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CRYSTAL STRUCTURE AND MAGNETIC ORDERING IN MAGNETOELECTRIC $KNiPO_4$ INVESTIGATED BY MEANS OF X-RAY AND NEUTRON DIFFRACTION

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The crystal structure of magnetoelectric $KNiPO_4$ was refined by single crystal X-ray diffraction methods at room temperature confirming orthorhombic space group $Pna2_1$. Powder neutron diffraction investigations showed that the room temperature structure is preserved down to 30 K. Consistent with magnetic susceptibility measurements, long-range antiferromagnetic ordering according to $\mathbf{K} = 0$ and Shubnikov space group $Pna2_1$ is established by neutron diffraction at temperatures below $T_N = (25.5 \pm 0.5)$ K. The ordered magnetic moments of $(3.00 \pm 0.04)\ \mu_B$, oriented along [1, 0, 0], indicate large orbital contributions to the magnetic moment of Ni^{2+}. DTA studies in the temperature range from 100–1000°C, showed two phase transitions, at 486.5°C and at 581.3°C.

Keywords: magnetic ordering, crystal structure, $KNiPO_4$, phase transitions.

1. INTRODUCTION

Compounds such as $LiMPO_4$ (where, $M = Fe^{2+}$, Co^{2+}, Mn^{2+}, Ni^{2+}) with orthorhombic symmetry corresponding to space group Pnma are known to be magnetoelectric.[1,2] First X-ray structure investigations and measurements of bulk magnetic properties in the temperature range from 1.8 to 900 K on the related compound $KNiPO_4$, were reported in References 3–5. The chemical structure of this compound, characterised by chains of five vertex NiO_5 polyhedra, was described to belong either to space group Pnma[4] or to $Pna2_1$.[5] The magnetic susceptibility corresponds to Ni^{2+} ions, but the effective magnetic moment, determined from magnetic susceptibility measurements, shows major orbital contributions. The negative value of the paramagnetic Curie-Weiss temperature $\theta_p = -50$ K indicates antiferromagnetic interactions between the Ni ions.

In order to obtain information on the magnetically ordered phase and to study magnetoelectricity in more detail, new single crystal X-ray measurements at room temperature and low temperature powder neutron diffraction investigations were started on $KNiPO_4$, together with measurements of bulk anisotropic magnetic and optical properties at low temperature.[6] Here we shall report on X-ray and neutron diffraction results and DTA studies on $KNiPO_4$.

2. EXPERIMENTAL

Single crystals of $KNiPO_4$ were synthesized in a KCl flux. Starting materials were anhydrous $NiCl_2$ and K_3PO_4 with KCl as solvent. A mixture of these three compounds (1:1:1 molar ratio) was placed into a sealed platinum crucible, heated to 1050°C and soaked for 4 h. Then cooling was realised in two stages, first at 0.5°C/h, till 900°C, and thereafter at 1.0°C/h down to 750°C. The flux was dissolved in hot water to separate the red crystals of $KNiPO_4$. The size of the largest crystal obtained was $1.2 \times 1.2 \times 2.0$ mm^3. A sample of 6.225 mg of these crystals was used in the DTA studies which were also performed with a DSC-Mettler apparatus.

The structure of $KNiPO_4$ was investigated at 20°C on a single crystal of dimensions $0.2 \times 0.16 \times 0.32$ mm^3. The intensity of 2937 reflections was measured by means of an automatic Enraf-Nonius CAD4 X-ray diffractometer with Cu radiation (λ = 1.54181 Å). The cell parameters were determined from 25 reflections with $18° < \theta < 30°$ and refined by diffractometer techniques and least-squares methods.

For neutron diffraction experiments, a 9 gr. powder sample was used. During the measurements the specimen was enclosed under He gas atmosphere into a cylindrical V container of 12.5 mm diameter and approximately 5 cm length. According to neutron diffraction, the sample consisted only of the $KNiPO_4$ phase. The neutron diffraction measurements were performed at the reactor Saphir of Paul Scherrer Institute, Würenlingen on the multidetector powder diffractometer DMC[7] in the high-intensity mode, using neutron wavelength λ = 1.7037 Å and a closed-cycle He refrigerator for cooling of the sample. In the paramagnetic state of $KNiPO_4$ the absorption corrected profile intensities were analysed by means of a modified Wiles-Young program,[8] using neutron scattering lengths published by Sears.[9] Magnetic neutron intensities were calculated with a standard Rietveld program,[10] based on the $\langle j_0 \rangle$ approximation of the Ni^{2+} neutron magnetic form factor.[11]

3. DTA STUDIES

Two phase transitions were found in the temperature range of 100–1000°C. A first transition occurs at 486.5°C and a second one at 581.3°C. The temperature of the second transition has the particularity that it shows almost no hysteresis between heating and cooling DSC experiments. This was observed for different temperature change rates (1°C/h, 4°C/h and 10°C/h). The two phase transitions were also followed by polarised light microscopy. During the first transition, a coexistence of two phases is seen, hence, it is a first order type phase transition; its phase transition enthalpy, determined from the DSC experiment, is 7.5 J/gr. The second transition is more difficult to see under optical observation, one has to examine a very thin plate (~20 μm). The transition appears as a slight change of colour, under normal light, from clear-violet to dark-violet, with crossed polarizers; no clear interface is visible. Therefore, and considering also the absence of hystersis, the transition at 581.3°C is second order-like, however, a latent heat of 6.2 J/gr. is measured from the DSC experiment. The changes in the crystal structure of $KNiPO_4$ upon the transition to these high temperature phases are still unknown.

4. CRYSTAL STRUCTURE OF $KNiPO_4$

As crystals of $KNiPO_4$ show a pyroelectric effect,[6] the noncentrosymmetric space group $Pna2_11'$ was used for the structure refinements. Absorption corrections were applied considering the crystal shape. The 2937 reflections measured were packed into 415 independent Friedel pairs to be used in the refinement. Calculations were made with the Xtal 3.2 program.[12] The model found by V. I. Lyutin *et al.*[5] was used to make the first refinements, subsequent anisotropic refinements converged to a final $R = 0.023$ ($Rw = 0.025$). The results, confirming with considerably improved accuracy Reference 5 are summarized in Tables Ia and Ib. The good agreement of observed and calculated neutron intensities of paramagnetic $KNiPO_4$ at 30 K, which is illustrated in Figure 2, shows that the room temperature structure model, with space group $Pna2_11'$, holds also at 30 K. The lattice constants given in Table Ia indicate anisotropic thermal contraction, i.e. mainly along the a-axis. A drawing of the structure is shown on Figure 1.

5. MAGNETIC Ni LONG-RANGE ORDER IN $KNiPO_4$

SQUID magnetisation measurements performed on $KNiPO_4$ single crystals (field and zero field cooled) suggest magnetic ordering at temperatures below approximately 25 K. Therefore neutron diffraction measurements were performed in the temperature range from 9 to 30 K. Figures 2 and 3 illustrate the increase of the intensities due to long-range antiferromagnetic ordering of Ni^{2+} ions, corresponding to propagation vector $\mathbf{K} = 0$, i.e. a magnetic unit cell being equal to the chemical cell. The temperature dependence of the dominant magnetic intensity shown in Figure 4 indicates an ordering temperature $T_N = (25.5 \pm 0.5)$ K, in excellent agreement with the bulk magnetic measurements.[3,6] (A certain hysteresis may be possible on the basis of the present neutron diffraction data.) Best agreement between observed and calculated magnetic neutron intensities (see Figure 3, agreement value concerning integrated magnetic intensities $R_{IM} = 22\% \approx$ statistically expected value R_{exp}, goodness of fit $\chi^2 = 1.7$) was achieved with an approximately collinear antiferromagnetic arrangement of Ni moments according to magnetic space group $Pna2_1$ (see Table II and Figure 5) with main component ($\mu_x = 2.99(4)\ \mu_B$; the other components are hardly significant) parallel to the *a*-axis. From the point of view of Shubnikov groups[13,14] this is the only antiferromagnetic configuration with full symmetry. The other possible Shubnikov groups $Pn'a2'_1$, $Pna'2'_1$, $Pn'a'2_1$ would have ferromagnetic *y*, *x*, or *z* components of the magnetic moments, respectively, and would not allow the experimentally determined antiferromagnetic *x* component configuration summarized in Table II. The [1, 0, 0] orientation of the antiferromagnetic moments is also consistent with almost no change in magnetisation along this direction between field and zero field experiments.[6] The ordered magnetic saturation moment at 9 K amounts to $\mu_{Ni} = (3.00 \pm 0.04)\ \mu_B$. This value considerably exceeds the spin only value of ($g = 2 + \delta$). ($S = 1$) μ_B of Ni^{2+} with $3d^8$ electron configuration which implies remarkably large orbital contributions to the ordered magnetic moment. The antiferromagnetic configurations of $KNiPO_4$ found by neutron diffraction consists of Ni chains parallel

TABLE Ia

Positional parameters and isotropic temperature factors U*j* of $KNiPO_4$, determined by X-ray (293 K, single crystal, $R = 0.023$, $R_w = 0.025$) and neutron diffraction (30 K, powder), second line; * without wavelength uncertainty. ** fixed parameter. Agreement values; $R_{wp} = 2.3\%$, $R_{exp} = 1.9\%$, $R_I = 2.0\%$, goodness of fit $\chi^2 = 4.3$. Space group $Pna2_1$, lattice parameters

Temp.	a [Å]	b [Å]	c [Å]
293 K	8.6333(5)	9.2565(5)	4.9064(9)
30 K	8.6071(3)	9.2501(3)	4.8992(2)*

Atom	x/a	y/b	z/c	U_{iso} [Å^2]
NI	0.15444(6)	0.04316(5)	0.9959**	0.0145(3)
	0.1549(2)	0.0423(1)	0.9959**	0.0005(4)
K	-0.00088(7)	0.31630(6)	0.5205(3)	0.0213(3)
	0.0000(5)	0.3143(4)	0.5220(9)	0.0035(10)
P	0.29081(9)	0.3743(1)	0.0602(4)	0.0131(4)
	0.2900(3)	0.3746(3)	0.0663(6)	0.0005(8)
O(1)	0.6836(3)	0.0185(3)	0.2037(9)	0.0196(8)
	0.6821(3)	0.0179(2)	0.2067(5)	0.0003(3)
O(2)	0.7867(3)	0.1114(3)	0.7499(8)	0.021(1)
	0.7879(3)	0.1143(2)	0.7523(5)	0.0003
O(3)	0.9525(3)	0.0846(3)	0.1822(7)	0.0161(8)
	0.9513(3)	0.0845(3)	0.1874(6)	0.0003
O(4)	0.2538(3)	0.2191(3)	0.1412(8)	0.0193(8)
	0.2547(3)	0.2190(3)	0.1460(6)	0.0003

TABLE Ib

Anisotropic Displacement Parameters [Å^2] at 293 K, from X-ray results

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
NI	0.0124(4)	0.0113(4)	0.0198(5)	-0.0001(2)	-0.0002(4)	-0.0010(4)
K	0.0173(4)	0.0188(4)	0.0278(7)	-0.0025(2)	0.0012(6)	-0.0031(5)
P	0.0112(4)	0.0107(5)	0.0174(9)	-0.0018(3)	-0.0009(4)	-0.0006(5)
O(1)	0.018(1)	0.019(1)	0.022(2)	-0.002(1)	-0.000(2)	0.003(2)
O(2)	0.018(1)	0.018(1)	0.026(3)	0.005(1)	-0.002(2)	-0.001(2)
O(3)	0.012(1)	0.019(1)	0.017(2)	0.0044(9)	-0.001(1)	0.000(2)
O(4)	0.025(1)	0.013(1)	0.020(2)	-0.006(1)	-0.002(2)	0.001(2)

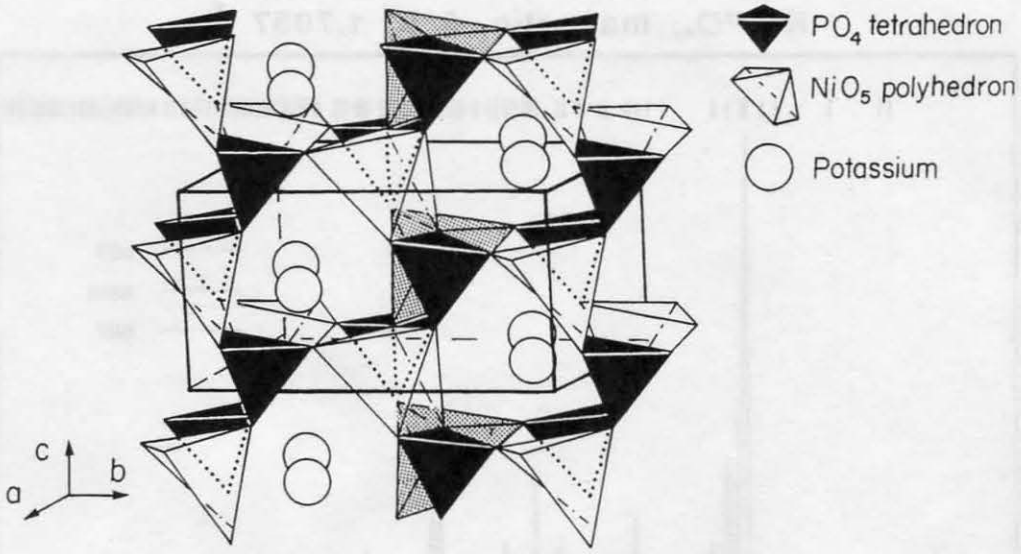

FIGURE 1 Chemical structure of $KNiPO_4$ at 293 K.

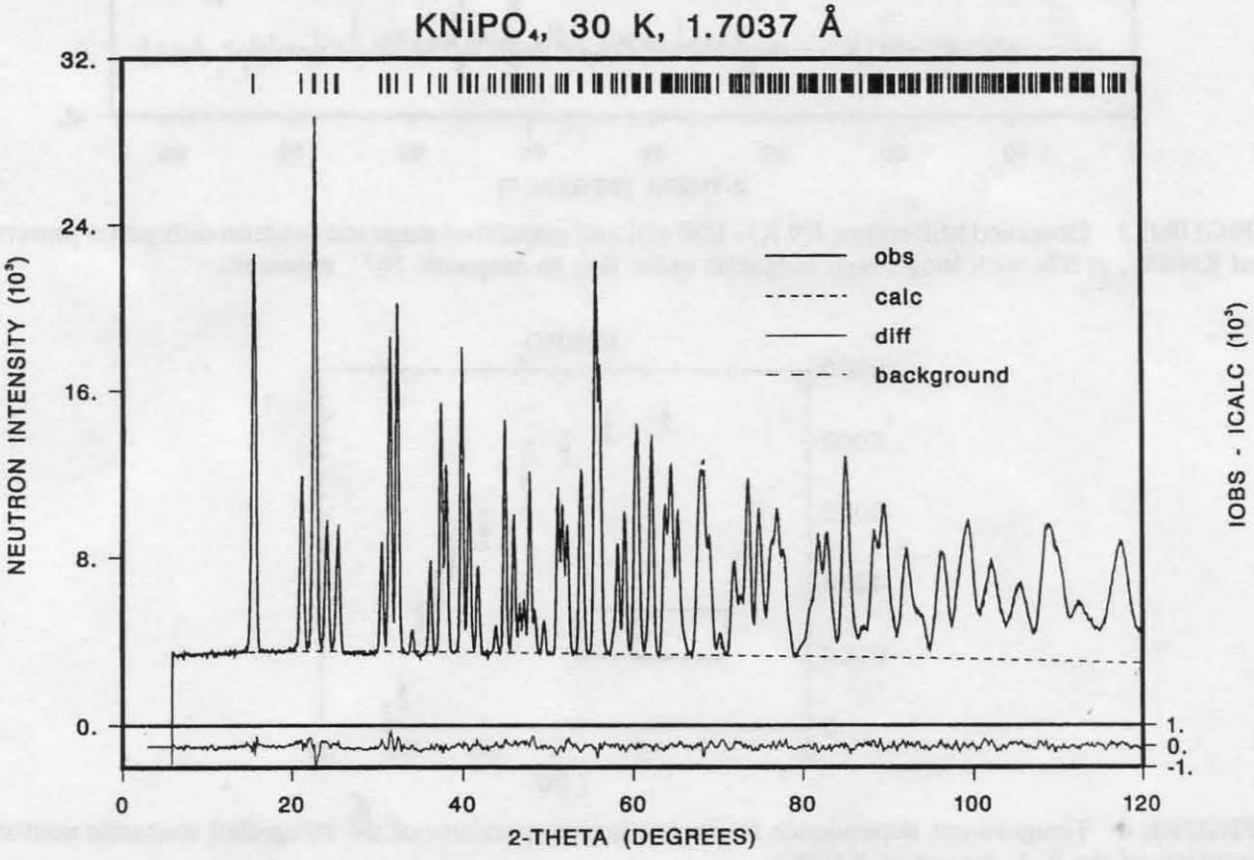

FIGURE 2 Observed, calculated and difference neutron diffraction patterns of paramagnetic $KNiPO_4$ at 30 K.

to the *c*-axis. There is antiferromagnetic coupling of nearest Ni ions and ferromagnetic coupling to second and third nearest neighbouring Ni ions (see Figure 5).

6. CONCLUSIONS

The single X-ray and powder neutron diffraction results allow to obtain an excellent fit for a description of the structure and magnetic ordering in the magnetic space

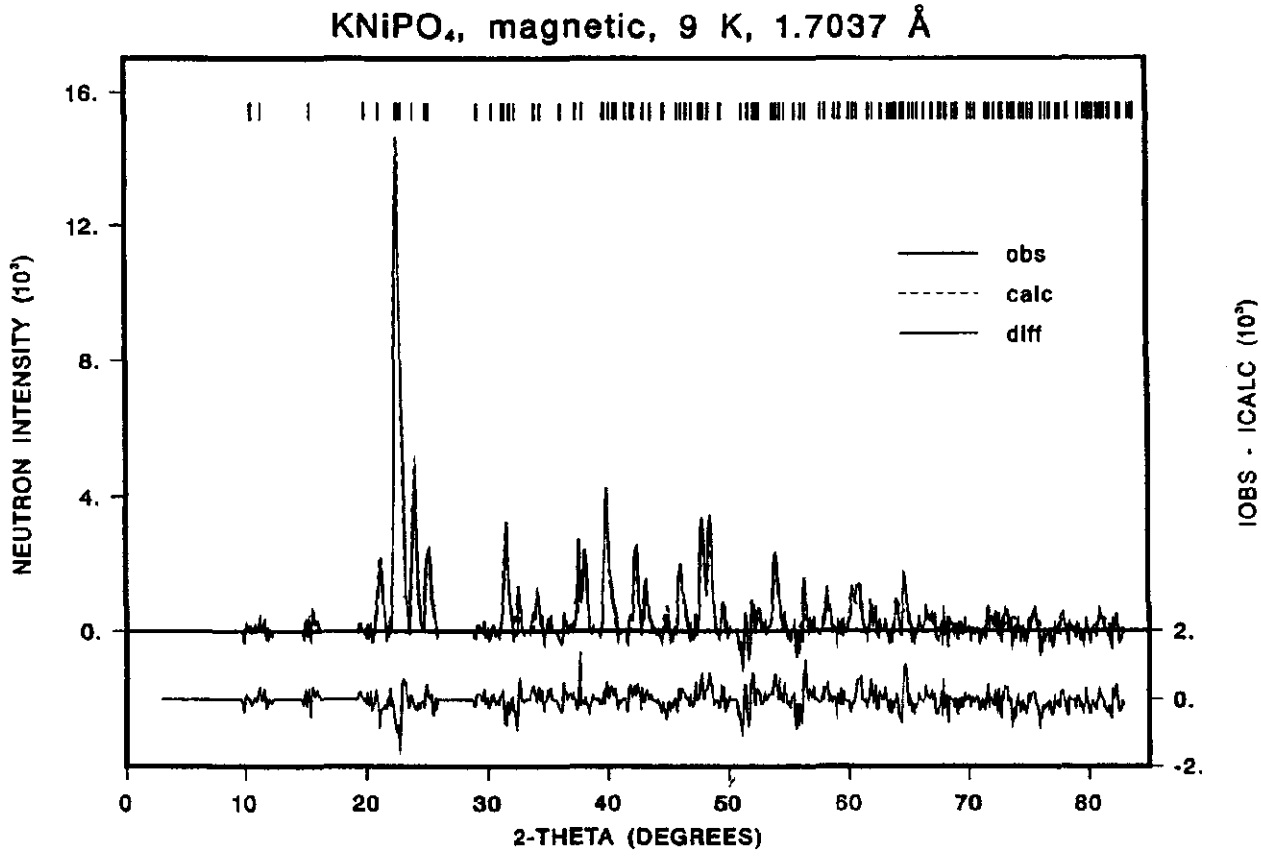

FIGURE 3 Observed [difference I(9 K)−I(30 K)] and calculated magnetic neutron diffraction patterns of $KNiPO_4$ at 9 K with long-range magnetic order due to magnetic Ni^{2+} moments.

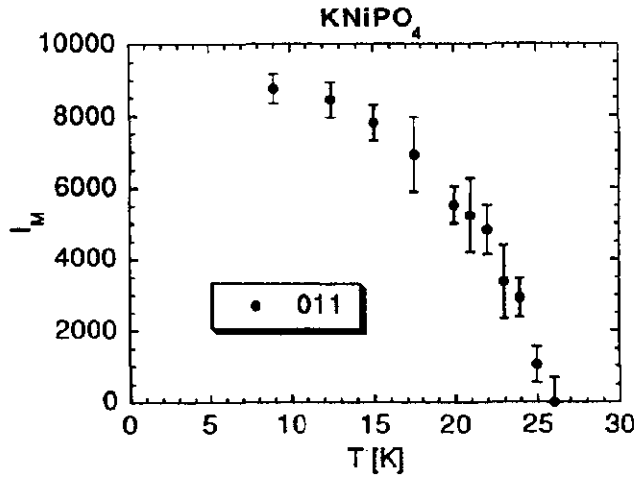

FIGURE 4 Temperature dependence for increasing temperature of the integrated magnetic neutron intensity of the 0, 1, 1 peak of $KNiPO_4$.

group $Pna2_1$ for the antiferromagnetic phase. This group only allows antiferromagnetism, but without permitting weak ferromagnetism[15] (The Shubnikov groups permitting the weak ferromagnetism for nearly uniaxial ferromagnets have been determined by Tavger[15]). In a concomitant paper[6] it is shown that the observation of the linear magnetoelectric coefficient α_{12} is consistent with group $Pna2_1$, but inconsistent with all the above mentioned orthorhombic groups permitting weak ferromagnetism. However, since a ferromagnetic moment has been measured both on powders[3] and single crystals,[6] we have to conclude that the true magnetic symmetry is lower than orthorhombic with the magnetic space group $Pna2_1$ as a very good approximation. DTA studies in the temperature range of 100–1000°C

TABLE II

Positions and magnetic moments of Ni in $KNiPO_4$ for space group $Pna2_1$

N° (Ni)	x	y	z	μ_x [μ_B]	μ_y	μ_z
1	x	y	z	+2.99(4)	+0.06(22)	-0.21(12)
2	-x	-y	1/2+z	-2.99	-0.06	-0.21
3	1/2+x	1/2-y	z	-2.99	+0.06	+0.21
4	1/2-x	1/2+y	1/2+z	+2.99	-0.06	+0.21

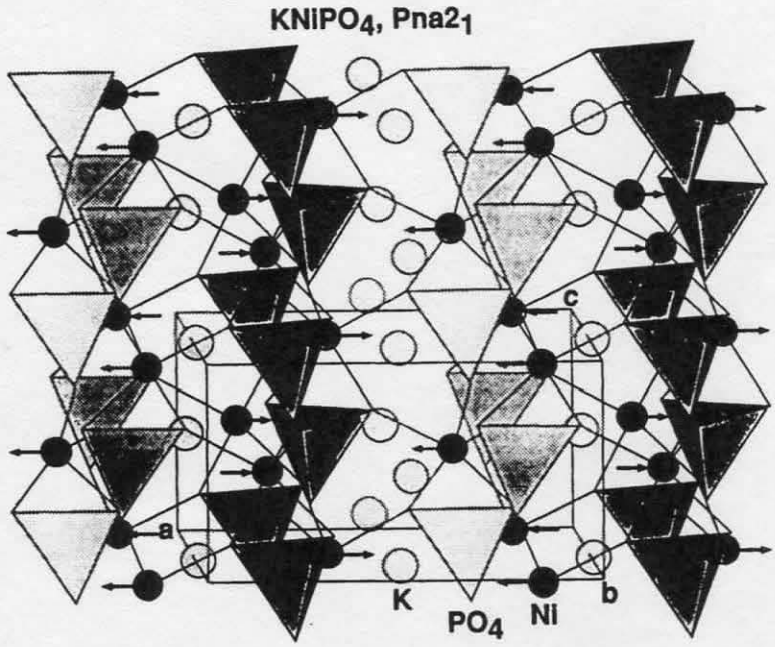

FIGURE 5 Orientation of ordered magnetic Ni moments in the chemical cell of $KNiPO_4$ at 9 K (see also Table II).

showed two additional phase transitions, at 486.5 and at 581.3°C, which require further investigations.

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