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New investigation of the magnetic structure of $CoNb_2O_6$ columbite

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The structural and magnetic properties of the $CoNb_2O_6$ 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 *Pbcn* symmetry, typical of a columbite 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_2O_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_2O_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_2O_6 compounds are considered as prototype materials since they exhibit low dimensional magnetic characteristics. Whereas tetragonal ATa_2O_6 phases are model two-dimensional magnetic systems,[9,11,12] the orthorhombic ANb_2O_6 phases exhibit weakly interacting one-dimensional magnetic chains.[17–20]

The $CoNb_2O_6$ 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 $0.37 \leq k_y \leq 0.5$. 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 $CoNb_2O_6$ 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 $CoNb_2O_6$ samples were prepared with appropriate amounts of Co_3O_4 and Nb_2O_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 Kα radiation, $\lambda(K\alpha_1) = 1.7890$ Å and $\lambda(K\alpha_2) = 1.7928$ Å, with scan step of 0.05° and an angular 2θ range from 10–80°. The XRD diffraction pattern confirms the purity of the $CoNb_2O_6$ phase as well as the *Pbcn* 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

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measurements.[25] χ(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° (in 2θ). 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 (2θ) 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 0.7054×10^{-12} cm for Nb, 0.2490×10^{-12} cm for Co and 0.5803×10^{-12} cm for O, values taken from Ref. 29.

The magnetic susceptibility χ 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 χ(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 measurement reported by Hanawa *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

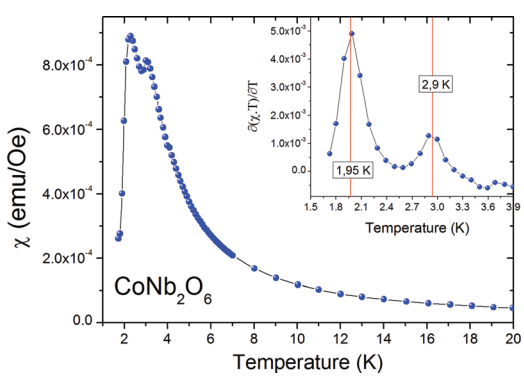

FIG. 1. (Color online) Magnetic susceptibility and derivation of temperature and susceptibility multiplication in detail.

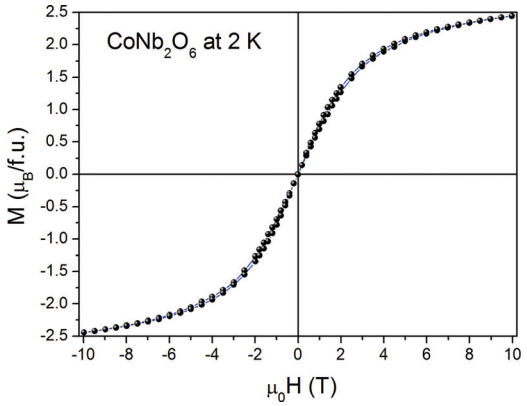

FIG. 2. (Color online) Hysteresis cycle recorded at 2 K for the $CoNb_2O_6$ powder.

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 $CoNb_2O_6$ 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 $CoNb_2O_6$ 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 *et al.*[18] A comparison with the pattern recorded at the lower temperature of 1.4 K

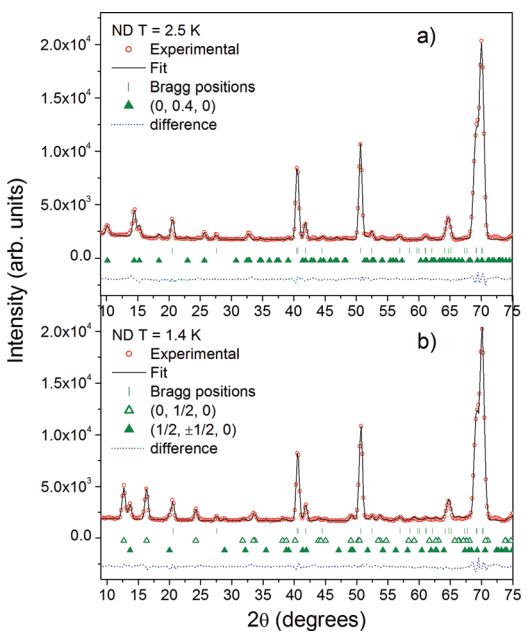

FIG. 3. (Color online) The Rietveld refinement results of the neutron diffraction pattern taken at (a) 2.5 K and (b) 1.4 K for $CoNb_2O_6$. The rows of ticks and triangles refer to the nuclear and magnetic Bragg reflections, respectively. The difference between the observed experimental points and the calculated fit (continuous line) is plotted at the bottom of each figure. Note the different magnetic-structure k vectors of $CoNb_2O_6$ at each temperature.

TABLE I. Structural parameters and magnetic moments obtained from the Rietveld analysis of the neutron diffraction data. The first and second rows refers to the 2.5 and 1.4 K results, respectively.

a(Å)	b(Å)	c(Å)	R_{wp}(%)	R_B(%)	R_B^{Mag}(%)
14.125(2)	5.701(3)	5.038(4)	3.6	2.4	25.7
14.124(5)	5.701(2)	5.037(1)	4.1	2.2	15.5 and 20.5
Atom	***x***	***y***	***z***	μ_{Co} (μ_B)	
Co	0	0.158 2(2)	0.25	0.94+2.98*i*	(0, 0.4, 0)
					(0, 1/2, 0) 80%
	0	0.157 9(4)	0.25	3.02(±0.3)	(1/2, ±1/2, 0) 20%
Nb	0.161 2(2)	0.361 1(2)	0.780 9(4)		
	0.161 3(1)	0.362 8(2)	0.782 1(2)		
O1	0.094 1(2)	0.372 2(3)	0.447 4(3)		
	0.094 1(4)	0.372 2(1)	0.447 4(1)		
O2	0.082 8(3)	0.117 0(5)	0.897 8(1)		
	0.082 9(1)	0.118 4(2)	0.897 7(3)		
O3	0.238 1(0)	0.151 3(3)	0.594 9(2)		
	0.237 2(2)	0.153 1(4)	0.595 2(2)		

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,[17,18] 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 the vectors described above. As indicated in Table I, a value of 3.02 μ_B per Co ion has been refined for both phases, whereas the obtained proportion of each phase is 80 and 20% for (0, 0.5, 0) and (0.5, ±0.5, 0), respectively.

Earlier studies of the magnetism in $CoNb_2O_6$ 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 $FeNb_2O_6$ and $NiNb_2O_6$. 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 $CoNb_2O_6$ in order to achieve a deeper understanding of the low temperature magnetic properties of this compound.

We have investigated the magnetic properties of $CoNb_2O_6$ with our main focus on the low-temperature ordered phases. Our neutron-diffraction and susceptibility results clearly reveal the presence of two magnetic transitions at 2.9 and 1.95 K which is in agreement with earlier reported measurements. At 2.5 K a magnetic structure described by a (0, 0.4, 0) propagation vector has been obtained whereas at 1.4 K the coexistence of two magnetic phases with propagation vectors (0, 0.5, 0) and (0.5, ±0.5, 0), have been inferred from the ND data. The rich variety of the magnetic behavior of AB_2O_6 compounds certainly deserves further investigation, preferably with the emphasis on the relative roles of inter- and intrachain couplings.

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