Acta Cryst. (1977). B**33**, 3401–3406

$LaFe_4P_{12}$ with Filled $CoAs_3$-Type Structure and Isotypic Lanthanoid–Transition Metal Polyphosphides

BY W. JEITSCHKO AND D. BRAUN

Institut für Anorganische und Analytische Chemie, Universität Giessen, D-6300 Giessen, Federal Republic of Germany

(*Received* 1 *April* 1977; *accepted* 30 *April* 1977)

The new compound $LaFe_4P_{12}$ was prepared by reaction of LaP and Fe powders with red P in evacuated silica tubes. Single crystals of $LaFe_4P_{12}$ were obtained by reaction of the elemental components in molten Sn. They are cubic, space group *Im*3, $a = 7{\cdot}832$ Å, $Z = 2$. The structure was determined from single-crystal counter data by Patterson and Fourier methods and refined to $R = 0{\cdot}028$ for 193 unique structure factors. It represents a new structural type which can be derived from the $CoAs_3$ and WAl_{12}-type structures by filling the (somewhat distorted) icosahedral and octahedral voids with La and Fe atoms respectively. The P atoms are coordinated by two Fe and two P atoms forming a distorted tetrahedron augmented by a La atom outside one face of that tetrahedron. In the polyanionic $[Fe_4P_{12}]^{3-}$ framework the P–P bonding distances are somewhat expanded, to accommodate the large La^{3+} cation, which in turn has shorter La–P distances than would be expected from the La–P distances in LaP, LaP_2, and LaP_5. The new compounds $LnFe_4P_{12}$ (Ln = Ce, Pr, Nd, Sm, Eu), $LnRu_4P_{12}$ (Ln = La, Ce, Pr, Nd, Eu), and $LnOs_4P_{12}$ (Ln = La, Ce, Pr, Nd) are isotypic with $LaFe_4P_{12}$. Their lattice constants indicate valencies IV and II for Ce and Eu, respectively, in the compounds. In $CeFe_4P_{12}$ the polyanion $[FeP_3]^-$ is isoelectronic and isostructural with CoP_3.

Introduction

Although most binary metal–P systems have been explored (Rundqvist, 1962; Lundström, 1969; Wilson, 1971; von Schnering, 1977), little is known about ternary phosphides involving two metals (Corbridge, 1974; Jeitschko, 1974). We have now started to synthesize and characterize such ternary compounds.

Synthesis and crystal growth

Starting materials were filings of the Ln elements obtained from ingots under Ar, freshly reduced Fe powder, powders of Ru and Os (all of purity >99·5%) and red P (>98·5%) which was treated with boiling, diluted NaOH (Brauer, 1960). Stoichiometric mixtures of the components (sometimes with excess P) were sealed in evacuated silica tubes, rapidly heated to 1250 K and annealed for one week at 1050 K. X-ray powder photographs of the products frequently showed, in addition to the ternary compound, weak lines of the binary phosphides. Better results were obtained by introducing the Ln in the form of its prereacted monophosphide which can easily be ground to fine powder. The products thus obtained are microcrystalline, black, and insensitive to air or moisture.

Single crystals of $LaFe_4P_{12}$ were grown from a Sn flux. This solvent has been used by Jolibois (1910) to grow crystals of NiP_2 and NiP_3. Starting materials were La filings, Fe powder, red P, and Sn (>99·9%) in the atomic ratio 1:4:20:50. The mixture was sealed in evacuated silica tubes and annealed for one week at 1050 K. After slow cooling (2 K h^{-1}) the samples were treated with moderately dilute HCl acid (1:1) to dissolve the Sn matrix. The resulting crystals of $LaFe_4P_{12}$ have truncated octahedral habit with diameters up to 0·2 mm.

For an analysis of Sn the crystals were dissolved in a melt of Na_2CO_3 and Na_2O_2 (1:3). After cooling, the melt was dissolved in hydrochloric acid. A flame absorption analysis resulted in 0·035 at.% Sn. It can be assumed that some of this is due to heterogeneous inclusions.

Crystal structure of $LaFe_4P_{12}$

Crystals of $LaFe_4P_{12}$ were examined in Weissenberg and precession cameras. They are body-centred cubic with *m*3 Laue symmetry. Lattice constants were obtained by least-squares refinement of Guinier data with α-quartz ($a = 4{\cdot}91304$, $c = 5{\cdot}40463$ Å) as standard. For heterogeneous samples with greatly varying overall compositions lattice constants between 7·8300 and 7·8332 Å were obtained for $LaFe_4P_{12}$ with individual standard deviations of about 0·0005 Å. This indicates that the compound has only a small homogeneity range. Besides the extinctions characteristic of body centring, no other extinctions were observed. Thus, space groups *I*23, $I2_13$, and *Im*3 were allowed, of which *Im*3 was found to be correct during the structure determination.

Intensities were collected from an approximately spherical crystal, 0·10 mm diameter, on an automated four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation, scintillation counter, and pulse-height discriminator. ω-scans were taken with a speed of 0·04° s^{-1} and a scan angle of 1·2°. Background was counted at both ends of the scan for 23 s. All reflexions within one octant up to $(\sin\theta)/\lambda = 0{\cdot}7$ were measured. An absorption correction was applied ($\mu = 116$ cm^{-1}) assuming spherical crystal shape. Equivalent reflexions were averaged.

Even though the composition of the crystal was not known, it was possible to obtain a complete interpretation of the Patterson function in space group $Im3$. The structure was refined by full-matrix least squares

Table 1. *Positional and thermal parameters of* $LaFe_4P_{12}$

Numbers in parentheses are e.s.d.'s in the least significant digits. Vibrational parameters are defined by $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + \cdots)]$; equivalent isotropic thermal parameters, B, are in Å^2.

	La	Fe	P
$Im3$	2(*a*)	8(*c*)	24(*g*)
x	0	$\frac{1}{4}$	0
y	0	$\frac{1}{4}$	0·3539 (1)
z	0	$\frac{1}{4}$	0·1504 (1)
U_{11}	0·0051 (2)	0·0030 (2)	0·0046 (3)
U_{22}	U_{11}	U_{11}	0·0046 (3)
U_{33}	U_{11}	U_{11}	0·0052 (3)
U_{12}	0	0·0003 (2)	0
U_{13}	0	U_{12}	0
U_{23}	0	U_{12}	−0·0001 (3)
B	0·40 (1)	0·24 (2)	0·37 (2)

Table 2. *Interatomic distances* (Å) *and selected interatomic angles* (°) *in* $LaFe_4P_{12}$

All distances shorter than 3·5 Å are listed. Standard deviations are all less than 0·002 Å and 0·1°.

La–P	3·012	(12×)	P–Fe–P	180·0	(3×)
Fe	3·391	(8×)	P–Fe–P	82·1	(6×)
Fe–P	2·259	(6×)	P–Fe–P	97·9	(6×)
La	3·391	(2×)	P′–P–P″	90·0	(1×)
P–Fe	2·259	(2×)	Fe–P–Fe	120·1	(1×)
P′	2·288	(1×)	Fe–P–P′	111·1	(2×)
P″	2·356	(1×)	Fe–P–P″	110·2	(2×)
La	3·012	(1×)	La–P–P′	157·0	(1×)
P	2·968	(4×)	La–P–P″	67·0	(1×)
P	3·284	(1×)	La–P–Fe	78·7	(2×)
P	3·407	(4×)			

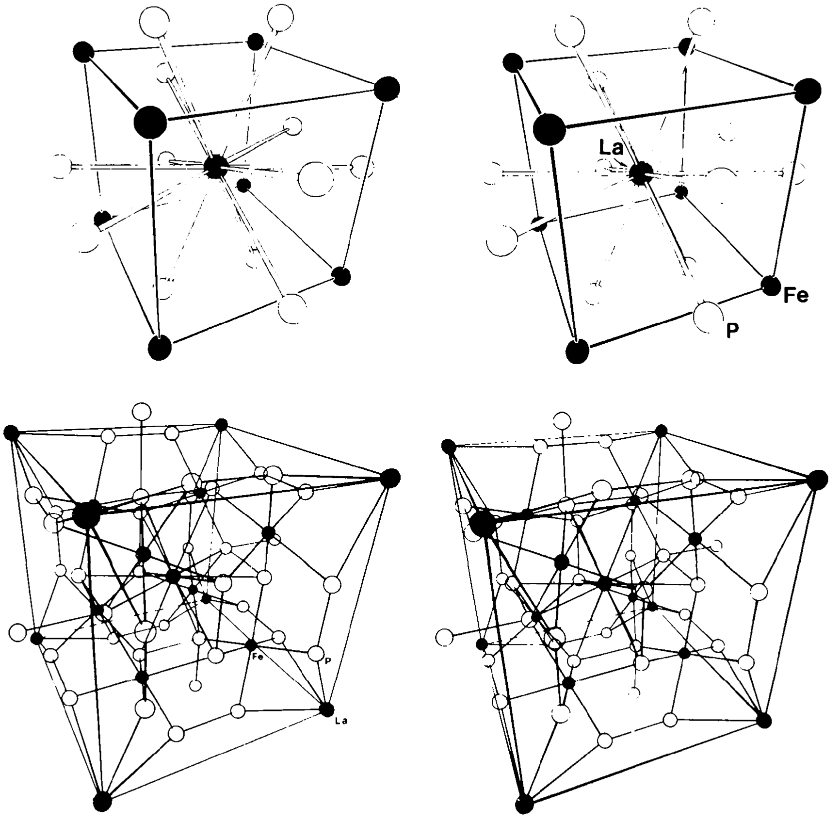

Fig. 1. Stereogram of one cell of $LaFe_4P_{12}$ and near neighbours of La, drawn with Johnson's (1965) program. The sizes of the atoms correspond to isotropic thermal parameters at the 90% probability limit.

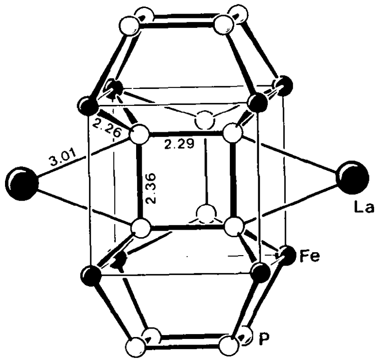

Fig. 2. Near neighbours of the P_4 groups in $LaFe_4P_{12}$. Interatomic distances are in Å.

(Sheldrick, 1976). Scattering factors for neutral atoms were used (Cromer & Mann, 1968), corrected for anomalous dispersion (Cromer & Liberman, 1970). The weighting scheme was $w = 1/[\sigma^2(F_o) + 0{\cdot}0005|F_o|^2]$. An isotropic extinction parameter x refined to $1{\cdot}04 \times 10^{-6}$ where F_c is multiplied by $(1 - x|F_c|^2/\sin\theta)$. The final R is 0·037 for 210 unique reflexions. $R = 0{\cdot}029$ for 193 reflexions, excluding very weak reflexions and the six strongest most severely affected by secondary extinction.* A difference synthesis revealed no features lower than $-1{\cdot}3$ e Å^{-3} or higher than $+1{\cdot}2$ e Å^{-3}. Final positional and thermal parameters are given in Table 1. Drawings of the structure and near-neighbour environments are shown in Figs. 1 and 2 and Table 2.

Isotypic compounds

To explore the stability range of the new structural type, samples were prepared where La was replaced by other Ln elements and Fe substituted by Ru and Os. Sample preparation was as described above. The preferred method of preparation is that from a Sn flux. $NdRu_4P_{12}$ and $PrOs_4P_{12}$ were also prepared by direct reaction of the elements in evacuated silica tubes. Lattice constants of samples prepared by the two methods were the same within 0·001 Å. Table 3 shows typical powder patterns. Lattice constants of the new compounds are listed in Table 4.

Table 3. *Calculated (Yvon, Jeitschko & Parthé, 1977) and observed powder patterns of some* $LaFe_4P_{12}$*-type compounds*

A Guinier camera, and Cu $K\alpha$ radiation were used to obtain the experimental powder pattern.

	$PrFe_4P_{12}$				$PrRu_4P_{12}$				$PrOs_4P_{12}$			
hkl	d_c	d_o	I_c	I_o	d_c	d_o	I_c	I_o	d_c	d_o	I_c	I_o
110	5.5260	5.5285	38	s	5.6866	5.6861	17	m	5.7070	5.7092	6	vw
200	3.9074	-	2	-	4.0210	5.0196	24	s	4.0355	4.0355	51	s
211	3.1904	3.1911	26	m	3.2831	3.2841	12	w	3.2950	-	4	-
220	2.7630	2.7629	87	vvs	2.8433	2.8431	100	vvs	2.8535	2.8538	100	vvs
310 130	2.4713	2.4711	0 100	vvs	2.5431	2.5426	0 48	s	2.5523	2.5526	0 17	w
222	2.2560	-	1	-	2.3215	2.3214	9	vw	2.3299	2.3298	19	m
231 321	2.0886	2.0886	53 20	vs	2.1493	2.1485	25 10	m	2.1571	2.1569	9 3	vw
400	1.9537	1.9532	14	m	2.0105	2.0099	18	m	2.0177	2.0168	19	m
411 330	1.8420	-	5 1	vw	1.8955	-	3 0	-	1.9023	-	1 0	-
420 240	1.7475	1.7473	8 10	m	1.7982	1.7990	15 16	s	1.8047	1.8053	20 21	s
332	1.6661	-	1	-	1.7146	-	0	-	1.7207	-	0	-
422	1.5952	1.5954	68	s	1.6416	1.6419	66	vs	1.6475	1.6477	58	vs

Table 4. *Lattice constants and calculated densities of* $LaFe_4P_{12}$*-type compounds*

Standard deviations (in the least significant digits, given in parentheses) obtained in the least-squares refinements do not reflect possible homogeneity ranges.

	a (Å)	V (Å^3)	D_c (g cm^{-3})
$LaFe_4P_{12}$	7·8316 (5)	480·3	5·07
$CeFe_4P_{12}$	7·7920 (10)	473·1	5·16
$PrFe_4P_{12}$	7·8149 (9)	477·3	5·12
$NdFe_4P_{12}$	7·8079 (7)	476·0	5·16
$SmFe_4P_{12}$	7·8029 (3)	475·1	5·21
$EuFe_4P_{12}$	7·8055 (11)	475·6	5·22
$LaRu_4P_{12}$	8·0561 (7)	522·9	5·81
$CeRu_4P_{12}$	8·0376 (5)	519·3	5·86
$PrRu_4P_{12}$	8·0420 (9)	520·1	5·86
$NdRu_4P_{12}$	8·0364 (3)	519·0	5·89
$EuRu_4P_{12}$	8·0406 (5)	519·8	5·93
$LaOs_4P_{12}$	8·0844 (4)	528·4	7·99
$CeOs_4P_{12}$	8·0626 (11)	524·1	8·06
$PrOs_4P_{12}$	8·0710 (10)	525·7	8·04
$NdOs_4P_{12}$	8·0638 (8)	524·3	8·09

Discussion

Geometric relations

The structure of $LaFe_4P_{12}$ is best described as a filled $CoAs_3$, skutterudite structure (Oftedal, 1928), where the two (nearly) icosahedral voids at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ are filled with La atoms. It can also be considered as a filled WAl_{12}-type structure (Adam & Rich, 1954) where La and P correspond to W and Al and Fe occupies octahedral P interstices which are empty in WAl_{12}. The derivation of the three structure types from the ReO_3 and $CaTiO_3$-type structures is summarized in Fig. 3. The $CoAs_3$ structure derives from ReO_3 by doubling the cell edge of ReO_3 and tilting the corner-sharing ReO_6 octahedra (Rundqvist & Ersson, 1968). With the doubled cell edge the ReO_3 structure contains eight voids which are occupied by Ca atoms in the perovskite ($CaTiO_3$) structure. The tilting of the ReO_6 octahedra reduces six of these voids: they become the centres of the rectangular As_4 or P_4 groups respectively (Fig. 2). The remaining two voids are greatly enlarged and are filled with W and La atoms in WAl_{12} and $LaFe_4P_{12}$.

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32698 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

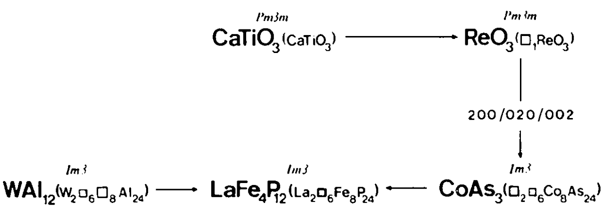

Fig. 3. Structural and space-group relations of $LaFe_4P_{12}$-related compounds. Chemical formulae in parentheses indicate the content of the cell. Vacant sites are indicated by squares.

Like $CoAs_3$ and WAl_{12}, the $LaFe_4P_{12}$-type structure has only two positional parameters. Thus, including the lattice 'constant', there are only three variables, which does not allow optimization of all interatomic distances and angles (Kjekshus, Nicholson & Rakke, 1973). Besides the condition for equal P—P bonding distances (Oftedal's relation: $y + z = \frac{1}{2}$), and the conditions for ideal octahedral ($y - 2yz = \frac{3}{8} - z$) and icosahedral ($y^2 = z^2 + yz$)[*] environment of the metal atoms, the distances between the metal and the P atoms need to be optimized. Some optimal configurations, *e.g.* the tetrahedral P—P—P angle, cannot be obtained at all. Only small changes in the positional parameters are required to go from CN = 11 (10 Al + 1 W) for Al in WAl_{12} to CN = 4 for P in the skutterudite phosphides TP_3. The TAs_3 and TSb_3 skutterudite compounds form the transition from localized bonds for P atoms to delocalized bonds for Al (Fig. 4).

Interatomic distances and angles

In $LaFe_4P_{12}$ the P—P distances of 2·288 and 2·356 Å are greater than the ideal value of 2·21 ± 0·02 Å (Jeitschko & Donohue, 1975). This is also true for the binary TP_3 skutterudite phases, but to a lesser extent (Rundqvist & Ersson, 1968). The Fe—P distance of 2·259 Å is equal to the average Fe—P distance in marcasite type FeP_2 (Dahl, 1969). The La—P distances in $LaFe_4P_{12}$ and LaP (Iandelli, 1964) are the same (3·01 Å) even though their CN's (12 and 6 respectively) are different. With a higher CN in $LaFe_4P_{12}$ larger La—P distances would be expected. Larger La—P distances were indeed found in LaP_2 (von Schnering, Wichelhaus & Schulze-Nahrup, 1975) and LaP_5 (Wichelhaus & von Schnering, 1976). In LaP_2 the La—P distances of three different LaP_9 polyhedra cover the range 2·955 (10) to 3·197 (10) Å with average distances of 3·047, 3·044, and 3·089 Å. The two independent La atoms in LaP_5 with (distorted) tetragonal antiprismatic coordination, have average La—P distances of 3·069 and 3·073 Å [range 2·989 (3) to 3·121 (2) Å]. It thus appears that thc icosahedral voids offered by the Fe_4P_{12} framework are somewhat too small for La. This explains also the long P—P distances: the P atoms with a P—P distance of 2·356 Å belong to the same LaP_{12} polyhedron; in the binary skutterudite compounds this distance has the expected length of about 2·22 Å. The distortions of the FeP_6 octahedra are also consistent with this rationalization: the P—Fe—P angle of 97·9° is formed by P atoms which belong to the coordination of the same La atom; *i.e.* deviations from ideal P—P bonding distances and ideal octahedral P—Fe—P angles are such that more room is obtained for the large La^{3+} ion.

These distortions should become smaller with the decreasing size of Ce, Pr, and Nd. However, when the Ln ions become too small, the holes of the Fe_4P_{12}

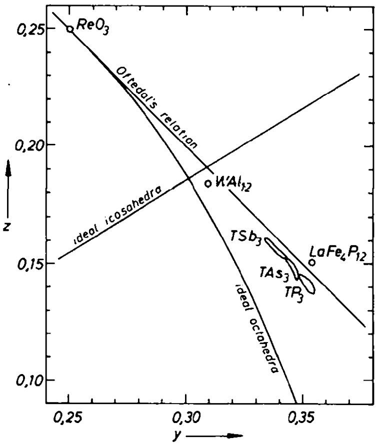

Fig. 4. Positional parameters for compounds with skutterudite and related structures.

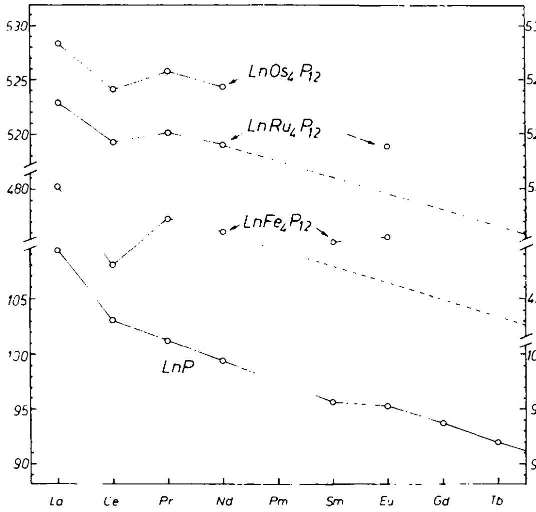

Fig. 5. Cell volumes of $LaFe_4P_{12}$-type compounds as compared with the volumes of lanthanoid phosphides with NaCl-type structure. All plotted volumes ($Å^3$) correspond to two lanthanoid atoms.

---

[*] This relation results when the P—P distances which correspond to 2·356 and 3·407 Å in $LaFe_4P_{12}$ are set equal.

framework are too large to obtain optimal bonding distances, and competing phases become more stable. This explains why we were not successful in preparing $LaFe_4P_{12}$-type compounds, where Ln = Gd or an even smaller Ln element. In the Ru and Os compounds the framework is even larger, which explains why we could prepare only $EuRu_4P_{12}$ and not $EuOs_4P_{12}$ or the corresponding compounds with Sm. The rigidity of the T_4P_{12} framework is also indicated by the relatively large volume of $CeRu_4P_{12}$ and $CeOs_4P_{12}$ compared with $CeFe_4P_{12}$ (Fig. 5).

Bonding

Binary skutterudite-type compounds are formed with all nine possible combinations of the elements Co, Rh, Ir with P, As and Sb (Kjekshus & Rakke, 1974; and references therein). In these compounds all near-neighbour interactions can be rationalized as two-electron bonds consistent with their diamagnetic and semiconducting behaviour (Hulliger, 1961). The only other well characterized compound with this structure is NiP_3 which has one more valence electron per formula unit and consequently shows metallic conductivity.

The small cell volume of $CeFe_4P_{12}$ suggests formal oxidation number IV for Ce and the formula can be written as $Ce^{4+}[Fe_4P_{12}]^{4-}$. In this formulation the polyanion $[Fe_4P_{12}]^{4-}$ ($\sim[FeP_3]^-$) is isoelectronic with CoP_3. In $LaFe_4P_{12}$, $EuFe_4P_{12}$, and $EuRu_4P_{12}$ where La^{3+} and Eu^{2+} can be assumed, the polyanions must be electron deficient.

When all bonding electrons are counted as belonging to P, the formula $Ce^{4+}Fe_4^{2+}[P_4]_3^{4-}$ results and thus Fe obtains d^6 configuration. The remaining two *d* functions participate in the d^2sp^3 hybrid which forms the bonds to the P atoms. In Fig. 6 we show a qualitative and simplified MO diagram for the polyanion $[FeP_3]^-$ in analogy with bonding models of pyrite type compounds (Bither, Bouchard, Cloud, Donohue & Siemons, 1968; Goodenough, 1971). Assuming the energy-level ordering is essentially as shown in the diagram, $CeFe_4P_{12}$ should be diamagnetic while $LaFe_4P_{12}$ should obtain d^5 configuration for one quarter of the Fe atoms.

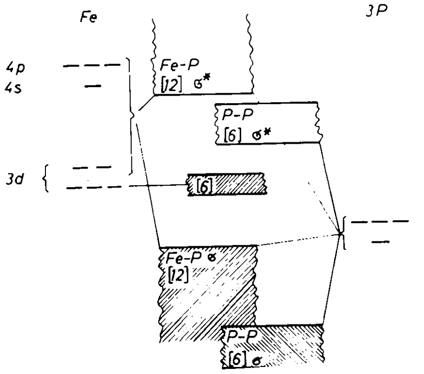

Fig. 6. Schematic MO energy-level diagram for the polyanion $[FeP_3]^-$ of the filled skutterudite compound $CeFe_4P_{12}$. Numbers in brackets refer to states per formula unit.

We have assumed sp^3 hybridization for P even though the P—P—P bonding angle is 90°. Bonding in the nearly quadratic P_4 groups is probably similar to cyclobutane where the angles between the bonding electrons are greater than the angles between the C atom nuclei (Harel & Hirshfeld, 1975).

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Dr M. Jansen for adapting several computer programs to the Giessen University computer centre and for supervising the single-crystal X-ray data collection.

References

Adam, J. & Rich, J. B. (1954). *Acta Cryst.* **7**, 813–816.

Bither, T. A., Bouchard, R. J., Cloud, W. H., Donohue, P. C. & Siemons, W. J. (1968). *Inorg. Chem.* **7**, 2208–2220.

Brauer, G. (1960). *Handbuch der Präparativen Anorganischen Chemie*. Stuttgart: Enke.

Corbridge, D. E. C. (1974). *The Structural Chemistry of Phosphorus*. Amsterdam: Elsevier.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Dahl, E. (1969). *Acta Chem. Scand.* **23**, 2677–2684.

Goodenough, J. B. (1971). *J. Solid State Chem.* **3**, 26–28.

Harel, M. & Hirshfeld, F. L. (1975). *Acta Cryst.* B**31**, 162–172.

Hulliger, F. (1961). *Helv. Phys. Acta*, **34**, 782–786.

Iandelli, A. (1964). *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.* **37**, 160–164.

Jeitschko, W. (1974). *MTP International Review of Science: Inorganic Chemistry, Series 2*, Vol. 5, pp. 219–281. London: Butterworths.

Jeitschko, W. & Donohue, P. C. (1975). *Acta Cryst.* B**31**, 575–580.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Jolibois, P. (1910). *C.R. Acad. Sci. Paris*, **150**, 106–108.

Kjekshus, A., Nicholson, D. G. & Rakke, T. (1973). *Acta Chem. Scand.* **27**, 1307–1314.

Kjekshus, A. & Rakke, T. (1974). *Acta Chem. Scand.* A**28**, 99–103.

Lundström, T. (1969). *Ark. Kem.* **31**, 227–266.

Oftedal, I. (1928). *Z. Kristallogr.* A**66**, 517–546.

RUNDQVIST, S. (1962). *Ark. Kem.* **20**, 67–113.
RUNDQVIST, S. & ERSSON, N.-O. (1968). *Ark. Kem.* **30**, 103–114.
SCHNERING, H. G. VON (1977). In *Homoatomic Rings and Chains*, edited by A. RHEINGOLD. Amsterdam: Elsevier. (In the press.)
SCHNERING, H. G. VON, WICHELHAUS, W. & SCHULZE-NAHRUP, M. (1975). *Z. anorg. allgem. Chem.* **412**, 193–201.
SHELDRICK, G. (1976). *SHELX* 76. Program system for crystal structure determination.
WICHELHAUS, W. & VON SCHNERING, H. G. (1976). *Z. anorg. allgem. Chem.* **419**, 77–86.
WILSON, A. (1971). *Supplement to Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 8, Suppl. 3, pp. 289–363. New York: John Wiley.
YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1977). *J. Appl. Cryst.* **10**, 73–74.

Acta Cryst. (1977). **B33**, 3406–3409

Y_3Ni_2: A New Tetragonal Phase with Ni-Centred Trigonal Prisms

BY JOËL LE ROY, JEAN-MICHEL MOREAU AND DOMINIQUE PACCARD

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 *quai Ernest Ansermet,*
CH-1211 *Genève* 4, *Switzerland and Centre Universitaire de Savoie, IUT Annecy et Laboratoire de Magnétisme,*
CNRS, Grenoble, France

AND ERWIN PARTHÉ

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 *quai Ernest Ansermet,*
CH-1211 *Genève* 4, *Switzerland*

(*Received* 6 *April* 1977; *accepted* 30 *April* 1977)

Y_3Ni_2 crystallizes with a new tetragonal structure type. Space group $P4_12_12$; a = 7·104 (1), c = 36·597 (5) Å, Z = 16, D_x = 5·52 g cm^{-3}, FW 384·1, $F(000)$ = 2768, μ(Mo $K\alpha$) = 463 cm^{-1}, R = 0·11. The structure is characterized by Ni-centred trigonal prisms of Y atoms. Always four prisms are joined to form a characteristic prism grouping which has been found before in the structure of Y_8Co_5. Y_3Ni_2 and Y_8Co_5 are members of a new structural series with formula $R_{2(n+1)}T_{n+2}$, where a block R_2T_2 (corresponding to a slice of the FeB type) is stacked with n blocks R_2T (corresponding to a slice of the As_2Nb or Ge_2Os type).

Introduction

Phase diagrams for the system Y–Ni have been published independently by Beaudry & Daane (1960) and by Domagala, Rausch & Levinson (1961). On the Y-rich side, two phases were reported on both diagrams: Y_3Ni with the Fe_3C type and Y_3Ni_2 with an unknown structure. Recently, compounds have been investigated in the rare-earth (R) rich part of the systems R–Ni and two new structure types have been discovered, corresponding to the same stoichiometry: rhombohedral Er_3Ni_2 (Moreau, Paccard & Gignoux, 1974) and monoclinic Dy_3Ni_2 (Moreau, Paccard & Parthé, 1974). In both types all Ni atoms are at the centres of trigonal prisms formed by R atoms. This crystallo-chemical feature appears in many other R–T (T = transition metal) structures (Parthé & Moreau, 1977) and it was of interest to determine whether or not the Y_3Ni_2 structure belongs to this family.

Experimental

The alloy was made from commercially available elements of high purity: Y 99·9%, Ni 99·99%. Samples were prepared by conventional arc melting techniques. Initial stoichiometries were such that the Ni content ranged from 35 to 45 at.%. X-ray photographs from powdered samples were obtained on a Guinier camera with Cu $K\alpha$ radiation. Small crystals suitable for X-ray analysis were isolated by mechanical fragmentation from the sample containing 40 at.% Ni. Weissenberg

Table 1. *Crystallographic data for* Y_3Ni_2

Space group $P4_12_12$	
a = 7·104 (1) Å	$F(000)$ = 2768
c = 36·597 (5)	D_x = 5·52 g cm^{-3}
Z = 16	μ(Mo $K\alpha$) = 463 cm^{-1}