Synthesis and Crystal Structure of a New Alkaline Earth Nickel Phosphide Phase: BaNi$_9$P$_5$

JOHN V. BADDING AND ANGELICA M. STACY[1]

Department of Chemistry, University of California, Berkeley, California 94720, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

A new barium nickel phosphide BaNi$_9$P$_5$ was synthesized in a tin flux. Single crystal X-ray methods revealed that the material has hexagonal Laue symmetry with unit cell dimensions $a = 6.5359(9)$ Å and $c = 10.854(3)$ Å. The structure was refined in the space group $P6_3/mmc$ to an R value of 2.3%. The structure is best described as hexagonal layers of Ba atoms with each Ba atom surrounded by Ni$_{18}$P$_{12}$ cages. The crystals have a silvery luster, and grow in an equidimensional, faceted habit. Magnetic measurements show temperature-independent Pauli paramagnetism, suggesting that BaNi$_9$P$_5$ is a metal. © 1990 Academic Press, Inc.

Introduction

A wide variety of metal-rich rare earth and alkaline earth transition metal phosphides have been synthesized in recent years because of their potentially interesting properties. The predominant structure types include Zr$_2$Fe$_{12}$P$_7$ (*1*), LaNi$_5$P$_3$ (*2*), LaCo$_8$P$_5$ (*3*), and YCo$_5$P$_3$ (*4*). All four of these classes of phosphides are highly anisotropic with the electropositive cations arranged in chains. The anisotropic nature of these compounds strongly affects their physical properties. For example, as a result of the europium chains, EuNi$_5$P$_3$ (*5*) exhibits an unusual series of magnetic phase transitions (*6*). Another common structural feature is the tricapped trigonal prismatic coordination about the phos-

phorus atoms (*7*). Here we report the synthesis of a new barium nickel phosphide, BaNi$_9$P$_5$, which crystallizes in a new structure type. In contrast to the four classes of phosphides listed above, BaNi$_9$P$_5$ is more isotropic, and the phosphorus atoms do not have trigonal prismatic coordination.

Synthesis

Single crystals of BaNi$_9$P$_5$ were prepared in a tin flux according to the method of Jeitschko and co-workers (*8*). The alkaline earth (99.99%), phosphorus (99.999%), nickel (99.999%), and tin (99.999%) were mixed in the ratio 1 : 5 : 3 : 20 and sealed in evacuated quartz tubes. The tubes were heated to 850°C, cooled at 2°C/hr to 500°C, and then cooled rapidly. After dissolution of the tin in concentrated hydrochloric acid, well-developed approximately equidi-

mensional crystals of $BaNi_9P_5$ remained. The crystals ranged in size from 40 μm to 3 mm.

Structure Determination

A Rigaku AFC-5 Rotating Anode diffractometer was used to collect single crystal intensity data. A primitive hexagonal cell was chosen from the results of preliminary precession photographs and automatic peak search and indexing procedures. The Laue symmetry is 6/mmm. Cell and data collection parameters are summarized in Tables I and II.

The 512 raw intensity data were converted to structure factor amplitudes and their e.s.d.'s by correction for background (9), Lorentz, and polarization effects (10). The magnitude of the intensity standard reflections varied less than 2%. The azimuthal scan data (36 reflections, 10° interval) showed a variation $I_{min}/I_{max} = 0.9$. An empirical absorption correction based on the azimuthal scan data, and a spherical absorption correction ($\mu R = 1.0$), were ap-

TABLE I

CRYSTAL PARAMETERS AT 23°C[a]

$a = 6.5359(9)$
$c = 10.854(3)$
$V = 401.5(1)$
$\mu_{calcd} = 265$ cm^{-1}
Size of crystal: $0.05 \times 0.05 \times 0.06$ mm

Space group: $P6_3/mmc$
Formula weight: 830.6 amu
$Z = 2$
$d_c = 6.80$ g/cm

[a] Unit cell parameters and their e.s.d.'s were derived by a least-squares fit to the setting angles of the resolved $MoK\alpha_1$ components of reflections with 2θ between 39 and 40° 2θ. In this and all subsequent tables the e.s.d.'s of all parameters are given in parentheses, right justified to the least significant digits given.

TABLE II

DATA MEASUREMENT PARAMETERS

Radiation:	$MoK\alpha_1$ ($\lambda = 0.7093$ Å)
Power level:	45 kV, 180 mA
Monochrometer:	Graphite
Detector:	Scintillation counter
2θ range:	0–60°
Scan type:	ω step scan, fixed monitor count
Scan width:	± 0.75°
Step size:	0.03
Effective scan speed:	4°/min
Background:	Lehman Larson

plied to the data. All $hh2\bar{h}l$ reflections with $l = 2n$ were very weak or absent, and there were no other systematic absences. Thus the possible space groups were $P6_3/mmc$, $P6_3mc$, or $P\bar{6}2c$. Refinement was successful in $P6_3/mmc$, so the other two possibilities were not considered. After averaging of redundant data and removal of systematically absent data, 256 unique data remained, of which 228 were observed.

The structure was solved using Patterson methods and refined using standard Fourier and least-squares techniques. Robust-Resistant weighting was used (11). A secondary extinction parameter (12) was included in the refinement. This parameter refined to a value of 16(3) × 10^{-6}; the strongest reflections were corrected by approximately 10%.

The final residuals for 21 variables refined against observations for which $F > 2\sigma(F)$ were $R = 2.3\%$, $R_w = 2.4\%$. The quantity minimized by the least-squares program was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The analytical forms of the scattering factors for neutral atoms were used (13), and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion (14). A listing of the values of F_o and F_c are available from the authors upon request.

Discussion

The BaNi₉P₅ structure can be described by hexagonal layers of Ba atoms at $z = 0$ with each Ba atom surrounded by a $Ni_{18}P_{12}$ "cage." The $Ni_{18}P_{12}$ cages, shown in Fig. 1, share six rhomboidal Ni_2P_2 faces to form the primitive hexagonal layer illustrated in the view down the c axis in Fig. 2. These layers are stacked parallel to the c axis with the Ba atoms collinear by sharing of hexagonal Ni_3P_3 faces which are in the mirror plane at $z = \pm\frac{1}{4}$. The positional parameters are given in Table III, and Table IV contains a listing of the interatomic distances and coordination numbers.
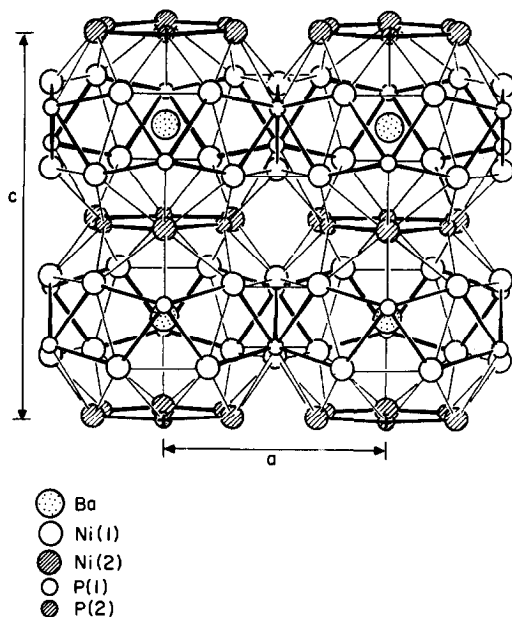

Ba
Ni(1)
Ni(2)
P(1)
P(2)

FIG. 1. ORTEP drawing of BaNi₉P₅ with the c axis vertical. The structure consists of shared cages of nickel and phosphorus of which four are shown. Barium atoms are at the center of each cage. The heavy lines connecting the Ni(2)–P(2) atoms indicate where the top and bottom faces of the cages are shared. The sides of the cages are shared along the rhomboids indicated by the heavy lines connecting the Ni(1)–P(1) atoms. Bonds are drawn between all atoms separated by less than 2.6 Å except for the Ni(1)–Ni(1) bonds in the center of the figure which were removed for clarity.
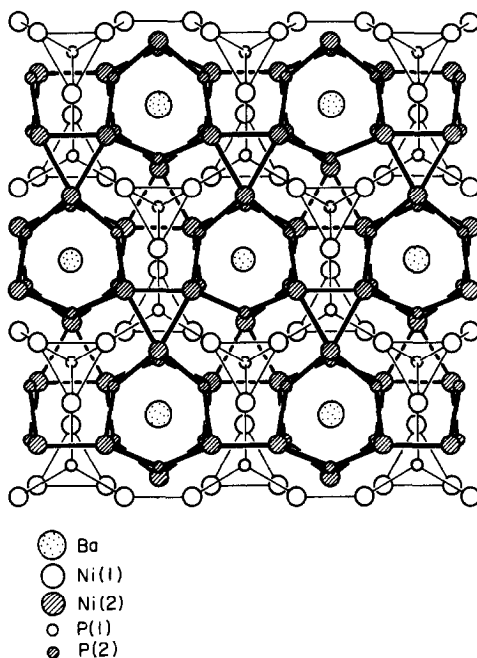

Ba
Ni(1)
Ni(2)
P(1)
P(2)

FIG. 2. View down the c axis of BaNi₉P₅. A single hexagonal layer of cages is shown. The barium atoms are in the middle of the layer at $z = 0$. The Ni(2) and P(2) atoms are connected by heavy lines at $z = \pm\frac{1}{4}$. The Ni(1) atoms and P(1) atoms are connected by light lines and are at $z = \pm0.1075$ and $z = \pm0.0608$, respectively.

TABLE III

TABLE OF POSITIONAL PARAMETERS AND THEIR
ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	$B(\text{Å}^2)$
Ba	0.000	0.000	0.000	0.66(2)
Ni(1)	0.53566(2)	$2\times$	0.392487(2)	0.60(2)
Ni(2)	0.203660(9)	$2\times$	$\frac{1}{4}$	0.58(3)
P(1)	$\frac{1}{3}$	$\frac{2}{3}$	0.060753(4)	0.52(3)
P(2)	$-.17426(1)$	$2\times$	$\frac{1}{4}$	0.53(4)

Note. The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as

$$(\tfrac{4}{3})^*[a^{2*}B(1,1) + b^{2*}B(2,2) + c^{2*}B(3,3) + ab(\cos \gamma)^*B(1,2) + ac(\cos \beta)^*B(1,3) + bc(\cos \alpha)^*B(2,3)].$$

TABLE IV

INTERATOMIC DISTANCES IN BaNi$_9$P$_5$

	Atom 1	Atom 2	Distance
12	Ba	Ni1	3.493(1)
6	Ba	Ni2	3.561(1)
6	Ba	P2	3.354(1)
2	Ni1	Ba	3.493(1)
1	Ni1	Ni1	2.470(1)
2	Ni1	Ni1	2.568(1)
2	Ni1	Ni2	2.536(1)
1	Ni1	P1	2.352(2)
1	Ni1	P1	2.346(1)
2	Ni1	P2	2.272(1)
2	Ni2	Ba	3.561(1)
4	Ni2	Ni1	2.534(1)
2	Ni2	Ni2	2.543(1)
2	Ni2	P1	2.525(2)
2	Ni2	P2	2.158(1)
3	P1	Ni1	2.352(2)
3	P1	Ni1	2.346(1)
3	P1	Ni2	2.525(2)
2	P2	Ba	3.354(1)
4	P2	Ni1	2.272(1)
2	P2	Ni2	2.158(1)

Each Ba atom is coordinated to 24 atoms, 12 Ni(1), 6 Ni(2), and 6 P(2) atoms, all approximately equidistant from the Ba atom (3.35 to 3.56 Å). In addition, there are 6 P(1) atoms at a distance of 3.83 Å from each Ba atom; these 6 P(1) atoms complete the Ni$_{18}$P$_{12}$ cage, but are not close enough to be within the coordination sphere of the Ba atoms. The coordination of 24 about the electropositive cation is unprecedented; in all previously determined structures of alkaline earth and rare earth nickel phosphides the coordination of the electropositive cation was less than 24. The smaller Eu^{2+}, Sr^{2+}, and La^{3+} ions are coordinated to 21 atoms in the LaNi$_5$P$_3$-type structure (2). It is interesting to note that BaNi$_5$P$_3$ is not known; Ba is probably too large to form in this structure type. In the Zr$_2$Fe$_{12}$P$_7$-type structure (1), the smaller trivalent rare earth ions, such as Gd^{3+}, are only 18-coordinate.

The barium–barium distances are 5.4 Å in the c direction and 6.5 Å in the a direction. Compared with other alkaline earth and rare earth nickel phosphides, these distances are long, and relatively isotropic. Other nickel phosphides, including SrNi$_5$P$_3$ (15), EuNi$_5$P$_3$ (5), LaNi$_5$P$_3$ (2), and those with the Zr$_2$Fe$_{12}$P$_7$ structure (1), have anisotropic structures. In all of these phosphides, the electropositive cations are arranged in chains. Whereas the interchain distance is over 6 Å, the intrachain distance is much shorter, typically 3.6 Å. This anisotropy is also evident in the morphology of the crystals. In contrast to the equidimensional growth habit of BaNi$_9$P$_5$, the other alkaline earth and rare earth nickel phosphides grow in the form of rods.

The two types of Ni atoms, labeled Ni(1) and Ni(2), lie in layers at $z = \pm 0.1075$ and $z = \pm\frac{1}{4}$, respectively. Both types of Ni atoms are in low symmetry environments which are difficult to describe simply. Ni(1) is 11-coordinate, and Ni(2) is 12-coordinate. The Ni(1) atoms are part of the rhomboidal Ni$_2$P$_2$ faces of the Ni$_{18}$P$_{12}$ cages; the Ni(2) atoms form the Ni$_3$P$_3$ hexagons above and below each Ba atom. The hexagonal faces are outlined with heavy lines in Fig. 1, and are easily seen in the view along the c direction shown in Fig. 2. The nickel–phosphorus distances range from 2.16 to 2.53 Å, and the nickel–nickel distances are all approximately 2.5 Å.

There are also two types of P atoms: P(1) at $z = \pm 0.0608$ associated with the rhomboidal Ni$_2$P$_2$ faces, and P(2) in the Ni$_3$P$_3$ hexagons at $z = \pm\frac{1}{4}$. P(1) is in a 9-coordinate environment of $3m$ symmetry which can be described as a distorted tricapped trigonal antiprism. The antiprisms and capping atoms can be seen in the view down the c axis in Fig. 2. The local symmetry of the 8-coordinate P(2) atoms is lower. In contrast, the phosphorus atoms in most

other metal-rich phosphides are typically in tricapped trigonal prismatic coordination (7). As in most metal-rich phosphides, the phosphorus–phosphorus distances in $BaNi_9P_5$ are long; there is no apparent homoatomic phosphorus bonding. Since the phosphorus atoms are isolated, according to the Zintl concept (16–18) phosphorus is in a formal oxidation state of -3. All of the previously mentioned structure types also have isolated phosphorus atoms with the exception of $LaCo_8P_5$. $LaCo_8P_5$ has $P_2^{2.5-}$ units in which the phosphorus atoms are joined by half bonds in addition to isolated P^{3-} atoms (19).

Magnetization measurements on $BaNi_9P_5$ revealed weak and almost temperature-independent paramagnetism. This indicates that the electrons are delocalized as is typical of alkaline earth and rare earth nickel phosphides. The shiny, metallic appearance of $BaNi_9P_5$ is also consistent with electron delocalization.

Acknowledgments

References

1. W. JEITSCHKO, D., J. BRAUN, R. H. ASHCRAFT, AND R. MARCHAND, J. Solid State Chem. 25, 309 (1978).

2. W. K. HOFMANN AND W. JEITSCHKO, J. Solid State Chem. 51, 152 (1984).

3. V. N. DAVYDOVAND AND YU. B. KUZ'MA, Dopov. Akad. Nauk, Ukr. RSR Ser. A. 1, 81 (1981).

4. U. MEISEN AND W. JEITSCHKO, J. Less-Common Met. 102, 127 (1984).

5. J. V. BADDING AND A. M. STACY, J. Solid State Chem. 67, 354 (1987).

6. J. V. BADDING AND A. M. STACY, Phys. Rev. B. 35, 8880 (1987).

7. E. PARTHE, B. CHABOT, AND E. HOVESTREYDT, Acta Crystallogr. B 39, 596 (1983).

8. W. JEITSCHKO AND B. JABERG, J. Solid State Chem. 467, 95 (1980).

9. M. S. LEHMAN AND F. K. LARSEN, Acta. Crystallogr. A 30, 584 (1974).

10. "Texsan," Molecular Structure Co.

11. W. L. NICHOLSON, E. PRINCE, J. BUCHANAN, AND P. TUCKER, in "Crystallographic Statistics" (S. Ramaseshan, M. F. Richardson and A. J. C. Wilson, Eds.), pp. 229–263, Indian Academy of Sciences, Bangalore (1982).

12. P. BECKER AND A. COPPENS, Acta Crystallogr. A 30, 129 (1974).

13. D. T. CROMER AND J. T. WABER, "International Tables for X-ray Crystallography," Vol. IV, Table 2.2B, Kynoch Press, Birmingham, England (1974).

14. D. T. CROMER, "International Tables for X-ray Crystallography," Vol. IV, Table 2.3.1, Kynoch Press, Birmingham, England (1974).

15. J. V. BADDING, P. D. VERNOOY, AND A. M. STACY, to be published.

16. H. SHÄFER, B. EISENMANN, AND W. MÜLLER, Angew. Chem. Int. Ed. 12, 694 (1973).

17. W. KLEMM, Proc. Chem. Soc. (London), 329 (1958).

18. R. MARCHAND AND W. JEITSCHKO, J. Solid State Chem. 24, 351(1978).

19. H. G. VON SCHNERING AND W. HÖNLE, Chem. Rev. 88, 243 (1988).