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New investigation of the magnetic structure of CoNb$_2$O$_6$ columbite

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The structural and magnetic properties of the CoNb$_2$O$_6$ compound have been investigated with a particular interest in their low-dimensional magnetic behavior which is characterized by the presence of weakly interacting ferromagnetic chains. We investigate this cobalt niobate by combining magnetic measurements; x-ray and neutron diffraction (ND). The ND was carried out on powder samples at different temperatures above (20 K) and below the ordering temperature (2.4, 1.8, and 1.4 K). The compound exhibits an orthorhombic crystal structure of Phcn, symmetry, of a columnite structure. Magnetic ordering at 2.5 K is found with the propagation vector (0, 0.4, 0), in agreement with earlier studies. However, at lower temperatures the present investigation shows the coexistence of two different magnetic phases; the propagation vector (0.5, 0.5, 0) is found to be necessary to refine the ND measurements at both 1.8 and 1.4 K, in addition to (0, 0.5, 0) which was the only one reported in earlier works. © 2011 American Institute of Physics. [doi:10.1063/1.3562516]

AB$_2$O$_6$ (A = Fe, Co, Ni; B = Ta, Nb) compounds have been the subject of many investigations due to their interesting structural and magnetic properties with a rich variety of magnetic phases.$^{1-12}$ Indeed, they have attracted the interest of scientists from many different communities; not only physicists,$^{2,4,8,14}$ but also chemists,$^{1,3,6}$ and biologists.$^{13}$ Compounds such as ANb$_2$O$_6$ have been proposed as potential materials for high performance microwave resonators.$^{15,16}$ Depending upon their atomic composition, they can crystallize in a wide range of crystal structures such as tetragonal or orthorhombic symmetry. They present magnetic ordering at low temperatures (typically below 10 K), and all the observed ordered phases can be classified as antiferromagnetic (AF) however they differ from a simple nearest-neighbor Néel structure. The AB$_2$O$_6$ compounds are considered as prototype materials since they exhibit low dimensional magnetic characteristics. Whereas tetragonal ATa$_2$O$_6$ phases are model two-dimensional magnetic systems,$^{9,11,12}$ the orthorhombic ANb$_2$O$_6$ phases exhibit weakly interacting one-dimensional magnetic chains.$^{17-20}$

The CoNb$_2$O$_6$ compound was found to order at 2.95 K with a transition from a paramagnetic phase to an ordered spin structure.$^{18}$ Its magnetic phase diagram was reinvestigated, combining powder and single-crystal neutron diffraction, by Schärf et al.$^{21}$ later by Heid et al.$^{18,19}$ and Kobayashi and co-workers.$^{17,20}$ Scharf et al.$^{21}$ first described the magnetic structure below 2.96 K as a screw structure with the y axis as the screw axis and a screw angle of 133°. This angle increases with decreasing temperature to a constant angle of 180° at and below 1.97 K. The magnetic structure below 1.97 K was reported as a noncollinear antiferromagnetic structure. More recently, Heid et al.$^{18}$ introduced an incommensurate propagation vector (0, k$_y$, 0), to describe the magnetic structure between 2.95 and 1.95 K where k$_y$ changes with temperature in the range 0.37 ≤ k$_y$ ≤ 0.5. Below 1.95 K a commensurate behavior is identified with the propagation vector (0, 0.5, 0). The magnetic properties of this compound have also been investigated by NMR,$^{22,23}$ ESR,$^{22}$ and IR transmission spectroscopy.$^{23}$

We present here a detailed investigation of low-temperature magnetic properties of CoNb$_2$O$_6$ by combining magnetic measurements and powder neutron diffraction experiments. Besides confirming the two transitions previously observed and the presence of an incommensurate ordering between them, we find that another phase coexists with the previously reported magnetic structure for temperatures below 1.97 K.

Powder CoNb$_2$O$_6$ samples were prepared with appropriate amounts of Co$_3$O$_4$ and Nb$_2$O$_5$. The mixture was ground, pressed into pellets, and heat treated in air at 1370 K for 30 h. Then, the obtained samples were slowly cooled and powdered to 320 meshes. A large amount of sample, at about 2.5 g, was prepared for the neutron diffraction measurements (ND). The sample purity was first checked by x-ray diffraction (XRD) analysis before magnetic and neutron measurements. XRD analysis has been performed in the Bragg-Brentano geometry, using Co K$_x$ radiation, $\lambda$(K$_{a_1}$) = 1.7890 Å and $\lambda$(K$_{a_2}$) = 1.7928 Å, with scan step of 0.05° and an angular 20 range from 10–80°. The XRD diffraction pattern confirms the purity of the CoNb$_2$O$_6$ phase as well as the Phcn space group symmetry.

Magnetic measurements have been undertaken on the powder sample in a wide temperature range, from 1.7–300 K, using the extraction method with an experimental setup described elsewhere.$^{24}$ Isothermal magnetization curves have been recorded in the magnetic field ranging from 0–10 T and magnetic susceptibility $\chi$(T) was measured in a magnetic field of 0.5 T in the temperatures range of 1.7–50 K. For better accuracy the measurement of the magnetic susceptibility above 50 K was confirmed using Arrott plots of the isothermal magnetization.
measurements. \( \chi(T) \) was thus obtained by extrapolating the magnetization data down to zero applied field at several temperatures between 50 and 300 K. In order to determine the magnetic transition temperature specific-heat measurements were performed with a Physical Properties Measurements System calorimeter,\(^{26} \) for temperatures ranging from 1.9 – 300 K.

Powder ND measurements were carried out with the double-axis multicounter high-flux diffractometer D1B, operated by the CNRS at the Institut Laue Langevin (ILL), Grenoble, France, using a 2.52 Å wavelength selected by a pyrolitic graphite monochromator. D1B is a powder diffractometer operating with the takeoff angle of the monochromator at 44° (\( 2 \theta \)). In the configuration used, the resolution was about 0.3° (full width at half maximum) and the multicounter is composed of 400 cells covering a total angular \( (2 \theta) \) range of 80°, which was chosen from 5–85° to collect the data with a detector step of 0.2°.

XRD and ND data analysis was performed using the FULLPROF refinement package\(^{27} \) in order to extract the crystallographic and magnetic parameters. The agreement factors used in this article are defined according to the guidelines of the Rietveld refinement that can be found elsewhere.\(^{28} \) The neutron scattering lengths used were 0.7054 \( \times 10^{-12} \) cm for Nb, 0.2490 \( \times 10^{-12} \) cm for Co and 0.5803 \( \times 10^{-12} \) cm for O, values taken from Ref.\(^{29} \).

The magnetic susceptibility \( \chi \) as a function of temperature is shown in Fig. 1. A double-peak structure is observed in the low temperature region within a broad maximum that indicates the presence of enhanced short-range correlations characteristic of low-dimensional materials. The AF transitions appear as inflection points in plots of the uniform susceptibility. These are better seen by plotting the derivative of the product \( \chi(T) \) with respect to \( T \), which shows well defined peaks at the transitions. This is shown for our data in the inset of Fig. 1, where two transitions are seen near 2.9 and 1.95 K, in fair agreement with earlier reported studies.\(^{30} \) The higher value may be identified as the Néel temperature, and coincides with the ordering temperature found from the specific-heat data. The peak at 1.95 K is indicative of a change of the magnetic ordering which will be discussed below in light of the neutron-diffraction investigation. An anomaly at the same point can also be observed on the specific-heat measurements reported by Hanawa \textit{et al.}\(^{31} \). We now turn to our neutron-diffraction analysis of the low-temperature magnetic structure. The refinement of the 20 K ND pattern indicates that the Co and Nb cations are fully ordered however, attempts to refine oxygen vacancies were unsuccessful within the experimental error bars. The columbite structure results from the stacking of slightly tilted oxygen octahedra surrounding the cations forming zig-zag chains along the \( c \) direction. The isothermal magnetization curve recorded at 2 K for CoNb\(_2\)O\(_6\) is shown in Fig. 2. The curve exhibits little hysteresis and no saturation of the magnetization is observed even below 10 T. This bears witness to the presence of antiferromagnetic interactions and possible magnetocrystalline anisotropy not completely overcome even in fields as high as 10 T.

According to Fig. 3(a), which presents the powder neutron diffraction data recorded at 2.5 K on the CoNb\(_2\)O\(_6\) phase, the indexation of the magnetic Bragg reflections can be done using a propagation vector \( k = (0, 0.4, 0) \). This is consistent with the previous observation of an incommensurate magnetic phase with propagation vector \( (0, k_y, 0) \), \( 0.37 \leq k_y \leq 0.5 \), as reported by Heid \textit{et al.}\(^{18} \). A comparison with the pattern recorded at the lower temperature of 1.4 K

![FIG. 1. (Color online) Magnetic susceptibility and derivation of temperature and susceptibility multiplication in detail.](image1)

![FIG. 2. (Color online) Hysteresis cycle recorded at 2 K for the CoNb\(_2\)O\(_6\) powder.](image2)

![FIG. 3. (Color online) The Rietveld refinement results of the neutron diffraction pattern taken at (a) 2.5 K and (b) 1.4 K for CoNb\(_2\)O\(_6\). The rows of ticks and triangles refer to the nuclear and magnetic Bragg reflections, respectively. The difference between the observed experimental points and the calculated fit (continuous line) is plotted at the bottom of each figure. Note the different magnetic-structure \( k \) vectors of CoNb\(_2\)O\(_6\) at each temperature.](image3)
reveals that the magnetic structure has evolved upon cooling, thus proving the occurrence of a magnetic transition between 2.5 and 1.4 K which is consistent with the observed peak at 1.95 K shown in the inset of Fig. 1. The low-temperature Rietveld refinement results are plotted in Figs. 3(a) and 3(b) for 2.5 and 1.4 K, respectively. It is worth mentioning that the diffraction patterns recorded at 1.8 or 1.4 K were barely identical and confirmed the coexistence of both (0, 0.5, 0) and (0.5, ±0.5, 0) propagation vectors.

In earlier studies, the magnetic structure below 1.95 K has been described as consisting of ferromagnetic chains that alternate antiferromagnetically along the b axis, with the propagation vector (0, 0.5, 0). Our analysis of the neutron powder diffraction patterns led us to consider the presence of two coexisting magnetic phases: besides (0, 0.5, 0), the propagation vectors (0.5, ±0.5, 0) were needed to account for the observed diffraction peaks. The refinement of the magnetic ND data recorded at 1.4 K has been carried out considering a unique Co\(^{2+}\) magnetic moment and the coexistence of two phases with propagation vectors (0, 0.5, 0) and (0.5, ±0.5, 0), respectively.

Earlier studies of the magnetism in CoNb\(_2\)O\(_6\) have reported only the (0, 0.5, 0) structure in temperatures below 1.95 K. However, it is interesting to mention that a coexistence between (0, 0.5, 0) and (0.5, 0.5, 0) phases has been reported\(^7\) for the related compounds FeNb\(_2\)O\(_6\) and NiNb\(_2\)O\(_6\). This magnetic structure change at low temperatures most probably originates from a temperature dependence of the magnetic interactions, since no crystal structure change has been observed in this temperature range and the lattice parameters have been found to be identical within the experimental errors (see Table I). This indicates the need for a precise determination of all the exchange interactions involved in CoNb\(_2\)O\(_6\) in order to achieve a deeper understanding of the low temperature magnetic properties of this compound.

We have investigated the magnetic properties of CoNb\(_2\)O\(_6\) with our main focus on the low-temperature ordered phases. Our neutron-diffraction and susceptibility results clearly reveal

<table>
<thead>
<tr>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>(R_{wp}(%))</th>
<th>(R_d(%))</th>
<th>(R_B^{Mag}(%))</th>
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<tr>
<td>14.125(2)</td>
<td>5.701(3)</td>
<td>5.038(4)</td>
<td>3.6</td>
<td>2.4</td>
<td>25.7</td>
</tr>
<tr>
<td>14.124(5)</td>
<td>5.701(2)</td>
<td>5.037(1)</td>
<td>4.1</td>
<td>2.2</td>
<td>15.5 and 20.5</td>
</tr>
<tr>
<td>Atom</td>
<td>x</td>
<td>y</td>
<td>z</td>
<td>(\mu_B)</td>
<td>(\mu_B)</td>
</tr>
<tr>
<td>Co</td>
<td>0</td>
<td>0.158 2(2)</td>
<td>0.25</td>
<td>0.94±2.98i</td>
<td>(0, 0.4, 0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0, 1/2, 0) 80%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>((\pi/), ±1/2, 0) 20%</td>
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<tr>
<td>Nb</td>
<td>0.161 2(2)</td>
<td>0.361 1(2)</td>
<td>0.780 9(4)</td>
<td>0.782 1(2)</td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>0.094 1(2)</td>
<td>0.372 2(3)</td>
<td>0.447 4(3)</td>
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<tr>
<td>O2</td>
<td>0.082 8(3)</td>
<td>0.117 0(5)</td>
<td>0.897 8(1)</td>
<td>0.897 7(3)</td>
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<tr>
<td>O3</td>
<td>0.238 10(0)</td>
<td>0.151 3(3)</td>
<td>0.594 9(2)</td>
<td>0.594 5(2)</td>
<td></td>
</tr>
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</table>

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