diffraction under magnetic fields up to 10 T. With an increasing magnetic field, the zero-field helical antiferromagnetic (AFM) phase, AF1, with \( \kappa = [0 \ 3/8 \ 1/2] \) is replaced by a simple ferromagnetic phase with \( \kappa = [0 \ 0 \ 0] \), the formation of which is, however, retarded by the appearance of a second AFM, AF2, with \( \kappa = [0 \ 1/8 \ 0.46] \). Upon further increasing of the magnetic field, the AF2 phase disappears and only the ferromagnetic phase persists. The results clearly show that the magnetization plateau, induced by the competition between field-induced ferromagnetic, F, and AF2 phases, is coincidentally situated at \( M = 1/3 \) of the dc magnetization curve. The AF1 and AF2 phases have strongly differing magnetic propagation vectors and are therefore not directly related.

DOI: 10.1103/PhysRevB.88.104401

PACS number(s): 75.30.Kz

I. INTRODUCTION

Several members of the Dion-Jacobson series of compounds \((\text{CuX})_{n-1}\text{B}_n\text{X}_{3n+1} (X = \text{Halide}, A = \text{La, Ca, Sr, Ba, and } B = \text{Nb, Ta, Ti})\) have lately been studied intensively as far as their crystal structure and magnetic behavior are concerned.\(^1^0\) Originally described in the \( P4/mmm \) symmetry,\(^7^8\) the crystal structure of these compounds is characterized by square lattices of \( \text{Cu}^{2+} \) ions in \( \text{CuX-Halide} \) layers separated by \( n \) slabs of nonmagnetic corner-sharing \( \text{BO}_6 \) octahedra. Interest in these compounds was stimulated as the compounds were believed to represent possible examples for the frustrated \( 2 \) \( D \) \( \times \) \( 2 \) \( D \) model for \( n = 2 \) compounds.\(^{10} \) The crystal structures of the \( n = 2 \) compounds \((\text{CuCl})\text{LaNb}_2\text{O}_7 \) (Refs. 1 and 11), \((\text{CuBr})\text{LaNb}_2\text{O}_7 \) (see Ref. 4), and \((\text{CuCl})\text{LaTa}_2\text{O}_7 \) (see Ref. 5) do not possess a tetragonal symmetry but have a small orthorhombic distortion introducing a manifold of different magnetic interactions going far beyond the simple \( J_1-J_2 \) model. The strongest magnetic coupling \( (J_4) \) was shown to connect the fourth-nearest \( \text{Cu}^{2+} \) neighbors in these compounds. The compound \((\text{CuCl})\text{LaNb}_2\text{O}_7 \) shows a nonmagnetic spin gap ground state and was described as a ferromagnetic Shastry Sutherland compound with spin dimers being about 8.5 Å apart.\(^{1,9,12}\) The appearance of magnetically long-range ordered states in \((\text{CuBr})\text{LaNb}_2\text{O}_7 \) and \((\text{CuCl})\text{LaTa}_2\text{O}_7 \) was linked to the increasing ratio between the sum of the numerous magnetic interdimer couplings and the intradimer coupling \( J_4 \) (see Ref. 5). The coupling between the 2D quasiquadratic lattice \( \text{CuX} \) layers through the nonmagnetic slabs of \( \text{BO}_6 \) octahedra is strong enough to lead to a three-dimensional long-range magnetic order in these \( n = 2 \) compounds.

Going to members of the Dion-Jacobson series that have \( n = 3 \), the coupling between the \( \text{CuX} \) layers should be further reduced as the 2D character of the magnetic \( \text{CuX} \) layers is increased by adding an additional nonmagnetic perovskite unit between the layers. Specific heat and magnetization measurements on \((\text{CuBr})\text{Sr}_2\text{Nb}_3\text{O}_{10} \) revealed, however, a unique magnetic behavior with the existence of two magnetic phase transitions at zero field and—most surprising—the existence of a magnetization plateau at 1/3 of the saturation magnetization \( M_s \).\(^{13} \) While magnetization plateaus at \( M = 1/3 \) \( M_s \) are predicted for lattices based on triangular symmetries,\(^{14} \) the frustrated square lattice with \( S = 1/2 \) should only allow a plateau at \( M = 1/2 \) \( M_s \) within the simple \( J_1-J_2 \) model.\(^{15} \) Our first study on this compound using neutron diffraction determined the zero-field magnetic structure below \( T_{N1} = 7.5 \) K to consist of an antiferromagnetic (AFM) alignment of \( \text{Cu} \) spins within the \( \text{CuBr} \) layers (helical magnetic structure) with a magnetic propagation vector \( \kappa = [0 \ 3/8 \ 1/2] \) and a magnetic moment value of about \( \mu_{\text{Cu}} = 0.8(1) \mu_B \) at 2 K.\(^{6} \) In order to explain the existence of the helical magnetic structure not foreseen in the \( J_1-J_2 \) model, the \( J_1-J_2-J_4 \) was invoked. Interestingly enough, a 1/3 plateau in the magnetization has been theoretically predicted within the \( J_1-J_2-J_4 \) model for \( J_1 = -1, J_2 = 1, \) and \( J_4 = 0.5 \) (see Ref. 16). No long-range magnetic order was found in the temperature range between \( T_{N1} = 7.5 \) K and \( 9 \) K, where the specific heat data\(^{13} \) showed a first magnetic phase. Earlier preliminary neutron-diffraction data under a magnetic field of 4.5 T (corresponding to the 1/3 magnetization plateau state) indicated the presence of a different magnetic propagation vector under the field without explaining the existence of the 1/3 magnetization plateau.\(^5 \)
In this paper, we present the results of a recent neutron-diffraction investigation under magnetic fields up to 10 T. The results clearly show that the magnetization plateau is induced by the competition between two field-induced magnetic phases (a ferromagnetic, F, phase and a AFM, AF2, phase with $\kappa = [0 \, \frac{1}{2} \, \gamma]$) and is only coincidentally situated at $M = \frac{1}{3} M_S$.

II. EXPERIMENTAL PROCEDURES

The sample of (CuBr)Sr$_2$Nb$_3$O$_{10}$ was prepared, as described previously, by a low-temperature ion-exchange reaction between the parent compounds RbSr$_2$Nb$_3$O$_{10}$ and CuBr$_2$. Neutron-diffraction data were taken at room temperature (RT) and at 20 K on the high-resolution powder diffractometer D2B ($\lambda = 1.594$ Å, $Q = 0.2-7.7$ Å$^{-1}$) at the Institut Laue Langevin (ILL), Grenoble, France, in order to check for the symmetry and the purity of the compound. High-intensity powder-diffraction data were recorded on the high flux instrument D20 as well, installed at the ILL ($\lambda = 2.419$ Å, $Q = 0.25-4.8$ Å$^{-1}$) as a function of temperature and magnetic field. Long measurements of 6 hours each were taken at 2 K for magnetic field values of $H = 0, 1, 2.5, 4.5, 5.5$, and 10 T. Additional scans were taken at zero field at 8.5, 15, and at 26 K and for $H = 4.5$ T at 5.5 and 8.5 K in order to verify the magnetic phase diagram proposed by Tsujimoto et al. Low temperatures and magnetic fields up to 10 T were achieved using an Oxford Instruments horizontal cryomagnet. A radially oscillating collimator was used to suppress the scattering of the cryomagnet. The sample was put inside a cylindrical vanadium sample holder in the form of pressed pellets in order to avoid any reorientation of powder grains under the effect of the magnetic field. The diffraction data were analyzed by the Rietveld method using the FULLPROF suite of programs. Magnetic symmetry analysis was done using the Program BASIREPS, which is included in the FULLPROF suite.

III. RESULTS AND DISCUSSION

A. Crystal structure

The crystal structure of (CuBr)Sr$_2$Nb$_3$O$_{10}$ has been reinvestigated by high-resolution neutron diffraction using the D2B diffractometer. Such a high-resolution diffraction pattern measured at RT is shown in Fig. 1. The data were first refined in space group $P4/mmm$ using the previously published crystal structure model. There is no evidence of a peak splitting as the unit cell parameters stay metrically tetragonal at RT and at 20 K. The refinement, however, leads to extremely elevated isotropic displacement parameters $U_{iso}$ for the bromine atom at the Wyckoff position 1$d$ and for the oxygen atom (O1) at the Wyckoff position 2$f$. The high value of $U_{iso}$ for the bromine position had been already found by Tsujimoto et al. from x-ray diffraction (XRD), whereas the same phenomena had not been determined for O1 as a single isotropic displacement parameter had been used for all four oxygen atoms, hiding thereby the unusual behavior of O1. The left inset of Fig. 1 displays part of the refined diffraction pattern at relatively high two-theta values (range $\sim 100-140^{\circ}$) where inconsistencies between the published model and the data become clearly visible. A high atomic displacement factor (ADP) of the halide was found in the $n = 2$ compound CuBrLaNb$_2$O$_7$ and had been interpreted as indicating the splitting of the Br position, with the major shift appearing within the Cu-Br layer. Consistently, when allowing a splitting of the Br position [1$d$; ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)] into either the 4o ($x$, $\frac{1}{2}$, $\frac{1}{2}$) or the 4k ($x$, $x$, $\frac{1}{2}$) positions, a clear improvement in the refinement of the present (CuBr)Sr$_2$Nb$_3$O$_{10}$ pattern is achieved. Both 4o and 4k sites allow a shift within the tetragonal basal plane. Relaxing the 1$d$ position of Br ions into the direction along the tetragonal axis (c axis) into the Wyckoff position, 2$h$ does not lead to any improvement of the refinement or reduction of the ADP. This confirms that the Br displacement occurs only within the ab-plane (Cu-Br layer). The splitting of the O1 position 2$f$ (0, $\frac{1}{2}$, 0) appears as well within the tetragonal basal plane with a statistical occupation of the Wyckoff site 4$n$ ($x$, $\frac{1}{2}$, 0). The final refinement, including the split Br (4o or 4k sites) and O1 (4$n$) positions, leads to normal ADPs and is shown in Fig. 1.

We have to recall here that for (CuBr)Sr$_2$Nb$_3$O$_{10}$ the tetragonal symmetry is preserved and that the originally proposed space group $P4/mmm$ with a square planar lattice of Cu atoms is still a valid description of the structure. In general, the deviations from the tetragonal symmetry can be detected in diffraction data not only through a splitting of certain Bragg peaks but also through the appearance of superlattice peaks. In the case of the $n = 2$ compound (CuCl)LaNb$_2$O$_7$, an orthorhombic splitting was observed in high-resolution synchrotron XRD while no splitting was detectable for (CuCl)LaTa$_2$O$_7$ by XRD. Neutron-diffraction data for both compounds revealed, however, weak superlattice reflections, which are indexable in a four times larger unit cell with...
2\sigma_i \times 2b_i \times c.\textsuperscript{15} For (CuBr)Sr\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}, the high intensity data of D20 were, therefore, used to verify and to confirm the absence of any superlattice reflections at RT and low temperatures (2 K). As a conclusion, one can state that the average crystal structure of (CuBr)Sr\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} stays tetragonal in space group \textit{P4}\textit{mmmm} over the studied temperature range between RT and 2 K. However, there exists a strong disorder of the Br atoms (within the Cu-Br layers) and of one of the oxygen atoms (within the NbO\textsubscript{6} perovskite blocks), which lowers the symmetry locally. Figure 2 displays this structure that leads to strong local deviations from a simple quadratic coordination of Br by Cu ions as the Br atom is statistically shifted from strong local deviations from a simple quadratic coordination symmetry locally.

### Magnetic structures

The magnetic structures of (CuBr)Sr\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} were studied as function of magnetic field and temperature using the high-intensity data taken on D20. Due to the very low intensity of the magnetic scattering as compared to that of the nuclear scattering, the magnetic peaks are only visible in the difference patterns. The magnetic difference patterns are obtained by subtraction from the relevant patterns of a pattern recorded at 15 K under zero magnetic field (within the paramagnetic phase). Using the crystallographic model and the atomic coordinates, as determined from the high-resolution D20 data at 20 K, this zero field 15 K nuclear-background pattern was refined. The so-determined scale factor served in the following for the refinement of the difference spectra.

FIG. 2. (Color online) (a) Crystal structure of (CuBr)Sr\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}. The Cu, Br, and Nb atoms are shown in yellow, green, and blue, respectively. The O atoms are shown in red except O1-atoms, which are shown in brown. The split Br 4o site and the split O1 4n site are also shown. Magnetic interaction pathways in the \textit{ab} plane (Cu-Br-layer) with Br on one of the four statistically occupied sites, (b) 4o or (c) 4k, are also shown.
corresponding to the AF1 structure are no longer visible. Under the maximum applied field of 10 T, a further qualitative change becomes apparent with the strong appearance of ferromagnetic Bragg peaks ($\kappa_3 = [0 1/3 0]$) and a decrease of the intensity of the AF2-type peaks. The detailed analysis of the data reveals that the ferromagnetic phase (F) is, in fact, already present in the data taken at 5.5 and 4.5 T, a possibility already mentioned before for the 4.5 T data.6

Below we discuss the magnetic structure of the field-induced AF2 phase. Magnetic symmetry analysis was done using the program BASIREPS18,19 for $\kappa_2 = [0 1/3 0.45]$; magnetic moments are confined in the $ac$ plane forming a cycloidal spiral. Along the $b$ axis, the spins turn by 120° between neighboring unit cells.

structure can be visualized as a cycloidal modulation of constant moment spins rotating within the $ac$-plane and is shown in Fig. 4. Using powder data, it is in principle not possible to discriminate between a helix and a sine-wave structure having the same components. If, however, the maximum amplitude of the magnetic moment in the sine-wave model is physically not reasonable, it is possible to exclude this model. This seems to be the case for (CuBr)Sr$_2$Nb$_3$O$_{10}$ where the refinement of the 5.5 T data using the helix model results in $\mu_{Cu} = 0.77(2)\mu_B$, whereas the sine-wave model using the same two basis vectors [0 1 0] and [0 0 1] gives $\mu_{Cu} = 1.09(3)\mu_B$. The moment value $\mu_{Cu} = 1.09(3)\mu_B$ is too large for Cu$^{2+}$ especially in the titled low-dimensional and partly frustrated system.

The clear presence of the (00$l$) reflections in the data taken at 10 T and the observed magnetic moment value of 0.8 $\mu_B$, which is in accordance with the maximum moment in the AF1 and AF2 magnetic structures, indicates that the magnetic moments of the ferromagnetic phase are aligned within the Cu-halide layers. This does not rule out the possibility of a small $c$ component for the magnetic moment not detectable in the current experiment.

With the knowledge of the three different magnetic structures, AF1, AF2, and F, the quantitative analysis of the purely magnetic diffraction patterns under different magnetic fields at 2 K has been performed to determine the degree of coexistence of these three magnetic phases. Figure 5 displays the results of the Rietveld refinements of the purely magnetic (difference) patterns under different magnetic fields at 2 K. Table II lists the determined magnetic-moment values for each phase as a function of magnetic field. One has to recall here that the magnetic moment values are determined using the scale factor determined from the refinement of the nuclear phase. In the case of coexisting magnetic phases, it is normally not possible to say whether the magnetic phases are present in different parts of the sample volume or whether they each embrace the whole sample volume. Only the presence of a strong magnetostriction effect, which would lead to nuclear phases having crystallographic unit cell parameters different for the different magnetic phases, would allow the determination of different scale factors and thereby the determination of

FIG. 4. (Color online) AF2 structure with $\kappa = [0 1/3 0.45]$; magnetic moments are confined in the $ac$ plane.
F(2 K, 0 T) - (15 K, 0 T)
AF1

AF1 + AF2

AF2 + F

AF2 + F

FIG. 5. (Color online) Rietveld refined magnetic diffraction patterns after subtraction of 15 K, 0 T diffraction pattern as nuclear background at 2 K under 1, 2.5, 4.5, and 10 T magnetic field. Observed, calculated, and difference patterns are shown by red points, black lines, and blue line, respectively. The calculated positions of the Bragg peaks are shown by vertical bars.

Now we discuss the phase diagram in details. Several observations can be made looking at the magnetic field dependence of the magnetic structures displayed in Fig. 6. With increasing magnetic field, the zero-field AF1 phase first persists (1 T), then decreases (2.5 T), and has disappeared at 4.5 T. The field-induced AF2 phase does not yet appear at 1 T, although it already represents the majority phase at 2.5 T. With further increasing field, the AF2 phase decreases significantly between 5.5 and 10 T, corresponding to the magnetic field range where the F phase increases strongly. The F phase starts to be noticeable in the data taken at 4.5 T but could be already present at lower fields at a level not detectable by the present neutron data.

TABLE II. Magnetic moment values of the different magnetic phases at 2 K as determined from the refinement of the difference spectra (after subtraction of the 15 K, 0 T pattern as nuclear background).

<table>
<thead>
<tr>
<th>$H$ (T)</th>
<th>0$^a$</th>
<th>1</th>
<th>2.5</th>
<th>4.5</th>
<th>5.5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF1 ($\mu_B$)</td>
<td>0.79(1)</td>
<td>0.75(2)</td>
<td>0.43(3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AF2 ($\mu_B$)</td>
<td>-</td>
<td>-</td>
<td>0.71(2)</td>
<td>0.78(4)</td>
<td>0.77(2)</td>
<td>0.53(2)</td>
</tr>
<tr>
<td>$F$ ($\mu_B$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.27(7)</td>
<td>0.31(4)</td>
<td>0.80(2)</td>
</tr>
<tr>
<td>$R_{mag}$ (%)</td>
<td>3.7</td>
<td>7.4</td>
<td>13.5/2.8</td>
<td>2.1/3.4</td>
<td>5.6/7.0</td>
<td>13.5/2.1</td>
</tr>
</tbody>
</table>

$^a$From Ref. 6.
different. The possibility to identify the AF2 phase as the magnetic phase responsible for the formation of the 1/3 plateau phase is supported by its temperature dependence as well. Figure 7 displays that the magnetic Bragg peaks (characteristic for the AF2 phase) at 4.5 T are still present at 8.5 K. This mirrors the temperature dependence of the 1/3 plateau phase shown in Fig. 4 of Ref. 13, which shows a maximum at this magnetic field value in opposition to the zero-field AF1 phase, which disappears already for T > 7.5 K.

IV. CONCLUSIONS

High-resolution and high-intensity neutron-diffraction data indicate that, contrary to some n = 2 members of the Dion-Jacobson series (CuX)\(A_{n-1}B_nO_{3n+1}\), the average crystal structure of the n = 3 compound (CuBr)\(Sr_2Br_3O_{10}\) does not show any signs of deviation from the tetragonal symmetry described in space group P4/mmm. The existence of a statistical distribution of the halide over a split site, however, disturbs the symmetrical surrounding of the Cu\(^{2+}\) ions by Br ions in the Cu-Br layers and calls for a magnetic interaction model going beyond the simple \(J_1-J_2\) model. The present detailed temperature and magnetic field-dependent neutron-diffraction investigation allows us to conclude that the existence of a plateau in the magnetization curve of (CuBr)\(Sr_2Nb_3O_{10}\) is only coincidentally situated at \(M = 1/3\) \(M_S\). Under the effect of the magnetic field, the zero-field AF1 phase is replaced by a simple ferromagnetic phase, the formation of which is, however, slowed down by the appearance of an AF2 phase, which is stable at intermediate field values. AF1 and AF2 phases have strongly differing magnetic propagation vectors and therefore, are not directly related.

ACKNOWLEDGMENTS

A part of this work was supported by FIRST program from JSPS. Support from EPSRC, STFC, and the Royal Society is also acknowledged.

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Due to the tetragonal symmetry, it is not possible to discriminate from powder-diffraction data between the magnetic propagation vectors $\kappa_2 = [0 \frac{1}{3} \gamma]$ and $\kappa_2 = [\frac{1}{3} 0 \gamma]$.

Instead of assuming a coexistence of AF2 and F magnetic phases in spatially different regions, it is also possible to explain the neutron data if the AF2 phase has an additional ferromagnetic component. This does not change the following discussion concerning the $\frac{1}{3}$ magnetization plateau; however, in Fig. 6, one would have to regard AF2 and F phases, respectively, as AFM and ferromagnetic components of the same phase. However, the magnetization data indicate that the F phase is induced as soon as a field is applied, whereas the AF2 phase seems to appear only above $\sim1$ T, which favors the two-phase model.

Unpublished data of Tsirlin et al. show that $(\text{CuBr})\text{Ba}_2\text{Ta}_3\text{O}_{10}$ adopts under a magnetic field the same AF2-type magnetic structure as $(\text{CuBr})\text{Sr}_2\text{Nb}_3\text{O}_{10}$. 