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The Magnetic Structure of $KNiAsO_4$: A Two-Dimensional Honeycomb Lattice

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IN HONOR OF C. N. R. RAO ON HIS 60TH BIRTHDAY

The magnetic structure of $KNiAsO_4$, an example of a two-dimensional honeycomb lattice, has been determined from neutron powder diffraction data collected at 1.5 and 30 K. The crystallographic unit cell ($R3$) is doubled along a ($k = \frac{1}{2}, 0, 0$) and the three observed magnetic reflections are indexed as 101, −102, 104 in the extended cell. The magnetic structure can be described as zig–zag antiferromagnetic chains parallel to a such that each moment has one nearest neighbor parallel and two antiparallel. This contrasts with the structurally related $BaNi_2(AsO_4)_2$, in which each magnetic ion has one antiparallel and two parallel neighbors. © 1994 Academic Press, Inc.

1. INTRODUCTION

Inorganic compounds whose structures contain well-developed layers of atoms have been intensively studied, both because their physical properties are highly anisotropic and because the layers may be separated chemically and become the site of intralamellar chemistry. Most of the compounds of interest for the latter reason, e.g., micas, are of no interest for the former, and indeed vice versa.

Potassium nickel arsenate, $KNiAsO_4$, is unusual in being of interest from both of these points of view. First, it is a close synthetic analogue of the silicate micas, containing octahedrally coordinated Ni and tetrahedral As in place of octahedral Mg, Al, and tetrahedral Si, and as such it undergoes a very similar series of intercalation reactions with water and organic amines (1, 2). Second, because of its pronounced layer structure, it is expected to be a useful model of a two-dimensional magnetic system, especially since the disposition of the magnetic Ni ions is a rare example of a honeycomb lattice. Earlier, we determined the crystal structure of $KNiAsO_4$ at 30 K by neutron powder diffraction (3), and showed by bulk susceptibility measurements that it underwent a transition at 19 K to a long-range ordered antiferromagnetic state (4). The structure of $KNiAsO_4$ is also related to the family of hexagonal layer compounds $BaNi_2(XO_4)_2$ (X = P,As,V) whose magnetostructural correlations were examined by Regnault (5) as examples of a honeycomb structure, a lattice type capable of sustaining an unusual variety of magnetic structures. In the present paper we report a study of the magnetic structure of $KNiAsO_4$ at 1.5 K by neutron powder diffraction and compare it with those of $BaNi_2(XO_4)_2$.

2. EXPERIMENTAL

Diffraction profiles of $KNiAsO_4$ were obtained at 1.5 and 30 K between scattering angles 2θ of 0° and 160° on the D2B diffractometer at the Institut Laue–Langevin, Grenoble, using a neutron wavelength of 1.5963 Å. The instrument was operated in "high intensity" mode, and the profile was accumulated over 5 hr. Comparing the profiles observed at 30 and 1.5 K between scattering angles of 8° and 30°, the three extra reflections observed may be indexed on a cell in which either the a_0 or b_0 axes or both are doubled (Table 1). As a result of the trigonal symmetry it is not possible to distinguish between these possibilities by indexing alone. Scans of 1 hr duration at 10 further temperatures between 1.6 and 21 K confirmed that the three peaks were magnetic in origin and identified T_N as 19.2(4) K, in agreement with susceptibility data (4).

3. STRUCTURE REFINEMENT

The crystal structure was first refined by the Rietveld powder profile refinement method based on the crystal structure obtained from an earlier experiment, data beyond $2\theta = 60°$ being excluded. The unit cell constants obtained were as follows (Å): a_0 4.9928(1), c_0 28.6709(7) (30 K); a_0 4.9768(8), c_0 28.5530(5) (1.5 K).

Initially, simple antiferromagnetic structures with collinear spin arrangements having the a_0 and/or b_0 axes

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TABLE 1

$KNiAsO_4$ Magnetic Reflections

Position (2θ)	I_{mag}	hkl (a_0)	hkl ($2a_0$)
11.34°	442	½01	101
12.66°	323	−½02	−102
16.93°	199	½04	104

doubled were considered. As a guide, the magnetic structures of the structurally similar $BaNi_2(XO_4)_2$ (X = As,P,V) compounds were examined. Of the four possible collinear spin arrangements for a two-dimensional honeycomb lattice (5), three are antiferromagnetic; two of these have been observed for $BaNi_2(AsO_4)_2$ and $BaNi_2(PO_4)_2$, respectively. Of the three antiferromagnetic spin structures shown in Fig. 1, (1) causes doubling of the a or b axis and (2) involves doubling of all three axes. No evidence of the latter is observed in the three magnetic reflections in Table 1, while in (3) the chemical unit cell is equivalent to the magnetic unit cell. The latter can be rejected since it would cause no extra magnetic reflections; (2) might be considered the most likely magnetic structure by analogy with $BaNi_2(AsO_4)_2$, but only (1) accounts for the observed magnetic peak intensities.

A magnetic unit cell was devised with the a_0 and b_0 axes doubled, in order to maintain the trigonal symmetry, and nine more symmetry operators were introduced to describe the unit cell with doubled a_0 and b_0 axes. Each symmetry operator had an associated magnetic rotation matrix, as indicated in Table 2. The atom positions in the second and third layers related by the rhombohedral translations $(\frac{2}{3}\,\frac{1}{3}\,\frac{1}{3})$ and $(\frac{1}{3}\,\frac{2}{3}\,\frac{2}{3})$ on the 23 symmetry positions

TABLE 2

Symmetry Operators and Respective Magnetic Rotation Matrices for a Unit Cell of $KNiAsO_4$ with Doubled a_0 and b_0 Axes

Symmetry operator			Diagonal elements of magnetic rotation matrix
x	y	z	(1 1 1)
$\bar{y}$	$x-y$	z	(1 1 1)
$\bar{x}+y$	$\bar{x}$	z	(1 1 1)
$x+\frac{1}{2}$	y	z	(−1 −1 −1)
$\bar{y}+\frac{1}{2}$	$x-y$	z	(−1 −1 −1)
$\bar{x}+y+\frac{1}{2}$	$\bar{x}$	z	(−1 −1 −1)
x	$y+\frac{1}{2}$	z	(1 1 1)
$\bar{y}$	$x-y+\frac{1}{2}$	z	(1 1 1)
$\bar{x}+y$	$\bar{x}+\frac{1}{2}$	z	(1 1 1)
$x+\frac{1}{2}$	$y+\frac{1}{2}$	z	(−1 −1 −1)
$\bar{y}+\frac{1}{2}$	$x-y+\frac{1}{2}$	z	(−1 −1 −1)
$\bar{x}+y+\frac{1}{2}$	$\bar{x}+\frac{1}{2}$	z	(−1 −1 −1)

shown in Table 2 have the same magnetic rotation matrix as the equivalent atom in the first layer.

A magnetic moment of 2 B.M. was placed on the Ni^{2+} in the x-direction, using the free ion form factor for Ni^{2+} (6), and the refinement converged with a magnetic R-factor, R_{mag} = 47.66% (overall R-factors: R_p = 11.33%,

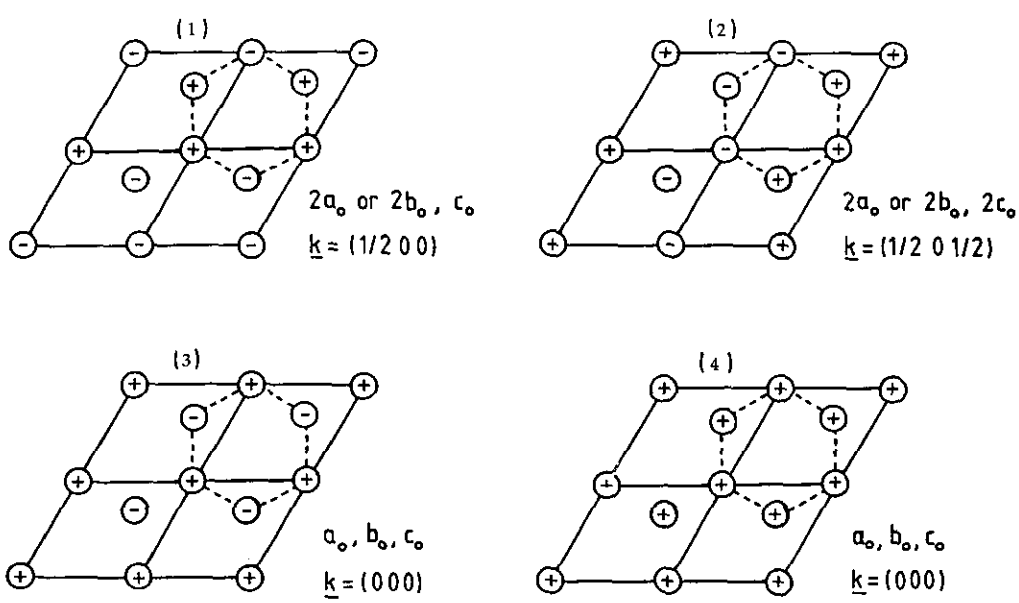

FIG. 1. Collinear spin structures in a two-dimensional honeycomb lattice.

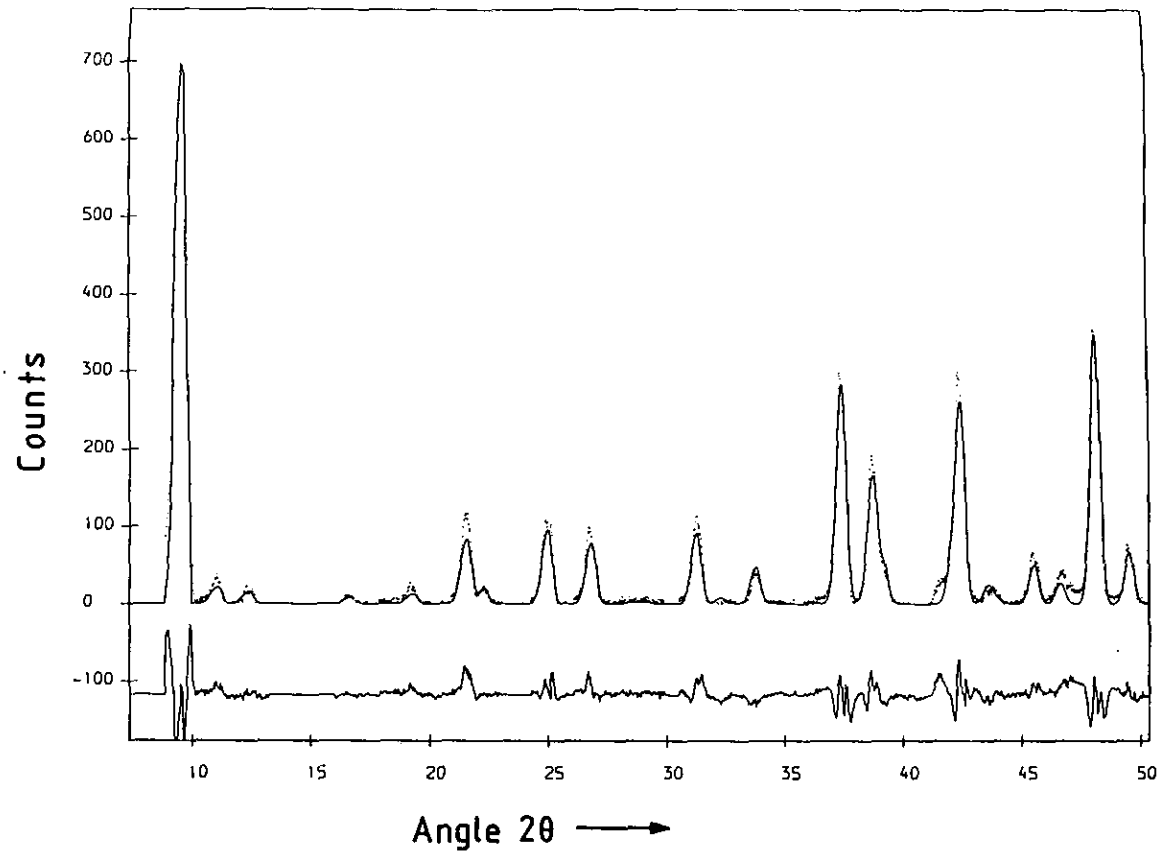

FIG. 2. Observed (dots) and calculated (full line) powder neutron diffraction profiles of $KNiAsO_4$ at 1.5 K.

R_{wp} = 19.66%), accounting for the observed magnetic reflections with $\mathbf{k}_x = 1.72$ (7). When $\mathbf{k}_x$ and $\mathbf{k}_y$ were refined, $\mathbf{k}_y$ was found to be insignificant compared to its standard deviation and was therefore discarded. The component of the moment in the z-direction could not be refined, either alone or with $\mathbf{k}_x$, so it was concluded that the moments lie in the a–b plane. The best fit obtained is shown in Fig. 2.

4. DISCUSSION

The low temperature neutron diffraction study of $KNiAsO_4$ revealed the magnetic structure (1) shown in Fig. 1. Although this is the only structure that accounts for the observed magnetic peaks, the R-factor is quite high, because of the small number of magnetic reflections observed. The magnetic structure consists of zig–zag antiferromagnetically arranged chains in either the a or the b direction. Each moment has one nearest neighbor parallel and two antiparallel, corresponding to one ferromagnetic and two antiferromagnetic bonds, if only near neighbor interactions are considered, in contrast to $BaNi_2(AsO_4)_2$, which has zig–zag ferromagnetic chains stacked antiferromagnetically in each sheet (Fig. 1(2)). In the latter each moment has one antiparallel and two parallel nearest neighbors corresponding to two ferromagnetic bonds and one antiferromagnetic bond. The magnetic ions in $BaNi_2(PO_4)_2$ have three antiferromagnetic bonds and antiferromagnetic chains in three directions within the sheet.

The refined value of the magnetic moment (1.72(7) B.M.) is reduced from the expected value of 2 B.M. as a result of zero-point spin deviations (7). The reduction of the magnetic moment calculated from spin wave theory is roughly given by $\frac{1}{2}\,z$ (8), where z is the number of nearest neighbor magnetic ions. Hence the true magnetic moment per site is $g\mu_B(S - \frac{1}{2}\,z)$, which in the present case (for $z = 3$ and $g \sim 2$) is 1.67 B.M., within the error of the observed value. The close agreement between the two values suggests that covalency effects that might further reduce the moment are negligible. Further evidence for the latter is given by the Ni–O bond lengths in Table 3, which are very close to the sum of the Ni^{2+} and O^{2-} ionic radii (9).

Regnault (5) made an extensive study of the magnetic properties of the layered compounds $BaM_2(XO_4)_2$ (M = Ni, Co; X = As, P), considering the exchange constants in the plane out to the third nearest neighbors (i.e., J_1, J_2, and J_3) and constructing phase diagrams for $J_1 > 0$ and $J_1 < 0$ as a function of $J_3/|J_1|$ versus $J_2/|J_1|$. The interlayer exchange constant J was treated as a perturba-

TABLE 3

Interlayer Bond Lengths (Å) and Bond Angles (°) in $KNiAsO_4$ and $BaNi_2(AsO_4)_2$

	$BaNi_2(AsO_4)_2$ (Ref. (5))	$KNiAsO_4$ (Ref. (3))
Ni–O(1)	2.049	2.054
Ni–O(1)	2.071	2.070
Ni–Ni	2.855	2.872
O(1)–Ni–O(1)	85.38	89.11
O(1)–Ni–O(1)	177.44	177.75
O(1)–Ni–O(1)	95.49	91.49
O(1)–Ni–O(1)	92.29	90.42
Ni–O(1)–Ni	87.71	88.30

tion and the anisotropy of the M^{2+} ions was neglected. Figure 3 shows a simplified version of the phase diagram for $J_1 < 0$.

The magnetic structure found in $KNiAsO_4$ is predicted by this phase diagram but has not been observed up till now. This is of interest since all three possible collinear structures are observed for different nickel arsenate/phosphate analogues. Whilst Regnault derived exchange constants for $BaNi_2(XO_4)_2$ (X = As and P) from spin wave measurements, no values are available at present for $KNiAsO_4$.

In $BaNi_2(PO_4)_2$ the nearest neighbor interaction is antiferromagnetic. However, the nearest neighbor interaction for a 90° Ni–O–Ni bridge would be expected to be ferromagnetic (10). In $BaNi_2(AsO_4)_2$ the magnetic structure consists of ferromagnetic chains because of the ferromagnetic nearest neighbor interaction (J_1 = 40 K). It might be thought that the latter is occasioned by the Ni–O–Ni angle of 87.71°, were it not for the fact that a high temperature series expansion fit to the bulk susceptibility of $KNiAsO_4$ (for which the 1 Ni–O–Ni angle is 88.30°) shows clearly that J_1 is antiferromagnetic.

It is noteworthy that $KNiAsO_4$ does not adopt the same magnetic structure as $BaNi_2(AsO_4)_2$ despite the fact that the $[NiAsO_4]^-$ sheets are structurally very similar in both compounds, the only substantial difference between the two structures being the interlayer separation: 9.508 Å for $KNiAsO_4$ and 7.81 Å for $BaNi_2(AsO_4)_2$. From the phase diagram (Fig. 3) a change in magnetic structure from (2) to (1) requires that the sign of $J_3/|J_1|$ change from negative to positive. That such a change should take place is surprising in view of the strong structural similarities between the two compounds. Table 3 compares bond angles and lengths in the two compounds.

Clearly, the second and third nearest neighbor exchange interactions are extremely sensitive to small changes in distance between the magnetic ions, as well as to their chemical environments and the precise bond angles. It is also possible that the interlayer interaction has a more important influence on the magnetic structures than has been recognized hitherto. The complexity of the magnetostructural correlations suggests that the series $MNi_n(XO_4)_y$ (for M = K and X = As, n = 1 and y = 1 or M = Ba, X = As or P and n = 2, y = 2) are far from simple magnetic model systems.

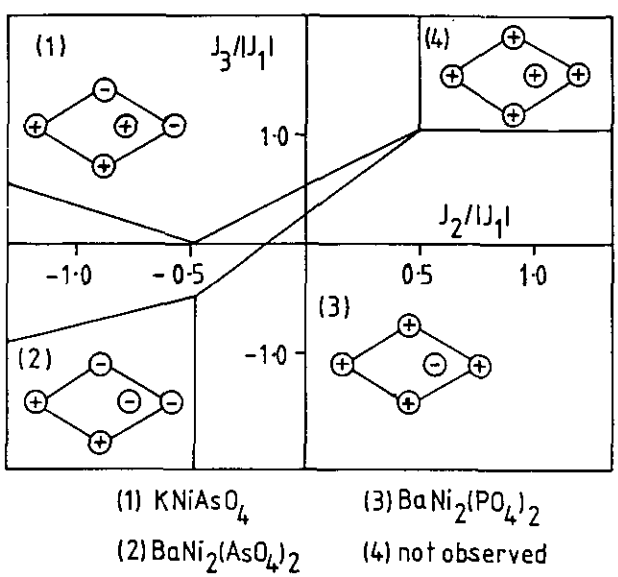

FIG. 3. Phase diagram indicating the stability of the four collinear spin structures in a two-dimensional honeycomb lattice shown in Fig. 1 in terms of the exchange constants J_1, J_2, J_3 (for $J_1 < 0$) (5).

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REFERENCES

1. K. Beneke and G. Lagely, *Clay Mineral.* **17,** 175 (1982).
2. A. M. Buckley, S. T. Bramwell, D. Visser, and P. Day, *J. Solid State Chem.* **69,** 240 (1987) and *Phys. Chem. Miner.* **15,** 446 (1988).
3. A. M. Buckley, S. T. Bramwell, P. Day, and W. T. A. Harrison, *Z. Naturforsch. B* **43,** 1053 (1988).
4. S. T. Bramwell, A. M. Buckley, P. Day, and D. Visser, *Phys. Chem. Miner.* **15,** 465 (1988).
5. L. P. Regnault. Thèse d'Etat, Grenoble (1981).
6. A. J. Freeman and R. E. Watson, *Acta Crystallogr.* **14,** 231 (1961).
7. P. W. Anderson, *Phys. Rev.* **86,** 694 (1982).
8. J. de Jongh and A. Miedema, *Adv. Phys.* **24,** 1 (1974).
9. P. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B.* **25,** 925 (1969) and *Acta Crystallogr. Sect. B* **26,** 1046 (1970).
10. J. B. Goodenough, "Magnetism and the Chemical Bond." Interscience, New York (1963).