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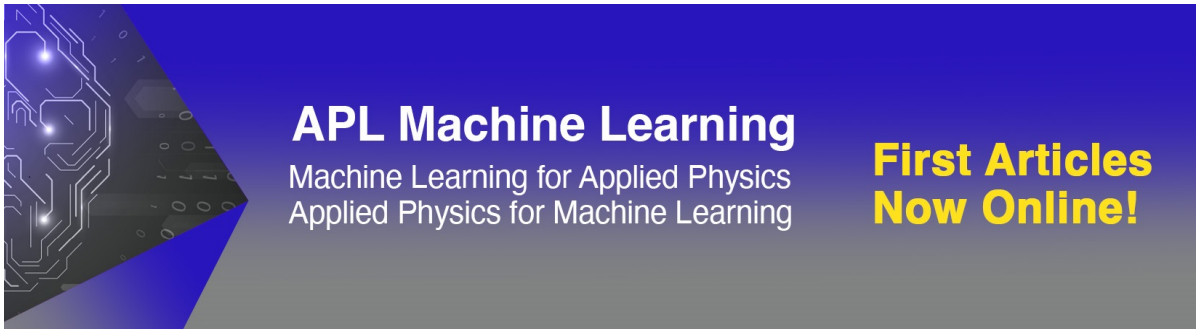

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ABSTRACT

Quasi-one-dimensional (Q1D) spin chain systems have great potential applications in high-density information storage devices, quantum information and computers, because of their quantum magnetism properties. The low-dimensional magnetic behavior has been investigated in ANb_2O_6, (A = Mn, Fe, Co or Ni) compounds, the structural and magnetic properties are very interesting because the system presents weakly interacting Ising chains, which leads to this quasi-one-dimensional magnetic order. Our investigation combines specific heat and magnetic measurements; x-ray and neutron diffraction (ND). In this work, we present a Co/Ni orthorhombic structure, called columbite, which crystallizes with *Pbcn* space group, whose formula is $Co_{0.4}Ni_{0.6}Nb_2O_6$. Co for Ni substitution induces a continuous lattice volume decrease, preserving the orthorhombic crystal structure. Magnetic susceptibility and specific heat measurements reveal that antiferromagnetic order occurs at 3.4 K, as a consequence of weak interchain interactions. Partial substitution of the magnetic ion tends to change the magnetic ordering observed in the $CoNb_2O_6$ and $NiNb_2O_6$. Lastly, we present this magnetic structure changes with the Ni-Co substitution.

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I. INTRODUCTION

Magnetism remains a theme that has absorbed humanity for numerous generations. However, the long-range interaction combined with the complex systems magnetism emerges in to make it an extremely challenging subject. The importance of this field is primarily due to the future appeal of the electronic industry down to the atomic level. Quantum effects get more imperative at short scales, notably in lower-dimensional materials such as sheets and wires.[1] Nowadays, numerous composites, as $CoNb_2O_6$, have been synthesized serving as a model for the quantum spin system's investigation with a one-dimensional arrangement of spins. This subject has proved therefore interesting that they been calling attention from many different scientific communities; like physicists,[2–6] engineers,[7–10] chemists[11–13] and biologists.[14] Indeed, ANb_2O_6 compounds are considered prototype materials, seeing as they present low dimensional magnetic characteristics. These orthorhombic materials exhibit weak interactions in one-dimensional magnetic chains.[15–18] They present magnetic ordering, typically, below 10 K, in ordered antiferromagnetic (AF) phase, but they diverge from a simple nearest-neighbor Néel structure.

Some of the traditional experimental techniques for detecting and identify magnetic order and dynamics in solid-state materials is neutron measurements as scattering and diffraction. The Néel temperature obtained for $CoNb_2O_6$ was 2.95 K with a transition to an ordered spin structure from the paramagnetic phase (PM).[17] Furthermore, its magnetic phase diagram was again investigated, linking powder and single-crystal neutron diffraction, by Schärf,[19] Heid,[17,18] Kobayashi and coworkers[15,16] and Sarvezuk *et al.*[6,20] Below 2.96 K Schärf[19] described as a screw magnetic structure, with the

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TABLE I. Succinct descriptions of magnetic structure for $CoNb_2O6$ and $NiNb_2O_6$ (SG/PV = Space Group/Propagation Vector. MM = Magnetic Moment. NDT = Neutron Diffraction Temperature. A/Y = Authors/year.).

	SG/PV	MM (μ_B)	NDT (K)	A/Y
$NiNb_2O_6$	Pbcn (0,½,0) (½,±½,0)	2.4	1.3	Heid, 1996[21]
	P42/n (½,½,½)	3.35	3.5	Munsie 2016 and 2017[22,23,a]
$CoNb_2O_6$	$P_b2_12_12_1$ (0,k,0) 0.3≤k≤0.6	3.05	1.5≤T≤2.6	Scharf 1979[19]
	Pbcn (0,k_y,0) 0.37≤k_y≤0.5	3.2	1.97≤T≤2.95	Heid 1995[17]
	Pbcn (0,½,0) (½,±½,0)	3.02	2.5	Sarvezuk 2011[6]
	Pbcn (0,0.4,0)	0.94+2.98i	1.4	Sarvezuk 2011[6]

[a]Single Crystal sample.

y-axis as a screw axis, and a screw angle of 133°. Such behavior changes because of the temperature decrease. In later work, Heid *et al.*[17] presented an incommensurate propagation vector, (0,k_y,0), for this system, which took place in a very specific temperature range between 2.95 and 1.95 K. The value of ky changes over the temperature and decreases from 0.37 to 0.5, respectively, this means: below 1.95 K a (0,½,0) commensurate propagation vector is used. We have in the past proposed a (0,½,0) and (½,±½,0) propagation vector for cobalt columbite at 2.5 K and an incommensurate magnetic structure (0,0.4,0) at a lower temperature, down to 1.4 K, and suggests a continuous evolution of this incommensurate propagation vector.[6]

On the other hand, investigations of $NiNb_2O_6$ compound present ordered magnetic structure, due to triangular coordination on the *ab* planes. This also leads to an unusual magnetic behavior influenced by a few different exchange couplings. Nickel columbite orders from the paramagnetic phase to an ordered spin structure at 5.7 K, the magnetic atomic structure for $NiNb_2O_6$ had been reinvestigated by Heid *et al.*,[17,21] who showed that $NiNb_2O_6$ exhibits antiferromagnetic order with a canted magnetic structure. They determined this nickel columbite compound had a magnetic structure with two propagation vectors (0,½,0) and (½,½,0), through the combination of magnetic measurements and neutron diffraction.

Not long ago Munsie *et al.*[22,23] described $NiNb_2O_6$ with a new $P4_2/n$ magnetic structure with propagation vector (½,½,½), showing that there is still much to investigate in this system. Compilation results obtained for magnetic structures of $CoNb_2O_6$ and $NiNb_2O_6$ are presented in Table I.

Here, we present a compilation of magnetic properties for $Co_{0.4}Ni_{0.6}Nb_2O_6$ by combining magnetic susceptibility, specific heat, and neutron diffraction studies, in this spin-chain compound, in order to reveal the magnetic structure present at low temperature.

II. EXPERIMENTS AND METHODS

$Co_{0.4}Ni_{0.6}Nb_2O_6$ powder sample was made with stoichiometric amounts of $CoNb_2O_6$ and $NiNb_2O_6$. The mixture of primary powders was pressed into pellets and heat-treated in the air at 1570 K for 30 h with a slow temperature decreasing to room temperature. Then, powdered to 44 microns. A large amount of sample is required for neutron diffraction (ND), about 2.5 g. Using X-ray diffraction (XRD), at room temperature, the sample pureness state was performed, before neutron diffraction measurements. The XRD

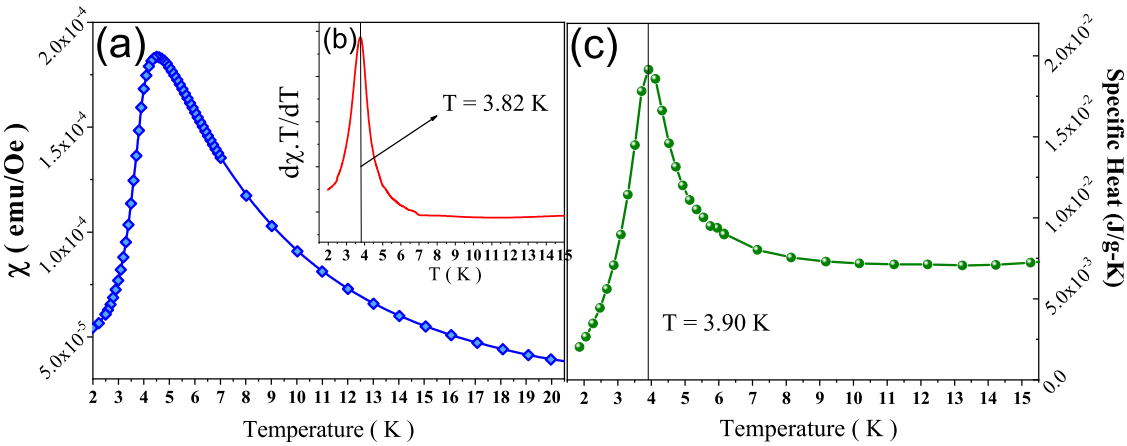

FIG. 1. (a) Magnetic susceptibility and (b) in detail derived from the multiplication between temperature and susceptibility. (c) Specific heat with assigned temperature transition.

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TABLE II. A summary of the bulk magnetic properties of $Co_xNi_{1-x}Nb_2O_6$.

x	θ_w ±2.5(K)	C (uem.k/mol/T)	μ_{eff} (μ_B)	T_N (K)
$NiNb_2O_6$[27]	11.3	1.3	3.25 (±0.9)	5.1
$Co_{0.4}Ni_{0.6}Nb_2O_6$	**4.3**	**1.49**	**3.45 (±0.9)**	**3.8**
$CoNb_2O_6$[6]	3.9	2.39	4.40 (±1.3)	1.9 2.9

pattern confirms the *Pbcn* space group symmetry and pure blended $Co_{0.4}Ni_{0.6}Nb_2O_6$ product. The ND was carried out at 2.5 Kelvin, with angular 2θ range from 10° to 80° and scan step of 0.05°, the wavelength was selected by a pyrolytic graphite monochromator using 2.52 Å, with the double-axis multi counter high-flux diffractometer D1B line, in collaboration with CNRS at the Institut Laue Langevin (ILL), Grenoble-FR.

Magnetic susceptibility ($\chi(T)$) has been undertaken on powder samples using SQUID Quantum Design. The $\chi(T)$ was measured in a magnetic field of 50 Oe in the temperatures range 1.7–300 K. A PPMS calorimeter[24] was used to add information on magnetic transition temperature, specific-heat measurements were made from 1.9 to 300 K.

To extract the crystallographic and magnetic parameters data analysis of XRD and ND was done with FULLPROF[25] refinement software using the Rietveld refinement method. This article uses agreement factors defined in the Rietveld's guidelines and can be found elsewhere.[26]

III. RESULTS AND DISCUSSION

The thermal evolution of magnetic susceptibility (χ) is displayed on the left side in Figure 1(a). A maximum on this curve is observed at low-temperature region (close to 4.5 K), which represents not a peak, but a broad maximum that characterizes low-dimensional magnetic materials. The antiferromagnetic transition does not occur at that point but the curve inflection region. These are better examined by plotting the derivative of the χ.T product with respect to T, which shows a well-defined peak at the temperature transition. This is shown in the inset, Figure 1(b), the transition is seen near 3.8 K which is an intermediate value between Co and Ni niobate.[6,17,21,27] This peak may be identified as the Néel temperature and coincides with the ordering temperature found from the specific-heat data showed at the right side of figure 1(c).

The Curie-Weiss law, $\chi(T) = C/(T - \theta_w)+\chi_o$ was fitted at sufficiently superior ordering temperature, higher than 40 K. The paramagnetic temperature θ_w, Curie constant C and effective magnetic moments μ_{eff} have been obtained by fitting the experimental data and are cataloged in Table II. The inclusion of χ_o corresponds to a tiny correction for the temperature-independent diamagnetic susceptibility signal whose value was close to 10^{-7} emu/Oe. The paramagnetic temperature θ_w is lower for the Co-pure sample and progressively increases for the Ni-pure sample. Another marked detail is the low and positive value of θ_w, reflecting the dominance of ferromagnetic exchange interactions along the chains and due balance between Ferro and antiferromagnetic exchange interactions.

Regarding the X-ray diffraction, the diffractogram pattern refinement indicates the Co and Ni cations are fully ordered and forms a pure $Co_{0.4}Ni_{0.6}Nb_2O_6$ sample, but we should note that attempts to refine oxygen vacancies were unsuccessful within the experimental sensitivity. The columbite structure results from the stacking of slightly tilted oxygen octahedra surrounding the cations, forming zig-zag chains along the *c* direction.

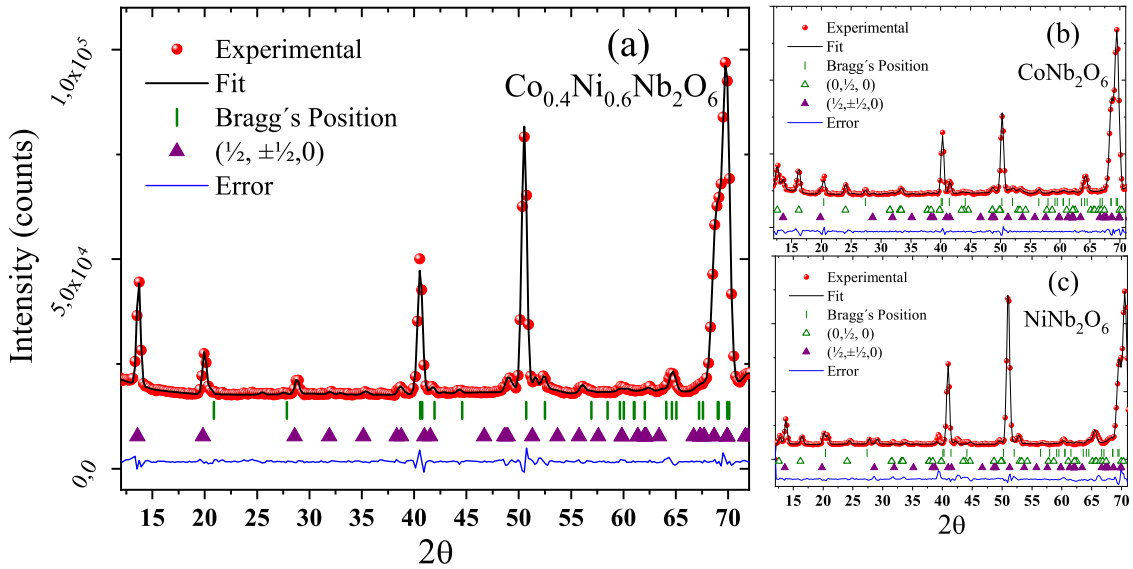

FIG. 2. Rietveld refinement results of the neutron diffraction pattern taken at 2.5 K for (a) $Co_{0.4}Ni_{0.6}Nb_2O_6$, (b) $CoNb_2O_6$[6] and (c) $NiNb_2O_6$.[27] The rows of ticks and triangles refer to the nuclear and magnetic Bragg reflections, respectively. The difference between the observed experimental points and the calculated fit (dotted line) are plotted at the bottom of each figure. Note the different magnetic peak intensity from $CoNb_2O_6$ and $NiNb_2O_6$.

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TABLE III. Unit-cell parameters and details of the crystallographic and magnetic structure study for $Co_{0.4}Ni_{0.6}Nb_2O_6$.

	a (Å)	b (Å)	c (Å)	R_{wp}(%)	R_B(%)
	14.009 (5)	5.661 (2)	5.020 (1)	2.4	6.4
Atom	x	y	z	$R_B{}^{Mag}$(%)	
Co	0	0.1705 (2)	0.25	17.1	
Nb	0.1599 (2)	0.3390 (2)	0.7957 (4)	**Propagation Vector**	
O1	0.0959 (2)	0.3863 (3)	0.4532 (3)	(½ ± ½ 0)	
O2	0.0823 (3)	0.1154 (5)	0.9031 (1)	$\mu_{CoNi}(\mu_B)$	
O3	0.2489 (2)	0.1427 (4)	0.5986 (2)	3.4	

Furthermore, low-temperature neutron diffraction measurement analysis can be seen in figure 2. This figure shows powder neutron diffraction data, recorded at 2.5 K, in $Co_{0.4}Ni_{0.6}Nb_2O_6$ (figure 2(a)), $CoNb_2O_6$ (figure 2(b)) and $NiNb_2O_6$ (figure 2(c)). For $Co_{0.4}Ni_{0.6}Nb_2O_6$ refinement, the identification of the magnetic Bragg reflections can be made by subtracting neutron diffraction pattern recorded at 20 K out of that at 2.5 K data,[23] and with the resulting pattern, only vector k = (½,±½,0) was required for indexing the magnetic phase.

Previous studies of magnetic structure in $CoNb_2O_6$ reported unique (0,½,0) or coupled (0,½,0) and (½,±½,0) propagation vector, for different temperatures. $NiNb_2O_6$, on the other hand, orders with (0,½,0) and (½,±½,0) and more recently a novel magnetic structure have been claimed (½,½,½), showing the contemporaneity of the research theme. Thus, comparing $CoNb_2O_6$ and $NiNb_2O_6$ magnetic structure, the pattern recorded at low temperature, reveals that $Co_{0.4}Ni_{0.6}Nb_2O_6$ has a peculiar behavior. Both Co and Ni pure columbite, present structures with two propagation vectors. For $Co_{0.4}Ni_{0.6}Nb_2O_6$ now we see one of them, that is (0,½,0), was annihilated, and only (½,±½,0) remain. This happens typically because of the cobalt and nickel spin correlation that makes the pattern peak reflection, relative to this propagation vector, fade. Accepting the importance of the ANb_2O_6 system into account, mainly due to its complex magnetic behavior, this result can further feed the experimental research of quantum criticality in Ising chains. The main results of the low-temperature neutron diffraction refinement are reported in Table III.

This magnetic structure changes most probably originate from Co-Ni combination, which modifies the magnetics interactions, since no crystal structure change has been observed, at this temperature. No significant lattice parameter deviation has been found from X-ray diffraction at room temperature data. This demands more exploration to better determine the exchange interactions involving Co and Ni cation substitution, to achieve a deeper understanding of the magnetic properties in this compound.

IV. CONCLUSIONS

We have investigated the magnetic properties of $Co_{0.4}Ni_{0.6}Nb_2O_6$ with the focus on the low-temperature ordered phases. The compounds show that substitution of Co for Ni in $NiNb_2O_6$ preserves the orthorhombic crystal structure. Our susceptibility and specific heat results reveal the presence of magnetic transitions at 3.8 K. Examination of the magnetic properties shows that all the compounds display small Néel and Weiss temperatures, persistent with the quasi-one-dimensional nature of their magnetic subsystem. The neutron diffraction at 1.8 K has a remarkable result. Despite the fact the two extreme compounds $CoNb_2O_6$ as well $NiNb_2O_6$ show, at some point, the same magnetic structure containing two propagation vectors (0,½,0) and (½,±½,0), chemical disorder promotes a change in the long-range magnetic order in $Co_{0.4}Ni_{0.6}Nb_2O_6$, resulting in a unique (½,±½,0) propagation vector. The disappearance of this propagation vector for this transitional compound may occur from cation disorder, and consequently, it amends the competing interactions that tend to influence the ordered state. The magnetic rich variety behavior of $Co_xNi_{1-x}Nb_2O_6$ compounds justifies further inspection, preferably with priority on the relative aspect of inter-and-intrachain couplings.

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