

Magnetic properties of the Kagomé mixed compounds $(\text{Co}_x\text{Ni}_{1-x})_3\text{V}_2\text{O}_8$

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The magnetic properties of the mixed compounds $(\text{Co}_x\text{Ni}_{1-x})_3\text{V}_2\text{O}_8$ (CNVO) investigated by magnetization and neutron diffraction measurements are presented. Unlike their parent compounds $\text{Ni}_3\text{V}_2\text{O}_8$ (NVO) and $\text{Co}_3\text{V}_2\text{O}_8$ (CVO), only one magnetic phase transition into an antiferromagnetic phase was detected for powder samples with $x=0.27$, 0.52 , and 0.76 . The magnetic structures are modulated according to a propagation vector $\vec{k}=(\delta, 0, 0)$ with δ being dependent on the composition parameter x . Furthermore, magnetization data of a CVO single crystal is featured, which is qualitatively different from previous publications and exhibits a controversial aspect concerning the behavior of the curve under an applied magnetic field along the b axis.

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I. INTRODUCTION

The orthooxovanadates of the $3d$ transition metals (M), which crystallize in the orthorhombic space group Cmca , represent magnetic lattices labeled as *Kagomé staircases*. The crystal structure of these $\text{M}_3\text{V}_2\text{O}_8$ compounds has been determined by Fuess *et al.*¹ and again by Sauerbrei *et al.*² The structure is characterized by edge-sharing MO_6 octahedra, which form buckled layers separated by nonmagnetic V^{5+} ions. Because of the structural anisotropy and two non-equivalent magnetic sites within the staircases (Fig. 1), these compounds differ from the ideal *Kagomé net*, which consists of corner-sharing equilateral triangles. The reduced symmetry relieves the geometrical frustration and results in long-range ordered magnetic structures and rich H-T phase diagrams.³ Although the parent compounds NVO and CVO have been exhaustively investigated,¹⁻¹⁰ only structural data about $(\text{Co}_{0.5}\text{Ni}_{0.5})_3\text{V}_2\text{O}_8$ has been published¹¹ concerning the cation distribution on the two M sites. In the present work, magnetization measurements of three powder samples of the mixed compounds with $x=0.27$, 0.52 , and 0.76 were carried out and compared to the pure Ni and Co compounds. The results were confirmed by neutron powder diffraction experiments revealing more information about the magnetic structures. In addition, magnetization measurements of CVO are presented that differ from previously published data.^{5,8} Possible reasons for this discrepancy will be discussed.

II. EXPERIMENTAL

Powder samples of CVO and CNVO were synthesized with a reported technique⁸ by mixing NiO and CoO in the

desired ratio. Single crystals of CVO were grown by the Czochralski method. The crystal structures of the powder samples were investigated by neutron diffraction experiments. Therefore, measurements were carried out at the high-resolution neutron powder diffractometers D1A (CNVO) and D2B (CVO) at the Institut Laue-Langevin using a wavelength of 1.911 \AA at 20 K and 2.3974 \AA at 14 K , respectively. The single-crystal structure was checked by x-ray diffraction on the single-crystal diffractometer Oxford Diffraction XCALIBUR with $\text{Mo K}\alpha$ at 100 K . The magnetic phase transitions were examined by magnetization measurements using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design). The magnetic structures of CNVO were studied at zero magnetic field by neutron powder diffraction experiments at D1A. Additionally, neutron single-crystal diffraction experiments on CVO (two-axis diffractometer E4 at the Hahn-Meitner-Institut in Berlin) were used to reveal the magnetic phase transitions due to the temperature dependence of the propagation vector.

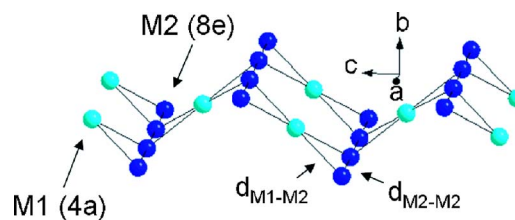


FIG. 1. (Color online) Visualization of a *Kagomé staircase* with the two crystallographic M sites [M1 light gray (blue), M2 dark gray (blue)] and the different distances between them.

TABLE I. Structural parameters of the investigated $(\text{Co}_x\text{Ni}_{1-x})_3\text{V}_2\text{O}_8$ powder (P) and single crystal (SC) samples.

Composition x	Cell	Position/Ion	M(1)	M(2)	V	O(1)	O(2)	O(3)
0.27 (P)	$a=5.9540(3)$	x	0	0.25	0	0	0	0.2674(9)
	$b=11.4094(7)$	y	0	0.1306(7)	0.3762	0.250(1)	0.002(1)	0.1197(6)
	$c=8.2530(6)$	z	0	0.25	0.1196	0.268(1)	0.244(1)	0.9998(6)
0.52 (P)	$a=5.9811(3)$	x	0	0.25	0	0	0	0.2683(7)
	$b=11.4359(5)$	y	0	0.1307(8)	0.3762	0.2509(9)	0.0030(9)	0.1197(5)
	$c=8.2704(5)$	z	0	0.25	0.1196	0.2687(9)	0.2443(9)	0.9989(9)
0.76 (P)	$a=6.0069(3)$	x	0	0.25	0	0	0	0.2683(7)
	$b=11.4648(6)$	y	0	0.132(1)	0.3762	0.250(1)	0.002(1)	0.1200(5)
	$c=8.2876(5)$	z	0	0.25	0.1196	0.2679(9)	0.2434(9)	0.9988(9)
1 (P)	$a=6.0255(1)$	x	0	0.25	0	0	0	0.270(1)
	$b=11.4843(4)$	y	0	0.128(4)	0.3786(7)	0.250(2)	0.003(2)	0.1215(9)
	$c=8.2975(2)$	z	0	0.25	0.121(1)	0.270(1)	0.246(1)	0.9976(9)
1 (SC)	$a=6.013(3)$	x	0	0.25	0	0	0	0.27003(9)
	$b=11.415(6)$	y	0	0.13226(1)	0.37715(1)	0.24975(7)	0.00116(6)	0.11849(5)
	$c=8.273(4)$	z	0	0.25	0.12031(2)	0.22937(9)	0.2449(1)	0.9984(7)

III. RESULTS

The structural investigation confirmed the correct phase formation of both the powder and single-crystal samples and showed close agreement to previously reported data.^{2,4,5,11} The cell constants of the mixed compounds behave according to Vegard's law. Like previously reported,¹¹ the Co ions were found to preferably occupy the more symmetric $4a$ sites, resulting in cation distribution factors of $K_D=0.73$, 0.81, and 0.76 for $x=0.27$, 0.52, and 0.76, respectively. Table I lists the structural parameters as well as the refined composition parameter x . Figure 2 shows the magnetization data of the three CNVO powder samples focusing the low-temperature region. For $x=0.27$ and $x=0.52$, a slight drop of the magnetization can be observed at $T=8.1$ K and $T=7.5$ K, respectively, whereas the curve for $x=0.76$ only exhibits a change of slope at $T=5.5$ K. From the characteristics of the curves, an antiferromagnetic ordering could be deduced and then confirmed by neutron powder diffraction ex-

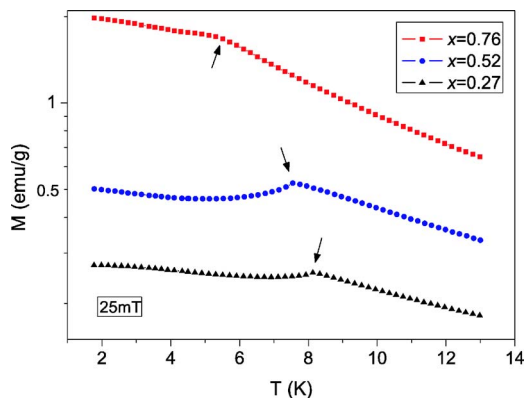


FIG. 2. (Color online) Magnetization in dependence on the temperature of $(\text{Co}_x\text{Ni}_{1-x})_3\text{V}_2\text{O}_8$ for $x=0.27$, 0.52, and 0.76 (logarithmic scale). Arrows mark the transition points.

periments. Because of the existence of multiple magnetic phases with temperature-dependent propagation vectors for NVO and CVO,^{3,6,10} patterns were collected at different temperatures below the respective transition points. In contrast to its parent compounds, CNVO does not exhibit temperature-dependent shifts of the magnetic reflections, which is illustrated in Fig. 3 for $x=0.27$. One can only note an increase of intensity of the magnetic reflections with decreasing temperature, which is an ordinary effect due to reduced thermal displacement. The magnetic reflections could be indexed by introducing a propagation vector $\vec{k}=(\delta,0,0)$ with δ being dependent on the composition parameter x . The shift of the magnetic reflections is clarified in Fig. 4. The values of δ are 0.372(5), 0.491(4), and 0.52(3) for $x=0.27$, 0.52, and 0.76, respectively, revealing an increase of δ with increasing amount of Co. It has to be mentioned that the increase of background at low angles for $x=0.76$ has also been observed for CVO at all investigated temperatures be-

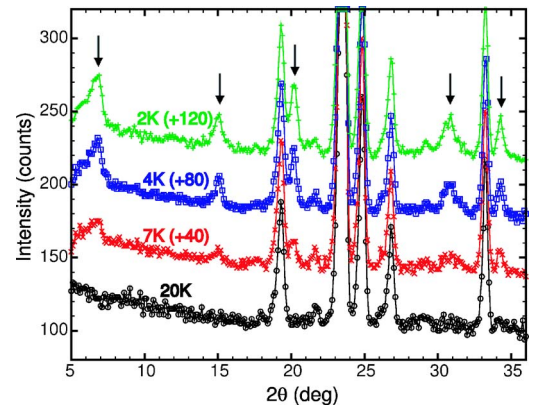


FIG. 3. (Color online) Powder diffraction patterns of $(\text{Co}_{0.27}\text{Ni}_{0.73})_3\text{V}_2\text{O}_8$ at different temperatures. Arrows mark the magnetic reflections. The numbers in brackets indicate the vertical shift to improve clarity.

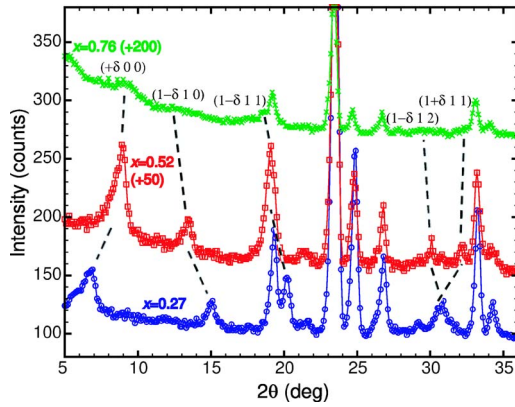


FIG. 4. (Color online) Powder diffraction patterns of $x=0.27$, 0.52 , and 0.76 at 2 K. The dashed lines indicate the shift of the magnetic reflections. Again the patterns are vertically shifted for clarity.

low 14 K and is depicted in Fig. 5 for $T=3.5$ K. The observed patterns could well be fitted (Fig. 6) based on a magnetic structure model similar to NVO with the antiferromagnetic vector along the a axis and weak ferromagnetism along c .

Magnetization measurements of CVO reveal the previously reported four magnetic phase transitions⁵ even on powder samples (inset in Fig. 5) in contrast to Refs. 4 and 6. The magnetic phase transitions are labeled according to Ref. 3. However, magnetization measurements performed on a single crystal with an applied magnetic field along each crystallographic axis only display the phase transitions $P \rightarrow \text{HTI}$ and $C \rightarrow C'$, although the same field strength and temperature step width have been used. But neutron diffraction experiments on the same single crystal confirm the larger variety of transitions, i.e., the HTI/LTI phases and the lock-in phase with $k_y = \frac{1}{2}$, by following the temperature dependence of the propagation vector obtained by measuring the $(020)^\pm$ reflections (Fig. 7).

The characteristics of the single crystal magnetization curves are qualitatively equivalent to Ref. 8, although the a and c axes are switched (Fig. 8).

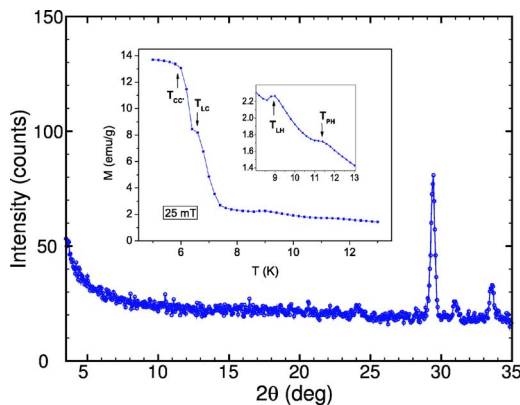


FIG. 5. (Color online) Powder diffraction pattern of ferromagnetic $\text{Co}_3\text{V}_2\text{O}_8$ at 3.5 K and zero field showing the increase of background at low diffraction angles. The inset displays the magnetization measurements of the same powder sample revealing four magnetic phase transitions.

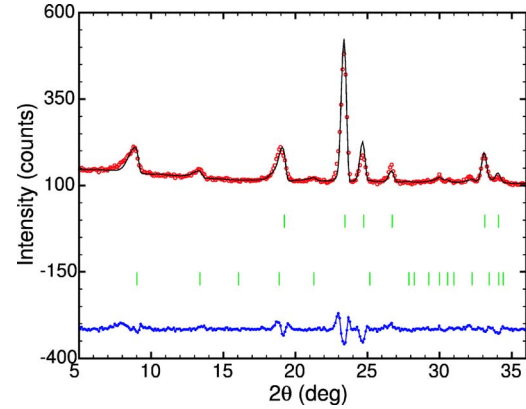


FIG. 6. (Color online) Observed pattern (red open circles), calculated pattern ([upper] black line) and difference plot ([lower] blue line) of $(\text{Co}_{0.52}\text{Ni}_{0.48})_3\text{V}_2\text{O}_8$ at 2 K and zero field.

These results are in contradiction to Ref. 5, where the magnetization curve with an applied field parallel to the crystallographic b axis exhibits a drop in the magnetization at the $C \rightarrow C'$ transition instead of increasing as in Fig. 8 or Ref. 8. This discrepancy can probably be explained by the orientation of the sample in the magnetometer. The field dependence of the transition points is able to elucidate this controversial aspect and will be discussed in Sec. IV.

IV. DISCUSSION

In contrast to NVO and CVO, the mixed compounds CNVO only exhibit a single-ordered magnetic structure deduced from magnetization and neutron diffraction experiments. Within the limits of the experimental precision, the modulation of the magnetic moments and the magnetic structure are similar to NVO, i.e., the magnetic moments propagate according to $\vec{k} = (\delta, 0, 0)$ with an antiferromagnetic vector along a and weak ferromagnetism along c , whereas CVO exhibits ferromagnetic coupling along a and a wave vector with a nonzero component along the b^* direction. For the three investigated samples, $x=0.27$, 0.52 , and 0.76 , the incommensurability δ has been found to be dependent on the

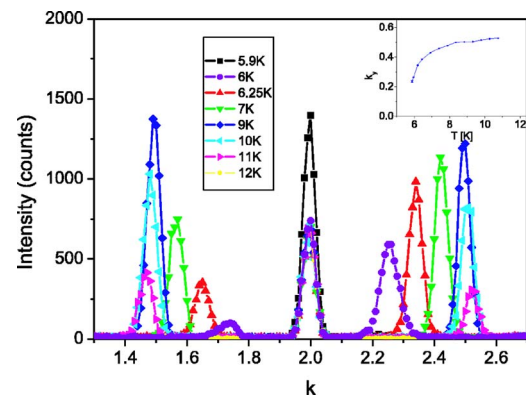


FIG. 7. (Color online) $(020)^\pm$ reflections at different temperatures. The inset shows the temperature dependence of the propagation vector $\vec{k} = (0, k_y, 0)$.

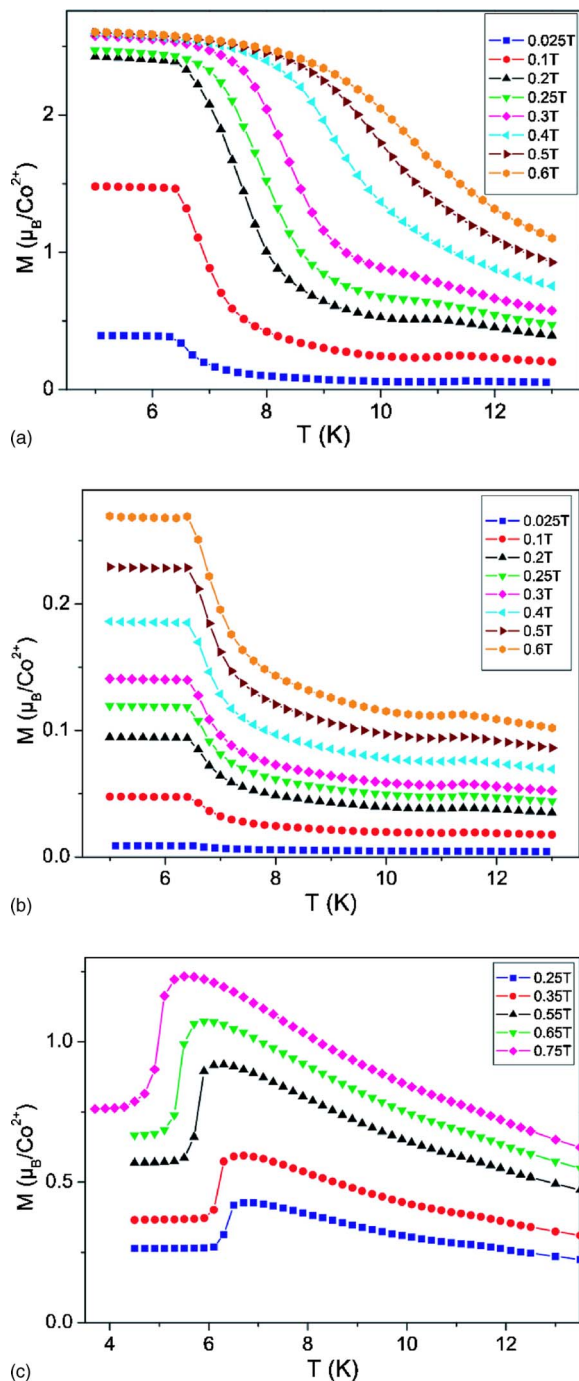


FIG. 8. (Color online) Temperature scans with different magnetic fields applied along the a - c axes for CVO.

composition factor x (δ increases with increasing x). The compound with $x=0.76$ seems to be close to a critical amount of Co, which disturbs the magnetic structure of NVO. A higher degree of frustration can be deduced due to the small and broad magnetic reflections (Fig. 4), which is well correlated with the less pronounced transition point in the magnetization curve (Fig. 2). More compositions with shorter steps in x will be investigated in order to specify the $\vec{k}(T)$ dependence and to spot the critical value of x where the magnetic structure switches from the NVO to the CVO type. Additional neutron diffraction experiments on single crystals will be carried out in order to extract precise information about the magnetic structure.

The magnetization measurements on a CVO single crystal yielded results differing from Ref. 5 concerning the curve with $H\parallel b$, which can be explained by the orientation of the single crystal in the magnetometer. Especially for the hard axis where small values of magnetization are observed, a deviation from the perfect crystal orientation would lead to different results because of measuring properties of another axis. In Fig. 8, one can clearly note the field dependence of the magnetic phase transitions with $H\parallel a$ and $H\parallel c$, whereas the transition points with $H\parallel b$ are not affected by the magnetic field. The fact that the characteristics of the curve for $H\parallel b$ are similar to the ones with $H\parallel a$ for small applied fields but do not exhibit the representative shift of the transition points with increasing field leads to the conclusion that, indeed, the properties of the b axis and no a axis contamination have been measured. Furthermore, in Ref. 5 the transitions points with $H\parallel b$ as well as $H\parallel c$ show the same tendency in the temperature region between 2 K and 6 K, i.e., a shift to smaller critical field strengths with increasing temperature. The authors do not state why their findings differ from Ref. 8. The magnetization curves with $H\parallel b$ in Ref. 5 possibly represent the properties of the c axis.

The crucial result of the present investigation is the compositional dependence (no temperature dependence) of the propagation vector, which modulates the magnetic moments of the antiferromagnetic structure of $(\text{Co}_x\text{Ni}_{1-x})_3\text{V}_2\text{O}_8$. Since the ground state of CVO is ferromagnetic, a quantum critical point is expected where the two types of magnetic interactions lead to a fully frustrated system for a certain composition with $x > 0.76$.

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¹H. Fuess, *et al.*, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **26**, 2036 (1970).

²E. E. Sauerbrei *et al.*, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **29**, 2304 (1973).

³G. Lawes *et al.*, Phys. Rev. Lett. **93**, 247201 (2004).

⁴N. Rogado *et al.*, Solid State Commun. **124**, 229 (2002).

⁵R. Szymczak *et al.*, Phys. Rev. B **73**, 094425 (2006).

⁶Y. Chen *et al.*, Phys. Rev. B **74**, 014430 (2006).

⁷A. B. Harris *et al.*, Phys. Rev. B **73**, 184433 (2006).

⁸G. Balakrishnan *et al.*, J. Phys.: Condens. Matter **16**, L347 (2004).

⁹G. Lawes *et al.*, Phys. Rev. Lett. **95**, 087205 (2005).

¹⁰M. Kenzelmann *et al.*, Phys. Rev. B **74**, 014429 (2006).

¹¹P. L. Wang *et al.*, Z. Kristallogr. **198**, 271 (1992).