Disorder in the Crystal Structure of NaNi$_4$(PO$_4$)$_3$

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NaNi$_4$(PO$_4$)$_3$ crystallizes in the space group *Amam*, $a = 9.892(1)$, $b = 14.842(2)$, and $c = 6.3576(2)$ Å. For $Z = 4$, the calculated density is 3.862 g/cm^3 ($V = 933.3$ Å^3). The presence of several weak reflections (of the class $2k0$ and $6k0$) which should be systematically absent in this space group has been attributed to a partial disorder of one of the phosphate tetrahedra. Two half-occupied $P(2)$ sites related by a mirror normal to the a axis result in a column of phosphate tetrahedra pointing either up or down in this direction. Nickel atoms occupy five- and six-coordinated sites while sodium is six-coordinated. © 1985 Academic Press, Inc.

Introduction

Kolsi (*1*), in a study of the system Na$_3$PO$_4$–Ni$_3$(PO$_4$)$_2$, reported the existence of four compounds: Na$_4$Ni(PO$_4$)$_2$, NaNiPO$_4$, Na$_6$Ni$_9$(PO$_4$)$_8$, and Na$_3$Ni$_9$(PO$_4$)$_7$. During our studies of the preparation and crystal chemistry of complex divalent transition metal orthophosphates, we have prepared and characterized, by growth from a NaCl–NiCl$_2$ flux, another compound in this system: NaNi$_4$(PO$_4$)$_3$.

The orthophosphate AB$_4$(PO$_4$)$_3$ stoichiometry (A = alkali metal ion, B = divalent metal ion) has been observed for KFe$_4$(PO$_4$)$_3$ (*2*) as well as the isostructural Ni and Co compounds (*3*), KZn$_4$(PO$_4$)$_3$ (*4*), and NaMg$_4$(PO$_4$)$_3$ (*5*). However, as will be shown, NaNi$_4$(PO$_4$)$_3$ is structurally related to NaMg$_4$(PO$_4$)$_3$ but represents a new structure which exhibits a distinct type of disorder.

Experimental

A mixture of 0.40 Ni$_3$(PO$_4$)$_2$, 0.40 NiCl$_2$, and 0.20 NaCl (mole fractions) in a tightly crimped platinum crucible was placed in a resistance heated furnace, heated to 1100°C, and cooled at 15°C/hr to 600°C. Inspection of the crucible revealed several different phases, including NiO. Red–orange crystals were present in the form of blocks up to 1 mm on edge. These blocks were irregular, but usually were single crystals. Several crystals of this red phase were selected for energy dispersive X-ray analyis which showed that the only elements present were Ni, P, Na, and O. A crystal (0.10 × 0.07 × 0.03 cm) was selected for X-ray diffraction to determine the lattice parameters and space group.

Initial precession photographs indicated that the crystal was orthorhombic, space group *Amam*; however, a close examination of the $hk0$ plane revealed several reflections from the groups $2k0$ and $6k0$ that violated the extinctions required for the *A*-

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centered group. To determine whether these additional weak spots were due to twinning or to some type of order–disorder in the crystal structure itself, additional crystals were examined which showed the same spots with intensities that were, to the eye, identical to those found on the original photograph. If these weak reflections are considered, the space group of NaNi$_4$(PO$_4$)$_3$ becomes *Pnam* or *Pna*2$_1$.

Lattice parameters were determined in a PICK-II least-squares refinement program, using 24 reflections within the angular range $44 < 2\theta < 47°$; the reflections were automatically centered on a Picker FACS-I four-circle diffractometer using MoKα radiation ($\lambda = 0.70930$ Å). At 22°C the lattice parameters were found to be $a = 9.892(1)$, $b = 14.842(2)$, and $c = 6.3572(6)$ Å, where the figures in parentheses represent the standard deviations in the last reported figure. The calculated volume is 933.3 Å^3, giving a calculated density, with $Z = 4$, of 3.862 g cm^{-3}.

Diffraction intensities were measured using Zr-filtered MoKα radiation at a take-off angle of 2.5° with the diffractometer operating in the θ–2θ scan mode. Scans were made at 1°/min with 20-sec background counts taken at both ends of the scan. Of the 2476 independent data investigated in the angular range $2\theta < 71°$, 1376 were considered observable according to the criterion $|F_o| > 3.0\sigma_F$, where σ_F is defined as $0.2|F_o| + [C + k^2B]^{1/2}/2|F_o|$Lp; the total scan count is C, k is the ratio of scanning time to the total background time, and B is the total background count. Of these 1376, 977 were reflections that satisfied the extinction criteria for the A-centered space group. The remaining weak, but observed, reflections were forbidden in that space group. Three reflections were systematically monitored; the maximum variation in intensity observed was never greater than $\pm3\%$ over the data collection period.

Intensity data were corrected for Lorentz and polarization effects, and absorption corrections ($\mu l = 85.4$, MoKα) were made for a crystal of general shape. The maximum relative absorption correction was 24% of $|F_o|$.

A Patterson map calculated using all the observable data and using primitive orthorhombic symmetry showed that the centering peak 0, $\frac{1}{2}$, $\frac{1}{2}$ was 92% as strong as the origin peak. Since this calculation confirmed the fact that this structure was almost centered, containing only a small amount of scattering that violated the higher symmetry space group, a decision was made to solve the structure in the higher symmetry space group before attempting to incorporate the weak data. Thus, only the reflections allowed in the space group *Amam* were used in the symbolic addition program MULTAN (6) to determine heavy atom positions. These positions were found with no difficulty, and least-squares refinements along with difference Fourier calculations were used to determine the lighter atom positions. Bond length and angle calculations at this point showed that two atoms, an oxygen and a phosphorus, had locations that could not possibly be fully occupied sites since they would result in face-sharing phosphate tetrahedra. In addition, the sodium atom showed a strong desire to move away from the special position that it occupied. Although these problems were present, the residual of 11% was most encouraging. The stoichiometry was determined at this point to be NaNi$_4$(PO$_4$)$_3$.

Full-matrix least-squares refinement (7) using a $1/\sigma^2$ weighting scheme, zero-valent scattering factors (8) for Ni, Na, P, and O, isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion, yielded a residual $R = 0.075$ and a weighted residual $R_w = 0.093$. The final anisotropic refinement, based on a data : parameter ratio of 14 with 67 independently varied parameters, yielded $R =$

TABLE I

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND ANISOTROPIC THERMAL PARAMETERS FOR $NaNi_4(PO_4)_3$ [a]

Atom	$10^4 x$	$10^4 y$	$10^4 z$	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni(1)	5605(1)	1281(1)	$\frac{1}{4}$	0.89(4)	0.87(4)	0.56(4)	0.13(3)	0	0
Ni(2)	$\frac{1}{4}$	2013(1)	7466(2)	0.83(4)	0.97(4)	0.62(3)	0	0	−0.08(3)
P(1)	327(2)	3132(1)	$\frac{1}{4}$	0.53(6)	0.60(7)	0.38(6)	−0.05(5)	0	0
P(2)	2916(4)	220(3)	$\frac{1}{4}$	0.33(10)	0.47(12)	1.06(14)	0.09(9)	0	0
Na	$\frac{1}{4}$	4737(7)	$\frac{1}{4}$	10.32(82)	2.59(40)	2.92(42)	0	0	0
O(1)	4303(6)	3664(4)	3084(7)	2.55(21)	2.02(19)	0.37(13)	0.75(17)	0.10(15)	0.46(14)
O(2)	1116(6)	2208(5)	$\frac{1}{4}$	0.85(20)	0.99(23)	1.85(25)	0.27(18)	0	0
O(3)	3807(6)	2153(5)	0	0.28(20)	2.01(29)	1.67(25)	0.19(19)	0	0
O(4)	$\frac{1}{4}$	703(5)	2983(11)	1.61(23)	0.80(20)	1.11(22)	0	0	0.08(18)
O(5)	$\frac{1}{4}$	4233(6)	0	0.73(27)	0.52(2)	1.22(31)	0	0	0
O(6)	514(11)	129(7)	$\frac{1}{2}$	0.54(35)	0.13(32)	1.71(45)	0.08(28)	0	0

[a] Numbers in parentheses are estimated standard deviations in the last significant figures. The B's are defined by the general temperature factor $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

0.062 and R_w = 0.078 for the observed data.[1] The maximum extinction correction (9) was 8% of $|F_o|$ for the 004 reflection.

Although these results completely ignore the weak data which are definitely present, the low residual demonstrates that this model for the structure is quite close to the real structure, and that the effect on the residual of the weak data will be small. Table I presents the final positional and anisotropic thermal parameters for the high symmetry model of $NaNi_4(PO_4)_3$.

The final positional parameters for the high symmetry model were transformed to *Pnam*. Isotropic refinement in *Pnam* was less successful than in *Amam*, yielding at best a residual of R = 0.123. A similar re-

[1] See NAPS document 04331 for 6 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $0.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

finement in *Pna2₁* produced results which were even less satisfactory, indicating that, for the data collected, the high symmetry model in *Amam* is the most accurate description of the structure. To demonstrate that $NaNi_4(PO_4)_3$ is not simply isostructural to $NaMg_4(PO_4)_3$, the positional parameters for the latter compound were transformed from *Pnma* to *Pnam* to agree with the indexing of our data. Isotropic refinement yielded R = 0.204. A Fourier difference map showed large peaks in the vicinity of the P position analogous to the position in $NaNi_4(PO_4)_3$ for which we propose disorder.

Discussion

Before an attempt to analyze the disorder that was producing the weak data, bond lengths and angles and the standard errors were calculated to see if any unusual results might help in understanding this situation. Before discussing these data, it is helpful to view the disorder in the structure so that the bond lengths and angles can be more easily understood. Figure 1 is a view of a slab of this structure on the *ab* plane. The
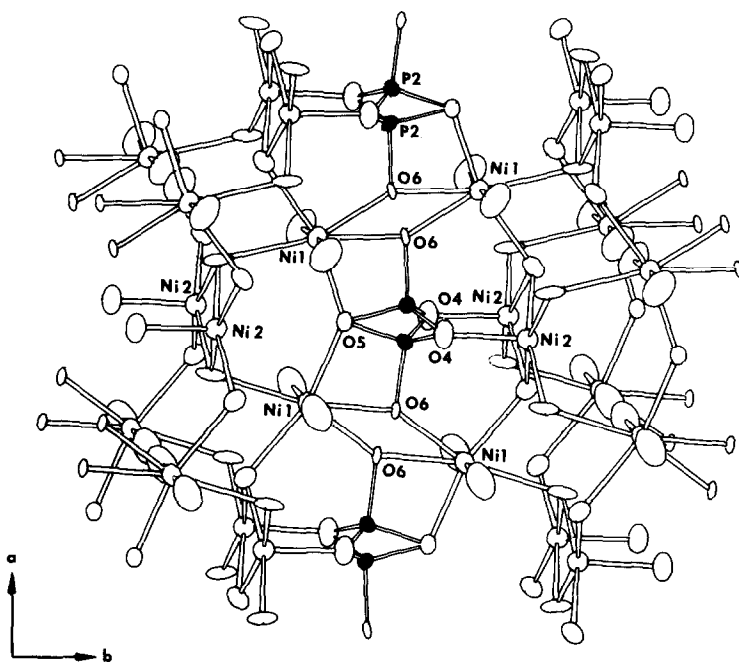
FIG. 1. A projection of a portion of the structure of NaNi₄(PO₄)₃ onto the *ab* plane showing the disorder of P(2) and O(6). The P(1) tetrahedra and Na octahedra are omitted. The projection has been rotated slightly for clarity.

vertical direction is *a* and the horizontal direction is *b* with a slight rotation for clarity. As can be seen, the P(2) tetrahedron is very close to a mirror plane. Three of the oxygens in the tetrahedron are actually on the mirror plane, and thus P(2) appears to form face-sharing tetrahedra. O(6) is the apex atom which also is in a position that is sterically impossible since the distance between apex O(6) atoms on different tetrahedra is only 1.12 Å. The sodium atom, although not disordered in this model, has a very large component of the temperature factor in the *a* direction, and it also appears to want to move to a disordered position off the mirror plane.

If the disorder is taken into consideration when analyzing the bond lengths and angles, none of the coordinating polyhedra are particularly unusual. Although Ni(1) has seven oxygens coordinating to it (Table II), only one of the O(6) atoms can bond to it in any given location (see above). It is interesting to note that both of the bond lengths for Ni(1)–O(6) are fairly similar. Bond-length bond-strength calculations using the method of Brown and Shannon (10) give values of 1.974 or 1.924 v.u. Thus, Ni(1) has a normal six-fold coordination in either case. Ni(2) is five-coordinated and is not involved in any of the disorder. (There are no additional oxygen atoms within 3.0 Å.)

The P(1) tetrahedron is not involved in the disorder. It is quite distorted with two relatively short bonds at 1.496 Å and longer bonds at 1.573 and 1.578. There is one distorted bond angle, 103.9°, between O(3) and O(2); the other bond angles fall in the normal range for orthophosphates. The P(2) tetrahedron, although disordered, has much more regular bond lengths (ranging from 1.522 to 1.559 Å) than the P(1) tetrahe-

TABLE II

BOND DISTANCES (Å), POLYHEDRAL EDGE LENGTHS (Å), AND BOND ANGLES (°) FOR THE Ni POLYHEDRA[a]

	Distance	Angle	Edge
Ni(1) polyhedron			
Ni(1)–O(1)	2× 1.964(5)		
Ni(1)–O(5)	2.023(4)		
Ni(1)–O(6a)	2.036(11)		
Ni(1)–O(6b)	2.094(11)		
Ni(1)–O(2)	2.189(7)		
Ni(1)–O(3)	2.396(7)		
O(1)–Ni(1)–O(5)		2× 88.3(2)	2.023(4)
O(1)–Ni(1)–O(6a)		2× 93.5(2)	2.914(9)
O(1)–Ni(1)–O(6b)		2× 92.5(2)	2.934(9)
O(1)–Ni(1)–O(2)		2× 90.6(2)	2.955(7)
O(1)–Ni(1)–O(3)		2× 87.0(2)	3.018(8)
O(5)–Ni(1)–O(6a)		100.8(4)	3.128(11)
O(5)–Ni(1)–O(6b)		70.3(4)	2.372(12)
O(5)–Ni(1)–O(3)		98.1(3)	3.347(12)
O(6a)–Ni(1)–O(2)		96.0(3)	3.142(13)
O(6b)–Ni(1)–O(2)		126.5(3)	3.842(13)
O(2)–Ni(1)–O(3)		65.1(2)	2.474(8)
O(1)–Ni(1)–O(1)		172.8(3)	3.921(10)
O(5)–Ni(1)–O(2)		163.2(4)	4.167(8)
O(6a)–Ni(1)–O(3)		161.1(3)	4.373(13)
O(6b)–Ni(1)–O(3)		168.4(3)	4.468(13)
Ni(2) polyhedron			
Ni(2)–O(4)	1.911(7)		
Ni(2)–O(3)	2× 2.022(4)		
Ni(2)–O(2)	2× 2.376(4)		
O(4)–Ni(2)–O(3)		2× 102.2(3)	3.146(9)
O(4)–Ni(2)–O(2)		2× 91.6(2)	2.916(9)
O(3)–Ni(2)–O(3)		77.0(3)	2.585(12)
O(3)–Ni(2)–O(2)		2× 99.2(2)	3.180(1)
O(3)–Ni(2)–O(2)		2× 166.2(3)	4.146(5)
O(2)–Ni(2)–O(2)		81.3(3)	2.738(13)

[a] Numbers in parentheses are estimated standard deviations in the last significant figures.

TABLE III

BOND DISTANCES (Å), POLYHEDRAL EDGE LENGTHS (Å), AND BOND ANGLES (°) FOR THE PHOSPHATE TETRAHEDRA[a]

	Distance	Angle	Edge
P(1) tetrahedron			
P(1)–O(1)	2× 1.496(5)		
P(1)–O(3)	1.563(6)		
P(1)–O(2)	1.578(7)		
O(1)–P(1)–O(1)		109.0(4)	2.436(9)
O(1)–P(1)–O(3)		2× 112.2(3)	2.540(7)
O(1)–P(1)–O(2)		2× 109.7(3)	2.514(8)
O(3)–P(1)–O(2)		103.9(4)	2.474(8)
P(2) tetrahedron			
P(2)–O(5)	1.522(10)		
P(2)–O(4)	2× 1.525(7)		
P(2)–O(6)	1.559(12)		
O(5)–P(2)–O(4)		2× 112.3(3)	2.530(10)
O(5)–P(2)–O(6)		100.7(5)	2.372(11)
O(4)–P(2)–O(4)		114.4(6)	2.564(10)
O(4)–P(2)–O(6)		2× 108.0(3)	2.496(10)

[a] Numbers in parentheses are estimated standard deviations in the last significant figures.

usual (see Fig. 2). For example, Co$_5$ (PO$_4$)$_2$(OH)$_4$ (*11*) has phosphate edge lengths of 2.425 and 2.429 Å in different tetrahedra. KCuPO$_4$ (*12*) has an even smaller phosphate edge length, 2.398 Å. Thus, there are no extraordinary bond distances involved in the coordination of the sodium. The oxygen environments are presented in Table V.

dron. There also is one distorted bond angle, 100.7°, between O(5) and O(6). These data are contained in Table III.

The sodium atom lies on a high symmetry site. It has only two different bond lengths, two to O(4) at 2.377 Å and four to O(1) at 2.684 Å (Table IV). Although the bond length–bond strength calculation for this octahedron is reasonable (0.85 v.u.), there is an unusually small O–Na–O bond angle of 54° between two of the O(1) atoms producing an O(1)–O(1) distance of 2.436 Å. This edge is actually the edge of the P(1) tetrahedron and, while short, is not that un-

TABLE IV

BOND DISTANCES (Å), POLYHEDRAL EDGE LENGTHS (Å), AND BOND ANGLES (°) FOR THE Na OCTAHEDRON[a]

	Distance	Angle	Edge
Na octahedron			
Na–O(4)	2× 2.377(9)		
Na–O(1)	4× 2.684(8)		
O(4)–Na–O(4)		105.9(5)	3.793(14)
O(4)–Na–O(1)		4× 136.1(1)	4.695(12)
O(4)–Na–O(1)		4× 89.8(2)	3.578(12)
O(1)–Na–O(1)		2× 54.0(2)	2.436(9)
O(1)–Na–O(1)		2× 83.3(3)	3.567(11)
O(1)–Na–O(1)		2× 107.1(4)	4.319(11)

[a] Numbers in parentheses are estimated standard deviations in the last significant figures.
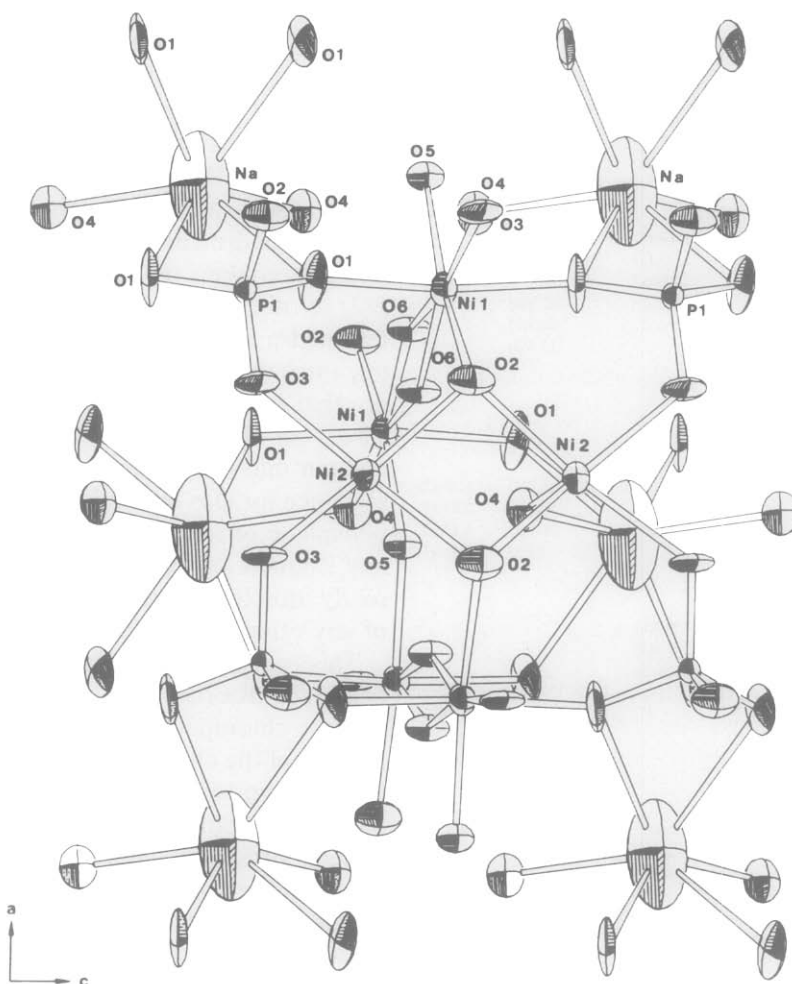
FIG. 2. A projection of a portion of the structure of $NaNi_4(PO_4)_3$ onto the ac plane showing the locations of the Na octahedra and P(1) tetrahedra. P(2) has been omitted for clarity. Note that each Ni(1) can only bond to one O(6) (see text).

Figure 1 also shows the bonding arrangement of the nickel-containing polyhedra. The five-coordinated nickel, Ni(2), forms edge-shared chains by sharing atoms O(2) and O(3) with other Ni(2) polyhedra. These chains are shown in Fig. 1 as coming out of the paper (the z direction). The fifth Ni(2) ligand, O(4), is one of the nondisordered oxygens in the P(2) tetrahedron. The Ni(1) octahedra link the Ni(2) chains together by corner sharing through O(2) and O(3). This is shown in Fig. 2 which also shows the

location of the sodium octahedra and P(1) tetrahedra. [The P(2) tetrahedra have been omitted for clarity.] Although it appears in Fig. 2 that Ni(1) forms edge-sharing dimers, only one of the two bonds to an O(6) atom can exist at any one time since that dimer is actually the result of the disordered oxygen atom. The linking of the nickel octahedra forms a plane normal to the b direction. These planes are separated by the disordered zone that contains the P(2) tetrahedra and the Na octahedra (which is not disor-

TABLE V

Bond Distances (Å), Polyhedral Edge Lengths (Å), and Bond Angles (°) for the Oxygen Polyhedra[a]

	Distance	Angle	Edge
O(1) polyhedra			
O(1)–P(1)	1.496(5)		
O(1)–Ni(1)	1.964(5)		
O(1)–Na	2.684(8)		
P(1)–O(1)–Ni(2)		145.4(4)	3.307(1)
P(1)–O(1)–Na		96.1(3)	3.208(8)
Ni(1)–O(1)–Na		117.3(2)	3.987(4)
O(2) polyhedra			
O(2)–P(1)	1.578(7)		
O(2)–Ni(2)	2× 2.101(4)		
O(2)–Ni(1)	2.189(7)		
P(1)–O(2)–Ni(2)		2× 116.2(3)	3.136(2)
P(1)–O(2)–Ni(1)		99.3(3)	2.899(2)
Ni(2)–O(2)–Ni(2)		96.5(3)	3.135(2)
Ni(2)–O(2)–Ni(1)		2× 114.9(2)	3.616(1)
O(3) polyhedra			
O(3)–P(1)	1.563(6)		
O(3)–Ni(2)	2× 2.076(4)		
O(3)–Ni(1)	2.396(8)		
P(1)–O(3)–Ni(2)		2× 124.9(2)	3.235(2)
P(1)–O(3)–Ni(1)		91.7(3)	2.899(2)
Ni(2)–O(3)–Ni(2)		101.8(3)	3.222(2)
Ni(2)–O(3)–Ni(1)		2× 104.4(3)	3.538(2)
O(4) polyhedra			
O(4)–P(2)	1.525(7)		
O(4)–Ni(2)	1.965(7)		
O(4)–Na	2.377(9)		
P(2)–O(4)–Ni(2)		125.9(4)	3.116(4)
P(2)–O(4)–Na		112.8(4)	3.284(3)
Ni(2)–O(4)–Na		118.7(4)	3.743(9)
O(5) polyhedra			
O(5)–P(2)	1.578(10)		
O(5)–Ni(1)	2× 2.101(4)		
P(2)–O(5)–Ni(1)		127.8(4)	3.191(5)
P(2)–O(5)–Ni(1)		96.5(2)	2.665(5)
Ni(1)–O(5)–Ni(1)		135.7(5)	3.748(2)
O(6) polyhedra			
O(6)–P(1)	1.559(11)		
O(6)–Ni(1)	2.036(11)		
O(6)–Ni(1)	2.094(11)		
P(1)–O(6)–Ni(1)		118.0(6)	3.091(4)
P(1)–O(6)–Ni(1)		92.5(5)	2.665(5)
Ni(1)–O(6)–Ni(1)		149.5(6)	3.985(3)

[a] Numbers in parentheses are estimated standard deviations in the last significant figures.

dered in the high-symmetry model although its very large temperature factor suggests that it may move off of the mirror when the structure starts to order).

Since there are no impossible, or even very unusual, coordinations in the high symmetry model of this structure, let us now look at the type of disorder that is possible in the real structure. As can be seen in Fig. 1, all of the disorder is confined to a zone normal to the b axis that contains the P(2) tetrahedron and the Na octahedron. In any one column of P(2) tetrahedra, if one P(2) tetrahedron points up, then all of the tetrahedra in that column must also point up, since the O(6)–O(6) distance of tetrahedra that point together is impossibly short. Thus, all the P(2) tetrahedra in a given column must be ordered since there is no evidence for less than full occupancy for all phosphate tetrahedra. Note, however, that any column of P(2) tetrahedra is not directly affected by the direction of ordering of any other column of P(2) tetrahedra.

This is a situation that is remarkably similar to the disorder of the chlorine atoms in calcium chlorapatite [$Ca_{10}(PO_4)_6Cl_2$], where the size of the chlorine atom forces a particular column to order. At low temperature, pure stoichiometric chlorapatite is completely ordered, with adjacent columns adopting the opposite site. This ordering is accomplished by a slight twist of phosphate tetrahedra that, in effect, transmits the location of a chlorine atom to adjacent columns. This mechanism has been described by Mackie et al. (13). At high temperature or if the crystal is slightly deficient in chlorine, the mechanism is incapable of maintaining long-range order, and the crystal transforms to the higher symmetry space group.

In $NaNi_4(PO_4)_3$, completely disordered P(2) tetrahedra (that is a random distribution of the direction of P(2) columns) will result in the adoption of the space group Amam. Thus, the higher symmetry model would be the true space group and there would be no additional reflections. Since additional reflections are observed for this compound, there must be a tendency for

the columns of P(2) tetrahedra to order. In chlorapatites, it is very easy for the chlorine atoms to move to the required position for ordering. However, in $NaNi_4(PO_4)_3$, a column of P(2) tetrahedra must break bonds in order to switch directions. Thus, a transformation to full ordering will be extremely sluggish if the crystal grew in a disordered state. Since the changes in cation coordination are minor whether a column of P(2) tetrahedra point up or down, the difference in energy for either state must be small. Since the crystals were grown relatively fast, (cooled at approximately 15°C/hr) large numbers of "mistakes" could easily be incorporated into the structure even though one particular arrangement of P(2) columns is more thermodynamically stable.

If the mistakes in the ordering of the P(2) columns occur only in planes, then the crystal is actually twinned, probably polysynthetically, with very thin individual regions of perfect order. The twin plane would obviously be the mirror plane (normal to the a axis) that contains the three basal oxygen atoms of the P(2) tetrahedra. If the regions of ordering are randomly scattered, then a perfectly ordered structure would be almost impossible to achieve.

Since the ordering is such a small part of the total scattering, meaningful refinements in a low symmetry space group in an attempt to determine the exact nature of the ordering are not possible, as we have demonstrated. Structure factor calculations were made for the weak reflections by using different models for ordering. These calculations using models that were completely ordered did not produce residuals as good as the residuals produced by the high symmetry model. Thus, the only valid conclusion from these calculations is that the structure is neither completely ordered or disordered.

Acknowledgment

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