Magnetic and powder neutron-diffraction studies of hexagonal β-$NaCoPO_4$: A possible geometrically frustrated magnet

N.P. Raju and J.E. Greedan

Abstract: Magnetic and powder neutron-diffraction studies were performed on a polycrystalline hexagonal compound β-$NaCoPO_4$ with space group $P6_5$ and lattice constants, a = 10.167 Å and c = 23.785 Å (1Å = 10^{-10} m). The susceptibility data display a magnetic transition below about 3.2 K and follow the Curie–Weiss law in the temperature range 5–300 K with a paramagnetic Curie temperature, θ_p, of −16.6 K indicating that the spins are strongly frustrated. The Co^{2+} ions form a helix about the c direction but due to the topology of the structure the helix can be decomposed into sets of six roughly triangular layers per unit cell. Thus, nearest-neighbor antiferromagnetic interactions can give rise to frustration within the pseudolayers. Low-temperature neutron-diffraction data reveal magnetic Bragg peaks below the ordering temperature. A Rietveld refinement of the data suggests a 120° magnetic structure of Co^{2+} spins within each pseudolayer.

Résumé : On a effectué des mesures de magnétisme et de diffraction des neutrons par la méthode des poudres sur un composé polycristallin hexagonal de β-$NaCoPO_4$, du groupe spatial $P6_5$ avec constantes de réseau a = 10,167 Å et c = 23,785 Å (1Å = 10^{-10} m). Les mesures de susceptibilité indiquent la présence d'une transition magnétique audessous de 3,2 K environ et une variation suivant la loi Curie–Weiss dans l'intervalle de température 5–300 K, avec une température de Curie paramagnétique, θ_p, de −16,6 K, ce qui indique que les spins sont fortement frustrés. Les ions Co^{2+} forment une hélice autour de la direction c, mais à cause de la topologie de la structure cette hélice peut être décomposée en ensembles de six couches approximativement triangulaires par maille élémentaire. Les interactions antiferromagnétiques entre plus proches voisins peuvent alors produire la frustration dans les pseudocouches. Les données de diffraction des neutrons à basse température révèlent la présence de pics magnétiques de Bragg au-dessous de la température de Curie. Un raffinement Rietveld des données suggère une structure magnétique à 120° des spins de Co^{2+} dans chaque pseudocouche.

[Traduit par la rédaction]

1. Introduction

Recently, there have been extensive studies of geometrically frustrated magnetic materials [1,2]. Geometrical magnetic frustration occurs when nearest-neighbor (nn) spins are subjected to anti-ferromagnetic exchange constraints, yet the topology of the spin lattice results in competing constraints on at least some sites. Lattices based on edge or corner sharing triangles in 2D (hexagonal or Kagomé) or tetrahedra in 3D (face-centred cube (fcc) or pyrochlore) provide such a topology. The ground state of an ordered, frustrated magnet depends on the dimensionality of the spins involved, i.e., Ising, XY planar, or Heisenberg. For XY planar and Heisenberg spins a long-range ordered structure, the so-called 120° structure, can result; this respresents a compromise for the nn constraints [3]. This structure can be thought of as three ferromagnetic sublattices oriented at 120° angles with each other such that the net magnetization is zero. In this work, we report magnetic and neutron studies on a new compound that appears to satisfy some of the criteria for frustrated magnetism.

Crystal structures of two different polymorphs of $NaCoPO_4$, namely α-$NaCoPO_4$ and β-$NaCoPO_4$, have recently been determined by R. Hammond and J. Barbier (private communication). The hexagonal β-$NaCoPO_4$ compound belongs to the large family of stuffed tridymites with space group $P6_5$ and unit cell constants: a = 10.166(1) Å, c = 23.881(5) Å (1Å = 10^{-10} m) with Z = 24. While the phosphorus and cobalt atoms occupy tetrahedral sites, the sodium atoms are located in the cavities. The structure consists of helical chains formed by alternating, corner-sharing CoO_4 and PO_4 tetrahedra, Fig. 1, which spiral about the c-axis. In such a geometry, the Co atoms form sets of edge-sharing triangular layers. However, these layers are not flat due to the distortion and also the tilting of the CoO_4 tetrahedra with in each layer. The triangular layers formed by the Co atoms are depicted in Figs. 2a and 2b as viewed along the [001] and [100] directions,

Received May 8, 1995. Accepted June 20, 1995.

N.P. Raju and J.E. Greedan. Institute for Materials Research, McMaster University, Hamilton, ON L8S 4M1, Canada.

Fig. 1. The structure of β-$NaCoPO_4$ viewed along the [110] direction. Open circles correspond to Na atoms. Shaded and unshaded tetrahedra represent PO_4 and CoO_4, respectively.

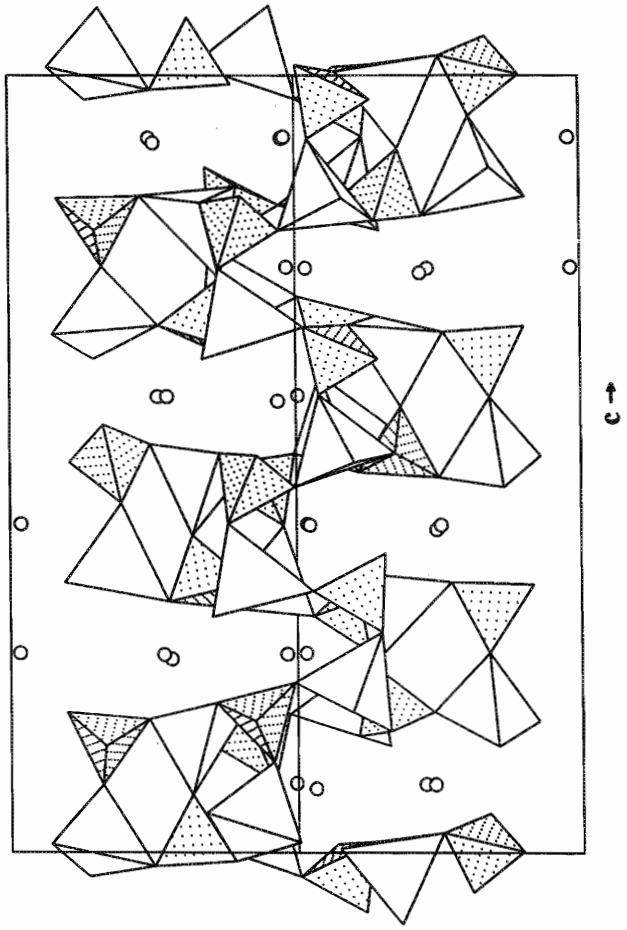


Fig. 2. (*a*) Two successive layers of the Co atoms in the *ab* plane connected by continuous and broken lines. (*b*) A view along the [100] direction illustrating tilted layers of the Co atoms.

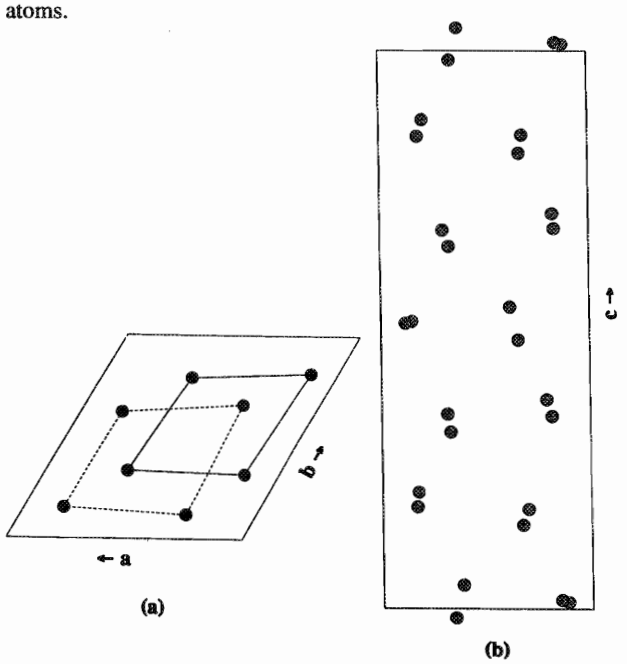
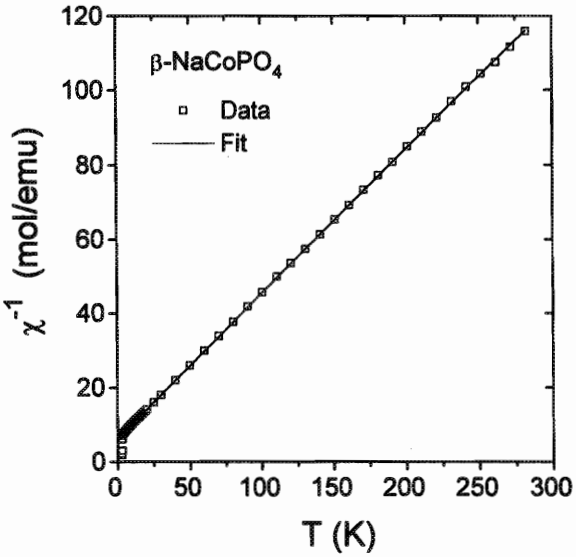


Fig. 3. Inverse magnetic susceptibility as a function of temperature.



respectively. Thus, this system represents sets of triangular layers of Co^{2+} ions with $S = 3/2$, and is a possible candidate for frustrated magnetism.

2. Experimental

2.1. Sample preparation

β-$NaCoPO_4$ was prepared in the form of polycrystalline powder. The starting materials of Na_2CO_3, $CoCO_3$, and $NH_4H_2PO_4$ were mixed in stoichiometric proportions and heated in air at 500°C for 16 h to pre-react the starting materials. Then the pre-reacted mixture was heated at 750°C for 2–5 days to obtain the dark-blue-coloured β-$NaCoPO_4$ compound. An analysis of powder X-ray diffraction data indicates that the sample formed was hexagonal and single phase.

2.2. Magnetic measurements

Magnetic susceptibility in the temperature range 2–300 K and magnetization up to 2.5 T were measured using a SQUID magnetometer (Quantum Design, San Diego).

2.3. Neutron diffraction

Powder neutron-diffraction data were collected at the DUALSPEC diffractometer at the Atomic Energy of Canada Limited facility in Chalk River, Ont. The powder sample was placed in a vanadium sample can and sealed with an indium gasket under a helium atmosphere. Diffraction data between 1.6 and 16 K, in the 2θ range 8°–85°, were collected by employing neutrons of wavelength 2.3141 Å. The data analysis was accomplished using the FULLPROF software system [4].

3. Results and discussion

3.1. Magnetic data

Magnetic susceptibility, χ, measured at 100 G obeys Curie–Weiss behavior over a wide temperature range, 5–300 K, as shown in the χ^{-1} vs. T plot in Fig. 3. The Curie constant, $C = 2.55$ emu K mol^{-1}, obtained from the fit, translates into an effective magnetic moment of 4.5(1) μ_B/Co, which is expected for a free Co^{2+} ion in tetrahedral symmetry. Also

Fig. 4. (*a*) Susceptibility vs. temperature below 5 K. (*b*) Negative temperature derivative of the product χT against temperature. The continuous line is guide to the eye.

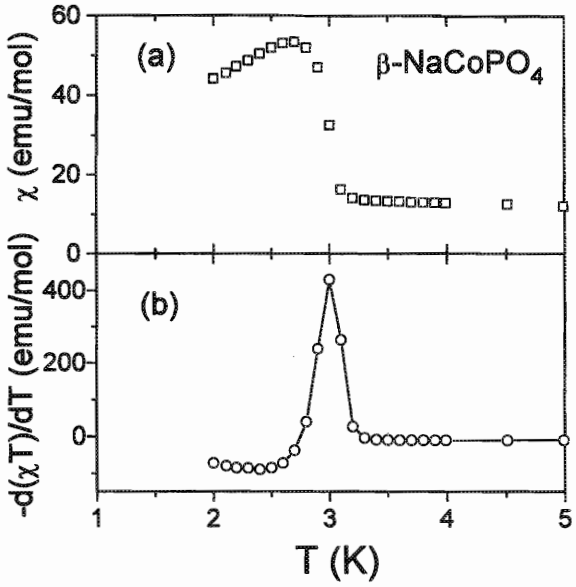
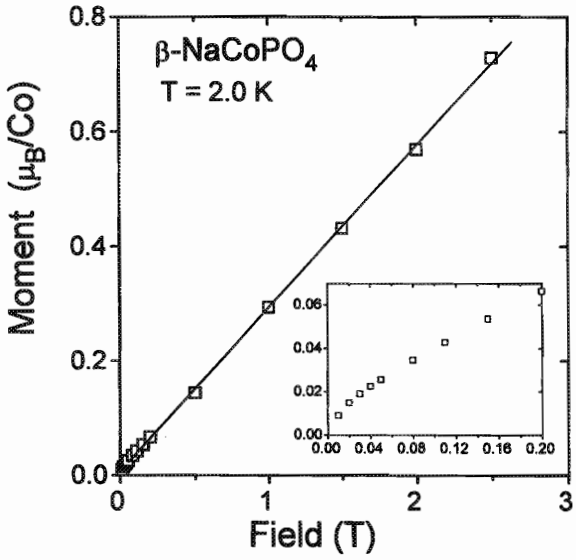


Fig. 5. Field dependence of magnetization at 2.0 K. The continuous line shows the linear behavior. Inset shows the same data below 0.2 T on an expanded scale.



the paramagnetic Curie temperature, θ_p, of $-16.4(2)$ K indicates the presence of anti-ferromagnetic exchange interactions among the Co^{2+} ions. χ as a function of temperature in Fig. 4*a* registers a sharp rise below about 3.2 K indicating a magnetic transition. A very sharp peak in $-d(\chi T)/dT$ vs. T provides a more accurate ordering-temperature of T_c = 3.0(1) K. The low ordering-temperature of 3.0 K compared with a negative θ_p of 16.6 K demonstrates that the spins are highly frustrated. Also note that in Fig. 3 the inverse susceptibility deviates from linearity in T only below ~5.0 K even though the θ_p is -16.6 K. This type of behavior is commonly observed in geometrically frustrated magnets [1]. Magnetization as a function of applied field at 2.0 K is shown in Fig. 5. The linear increase of the magnetization above 0.05 T and the absence of saturation behavior up to 2.5 T imply an anti-ferromagnetic-like ordering. However, the magnetization data at low applied fields, as shown in the inset of Fig. 5, indicate a small amount of ferromagnetic component in the ordered state that appears to be responsible for the steep increase in χ at the ordering temperature.

To understand the magnetic structure in the ordered state, neutron diffraction studies were performed above and below T_c and the results are presented in the next section.

3.2. Powder neutron-diffraction data

Neutron-diffraction measurements were carried out on a powder sample of β-$NaCoPO_4$ between 1.6 and 16 K and the results are shown in Figs. 6*a* and 6*b*. The crystal structure was refined by the Rietveld method using the FULLPROF program. The refinement parameters obtained are collected in Table 1. There is an impurity peak in the powder neutron-diffraction patterns at $2\theta = 31.4°$ that could not be detected in the powder X-ray diffraction data. Efforts to identify this impurity peak have not been successful. Examination of the data at 1.6 K (Fig. 6*b*) indicates the enhancement of four reflections that can be indexed as a-(101), b-(102), c-(103),

Fig. 6. Powder neutron-diffraction patterns at 16 and 1.6 K.

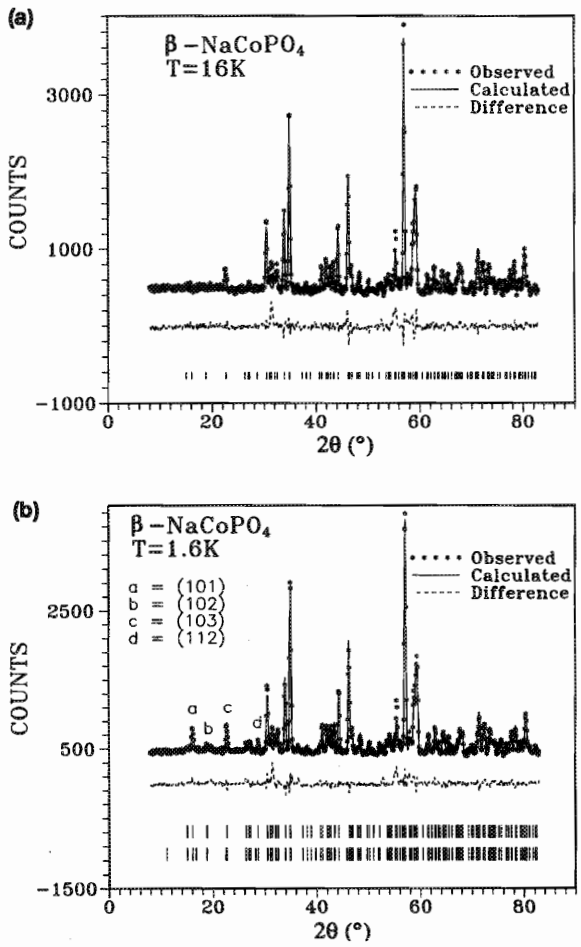
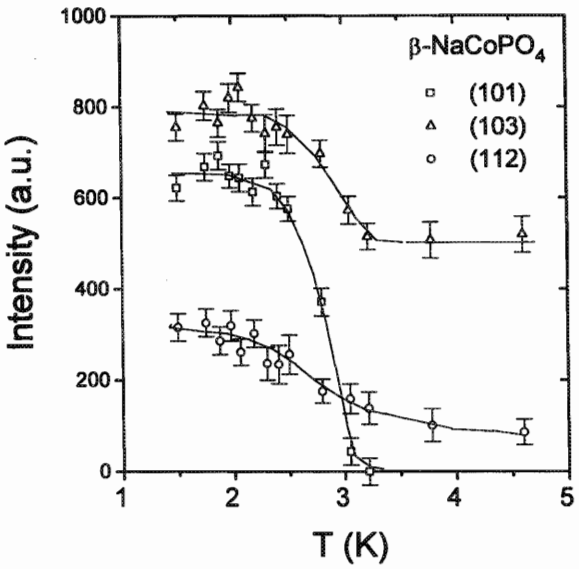


Table 1. Cell parameters, overall temperature factors, and Rietveld refinement agreement indices for $NaCoPO_4$ at 16 and 1.6 K.

	16 K	1.6 K
a(Å)	10.167(5)	10.169(5)
c(Å)	23.785(6)	23.795(5)
Volume (Å^3)	2128.796	2130.948
$B_{overall}$(Å^2)	0.1(4)	−0.3(3)
R_{wp}	7.6	6.9
R_{exp}	3.8	2.7
χ^2	4.0	6.3
Bragg R factor	10.7	9.6
R-F factor	8.3	7.4
Magnetic R factor	—	24.2
Moment (μ_B/Co)	—	1.8(1)

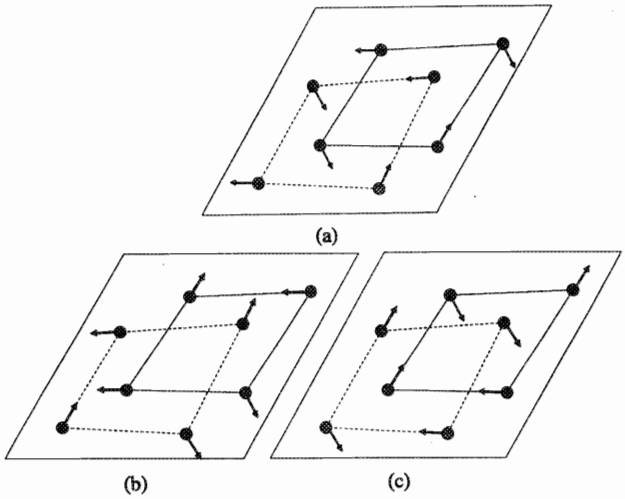
Fig. 7. Temperature dependence of the intensities of magnetic Bragg peaks. The continuous lines are to guide the eye.



and d-(112). The temperature evolution of the intensities of three of these peaks is displayed in Fig. 7. The increase in the intensity of these Bragg reflections below about 3.2 K is consistent with the magnetic data and suggests that they are associated with long-range magnetic ordering.

A variety of spin configurations (FM ordering in 2D and 3D, AFM ordering of alternating layers in 2D and 3D) have been tried to refine the magnetic Bragg reflections. These models not only gave high magnetic R factors (>55) but also did not contribute significant intensity to the (101) reflection. A model based on the 120° structure within the distorted ab planes is considered to be the most probable one on the basis of a much smaller magnetic R factor, Table 1. This magnetic spin structure is schematically depicted in Figs. 8a–8c representing three successive subcells. It can be seen that the corresponding spins from one subcell to the next rotate clock wise by 120°. An anti-clockwise rotation

Fig. 8. (a), (b), and (c) portray three successive subcells within the unit cell in order of ascent along c. The direction of the Co^{2+} spin at each site is indicated.



also produces the same refinement results. The 120° rotation of the corresponding spins from one subcell to the next one seems to arise owing to the helical chains of alternating, corner-sharing CoO_4 and PO_4 tetrahedra as mentioned in the introduction. Also because of this helical nature the superexchange paths with in and out of the pseudoplanes are similar (i.e., Co-O-O-Co). Another model, applicable to $CsMnBr_3$ [5,6], in which the in-plane spins with the 120° structure are coupled anti ferromagnetically with the nearest neigbors in the c-direction is found to be not satisfactory as it does not contribute any intensity to the (101) reflection. However, the magnetic structure shown in Fig. 8 may not be unique. The magnetic moment of Co^{2+}, $S = 3/2$, $g > 2.0$, has been obtained from the refinement at 1.6 K as 1.8(1) μ_B/Co^{2+}, which is significantly smaller than the expected value of 3.3–3.6 μ_B/Co^{2+}. This reduction in the moment is also consistent with the frustrated magnetic ordering as in the case of VBr_2 [7]. The Bragg intensities, obtained for VBr_2 with a 120° magnetic structure, are consistent with an average moment of 83% of the expected value for V^{2+}, also $S = 3/2$.

4. Summary and conclusions

Magnetic and neutron-diffraction studies on a powder specimen of β-$NaCoPO_4$ belonging to the family of stuffed tridymites have been reported. The observed Curie–Weiss behavior of the susceptibility data over a wide temperature range 5–300 K and the low magnetic-transition temperature of 3.0 K compared with the θ_p of −16.6 K imply magnetic frustration in β-$NaCoPO_4$ that was attributed to the nn anti ferromagnetic interactions among Co^{2+} spins on sets of triangular layers. The evolution of the magnetic Bragg peaks was observed as the sample was cooled below the T_c. An analysis of the neutron diffraction data at 1.6 K with the help of Rietveld refinement proposes a 120° magnetic structure of Co^{2+} spins in pseudo planes roughly normal to the c-axis.

Acknowledgments

We thank Rob Hammond for providing us with the sample,

Ronald Donaberger for assistance in obtaining the neutron data at DUALSPEC and C.V. Stager for use of the SQUID magnetometer. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

References

1. A.P. Ramirez. Annu. Rev. Mater. Sci. **24**, 453 (1994).
2. B.D. Gaulin. Magnetic systems with competing interactions (Frustrated spin systems). *Edited by* H.T. Diep. World Scientific, Singapore. 1994. pp. 286–326.
3. D.H. Lee, J.D. Joannopoulos, J.W. Negele, and D.P. Landau. Phys. Rev. Lett. **52**, 443 (1984).
4. J. Rodriguez-Carvajal. FULLPROF: A program for Rietveld refinement and pattern matching analysis. Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the International Union of Crystallography, Toulouse. 1990. p. 127.
5. M. Eibshutz, R.C. Sherwood, F.S.L. Hsu, and D.E. Cox. *In* Magnetism and magnetic materials (Denver, 1972). Proc. 18th Annual Conf. on Magnetism and Magnetic Materials, AIP Conf. Proc. No. 10. *Edited by* C.D. Graham Jr. and J.J. Rhyne. AIP, New York. 1973. p. 684.
6. B.D. Gaulin, T.E. Mason, and M.F. Collins. Phys. Rev. Lett. **62**, 1380 (1989).
7. H. Kadowaki, K. Ubukoshi, and K. Hirakawa. J. Phys. Soc. Jpn. **54**, 363 (1985).