

The Synthesis and Crystal Structure of the Polyphosphides $\text{La}_6\text{Ni}_6\text{P}_{17}$, $\text{Ce}_6\text{Ni}_6\text{P}_{17}$, and $\text{Pr}_6\text{Ni}_6\text{P}_{17}$

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The new compounds $\text{Ln}_6\text{Ni}_6\text{P}_{17}$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$) were prepared by annealing the elemental components in evacuated silica tubes. Single crystals were obtained by reaction of the components in molten tin at 900 K. They crystallize in the cubic system, space group $I43m$ (T_d^2), $Z = 2$, with lattice constants: $\text{La}_6\text{Ni}_6\text{P}_{17}$: $a = 10.168$ (1) Å; $\text{Ce}_6\text{Ni}_6\text{P}_{17}$: $a = 10.116$ (1) Å; $\text{Pr}_6\text{Ni}_6\text{P}_{17}$: $a = 10.073$ (1) Å. The structure was determined for $\text{La}_6\text{Ni}_6\text{P}_{17}$ from single-crystal counter data by Patterson and Fourier methods and refined to an R of 0.023 for 443 unique reflections. The structure of isotypic $\text{Ce}_6\text{Ni}_6\text{P}_{17}$ was refined to $R = 0.046$ for 419 reflections. Of the 17 P atoms per formula unit, 16 form trigonal-pyramidal P_4 groups. The remaining P atom is surrounded octahedrally by six Ln atoms. Ni has tetrahedrally distorted square-planar P coordination. The coordination of the Ln atom is unusual: nine P atoms form the main part of the coordination shell, and the remainder is formed by four Ni atoms, all at one side of the shell. The $\text{La}_6\text{Ni}_6\text{P}_{17}$ -type structure is closely related to the structure of tetrahedrite, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$. Bonding in these compounds is discussed within the framework of conventional bonding models. The Ni atoms in $\text{La}_6\text{Ni}_6\text{P}_{17}$ and its isotypic compounds, although in identical positions, have, at least on average, formal oxidation numbers of +1.5.

Introduction

Little is known about ternary phosphides. Recently we reported on $\text{LaFe}_4\text{P}_{12}$ and isotypic polyphosphides (Jeitschko & Braun, 1977). During the search for compounds with the $\text{LaFe}_4\text{P}_{12}$ -type structure, we have prepared samples with high P content in the systems lanthanoid(Ln)–Ni–P. We did not find compounds with the $\text{LaFe}_4\text{P}_{12}$ -type structure in these systems. However, in samples where $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$, we found polyphosphides of different composition. Their preparation and crystal structure are reported here.

Experimental

Synthesis

The starting materials for the sample preparation were ingots of La, Ce, and Pr (with stated purities higher than 99.9%), Ni powder (purity >99.9%) and red P (purity >98.5%) which was treated with boiling diluted NaOH (Brauer, 1975). Samples were prepared by several methods. One was the reaction of the components in evacuated silica tubes. For this purpose filings of the rare-earth elements, prepared and kept under Ar, were sealed in evacuated silica tubes with an equiatomic amount of red P, held at 950 K for 5 h and cooled. The product was then intimately mixed under Ar with the appropriate amounts of Fe and P and sealed again in evacuated silica tubes. Annealing times and temperatures varied. Typical conditions were 1 d at

1200 K followed by 7 d at 900 K. The products thus obtained were mostly microcrystalline.

Well-crystallized products were obtained by reaction of the elemental components in liquid tin (Jolibois, 1910). The Sn (purity >99.9%) content of the samples varied between 50 and 70 at.%. The single crystals of $\text{La}_6\text{Ni}_6\text{P}_{17}$ and $\text{Ce}_6\text{Ni}_6\text{P}_{17}$ used for the structure determination and refinement were taken from samples which were annealed for 1 week at 900 K. After the heat treatment, the tin matrix was dissolved in moderately dilute (1:1) hydrochloric acid, which did not greatly affect the crystals of the new compounds.

After we had determined and analyzed the unusual features of the structure, we considered the possibility that impurities like Si or Fe might possibly stabilize these compounds. We therefore prepared another sample of $\text{La}_6\text{Ni}_6\text{P}_{17}$ by reaction of the elemental components using semiconductor-grade red P (Knapsack–Hoechst). To avoid contamination with Si, the reaction was carried out in a closed alumina vessel, sealed under vacuum in a silica tube. The sample was annealed for 1 d at 1250 K, followed by 7 d at 900 K. After this treatment, X-ray powder photographs showed the product to be about 90% single-phase $\text{La}_6\text{Ni}_6\text{P}_{17}$. The remaining lines could be ascribed to LaP (NaCl type) and NiP_3 (CoAs_3 type). We therefore concluded that impurities, like Si or Fe, are not important in the formation of $\text{La}_6\text{Ni}_6\text{P}_{17}$. The possibility of accommodating O at interstitial sites is discussed below.

Lattice constants

X-ray powder diffraction patterns were recorded with a Guinier-Johansson camera of Enraf-Nonius-Delft design, using α -quartz ($a = 4.91304$, $c = 5.40463$ Å) as standard. They were indexed on the basis of a body-centered-cubic cell, which was refined by a least-squares treatment of the data.

The composition of the new compound as determined through the structure refinement is $\text{La}_6\text{Ni}_6\text{P}_{17}$. To obtain an indication for possible homogeneity ranges, lattice constants were refined for $\text{La}_6\text{Ni}_6\text{P}_{17}$ samples, prepared by a great variety of conditions and greatly varying overall composition. Typical compositions, where the $\text{La}_6\text{Ni}_6\text{P}_{17}$ pattern was observed, varied between $\text{La}:\text{Ni}:\text{P} = 1:3:10$ and $4:1:10$. In samples prepared by the Sn flux method, $\text{La}_6\text{Ni}_6\text{P}_{17}$ crystals were isolated from ingots with overall compositions $\text{La}:\text{Ni}:\text{P}:\text{Sn}$ of $1:1:8:20$ and $3:1:6:10$. The resulting lattice constants cover the range from 10.167 to 10.172 Å with standard deviations all somewhat less than 0.001 Å. No systematic correspondence of lattice parameter and composition was observed and we conclude that $\text{La}_6\text{Ni}_6\text{P}_{17}$ has only a very small homogeneity range. The lattice constant of the sample prepared from the high-purity elemental components in an alumina container was within the range given above. The $\text{La}_6\text{Ni}_6\text{P}_{17}$ crystals used for the structure determination, taken from a sample with overall composition $\text{La}:\text{Ni}:\text{P}:\text{Sn} = 1:1:8:20$, had a lattice constant of $a = 10.168$ (1) Å.

The lattice constant for $\text{Ce}_6\text{Ni}_6\text{P}_{17}$ is $a = 10.116$ (1) Å and for $\text{Pr}_6\text{Ni}_6\text{P}_{17}$, $a = 10.073$ (1) Å. The isotypism of $\text{Pr}_6\text{Ni}_6\text{P}_{17}$ is evident from its powder pattern (Table 1).

Space group and crystal data

Burger precession and Weissenberg diffraction patterns of $\text{La}_6\text{Ni}_6\text{P}_{17}$ and $\text{Ce}_6\text{Ni}_6\text{P}_{17}$ crystals confirmed the body-centered cell with Laue symmetry $m\bar{3}m$. No additional extinctions were present. Thus space groups

Table 1. Powder pattern of $\text{Pr}_6\text{Ni}_6\text{P}_{17}$

For the calculated intensities (Yvon, Jeitschko & Parthé, 1977) the positional parameters obtained in the single-crystal study of $\text{Ce}_6\text{Ni}_6\text{P}_{17}$ were assumed (Guinier camera, $\text{Cu } K\alpha$ radiation).

hkl	d_c	I_c	I_o	hkl	d_c	I_c	I_o	hkl	d_c	I_c	I_o
110	7.1230	1	-	440	1.7808	51	s	633	12	12	-
200	5.0367	11	vw	530	1.7276	2	m	552	1.3708	36	-
211	4.1125	21	w	442	1.6789	3	vw	721	1.3461	4	-
220	3.5615	15	w	600	1.6341	2	vw	642	1.3461	2	-
310	3.1855	48	s	532	1.5928	<1	-	730	1.3227	35	-
222	2.9080	100	vvs	611	1.5544	15	w	732	1.2793	18	-
321	2.6922	4	vvs	620	1.5186	64	vs	651	1.2592	3	-
400	2.5184	87	vvs	541	1.4853	11	vw	800	1.2400	6	-
330	2.3743	56	vvs	631	1.4540	19	w	811	1.2216	11	-
411	2.2525	12	w	710	1.4246	2	w	820	1.2040	3	-
420	2.2525	12	w	543	1.4246	2	w	822	1.1872	25	-
332	2.1477	10	vw	550	1.3969	16	w	660	1.1872	<1	-
422	2.0562	24	m								
431	1.9756	13	w								
510	1.8392	30	m								
521	1.8392	30	m								

$I\bar{4}32$, $I\bar{4}3m$, and $Im\bar{3}m$ were possible, of which $I\bar{4}3m$ was found to be correct during the structure determination.

The $\text{La}_6\text{Ni}_6\text{P}_{17}$ crystal used for the collection of the intensity data on an automated four-circle diffractometer was an approximate cube, with the corners and edges cut off. All reflections within one octant, up to $(\sin \theta)/\lambda = 1.0$ Å⁻¹, were measured, with graphite-monochromated $\text{Mo } K\alpha$ radiation, a scintillation counter, and a pulse-height discriminator. The θ - 2θ technique was used, with a scan speed of 0.04° (2θ) s⁻¹ and a scan angle of 1.5° (2θ). Background was counted at both ends of the scans for 19 s. Equivalent reflections were averaged. For the purpose of the absorption correction the shape of the $\text{La}_6\text{Ni}_6\text{P}_{17}$ crystal was approximated by a sphere [$\mu(\text{Mo } K\alpha) = 176$ cm⁻¹, $\mu_r = 1.05$]. The calculated density of $\text{La}_6\text{Ni}_6\text{P}_{17}$ is $\rho = 5.41$ g cm⁻³ for two formula units in the body-centered cell.

Data for the refinement of the structure for $\text{Ce}_6\text{Ni}_6\text{P}_{17}$ were collected under similar conditions and a similar absorption correction ($\mu_r = 0.75$) was applied.

Structure determination and refinements

The structure was solved and refined for $\text{La}_6\text{Ni}_6\text{P}_{17}$ with a program system by Sheldrick (1976). Although at the outset the composition of the crystals was not known, it was possible to obtain probable locations for the La and Ni atoms in space group $I\bar{4}3m$ from an inter-

Table 2. Positional and isotropic thermal parameters of $\text{La}_6\text{Ni}_6\text{P}_{17}$ and $\text{Ce}_6\text{Ni}_6\text{P}_{17}$

For comparison, parameters of tetrahedrite, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, as obtained by Wuensch (1964), are also listed. Numbers in parentheses are e.s.d.'s in the least significant digits.

	$I\bar{4}3m$	x	y	z	B (Å ²)
$\text{La}_6\text{Ni}_6\text{P}_{17}$					
La	12(e)	0.28997 (3)	0	0	0.36 (1)
Ni	12(d)	$\frac{1}{4}$	$\frac{1}{2}$	0	0.40 (1)
P(1)	24(g)	0.20148 (9)	x	0.43226 (13)	0.34 (2)
P(2)	8(c)	0.21483 (12)	x	x	0.37 (3)
P(3)	2(a)	0	0	0	0.46 (5)
$\text{Ce}_6\text{Ni}_6\text{P}_{17}$					
Ce	12(e)	0.28934 (6)	0	0	0.36 (2)
Ni	12(d)	$\frac{1}{4}$	$\frac{1}{2}$	0	0.37 (2)
P(1)	24(g)	0.2021 (2)	x	0.4323 (3)	0.27 (3)
P(2)	8(c)	0.2147 (3)	x	x	0.36 (5)
P(3)	2(a)	0	0	0	0.47 (9)
$\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$					
Cu(2)	12(e)	0.2150 (5)	0	0	4.19
Cu(1)	12(d)	$\frac{1}{4}$	$\frac{1}{2}$	0	1.19
S(1)	24(g)	0.1152 (3)	x	0.3609 (5)	1.23
Sb	8(c)	0.2682 (1)	x	x	1.11
S(2)	2(a)	0	0	0	1.14

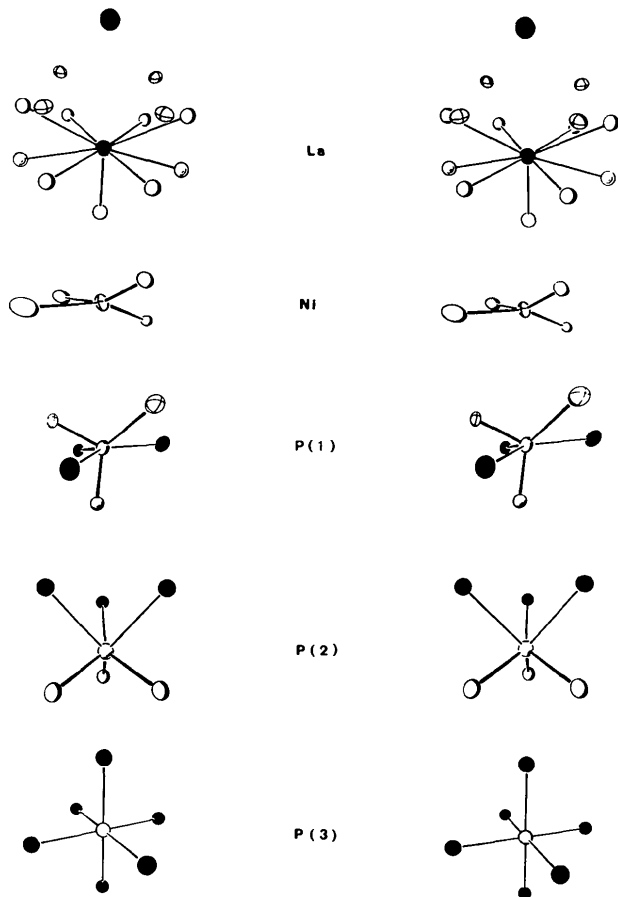


Fig. 1. Stereodrawings of near-neighbor coordinations in $\text{La}_6\text{Ni}_6\text{P}_{17}$, (ORTEP, Johnson, 1965).

pretation of the Patterson function. The P atoms were located on difference Fourier maps.

The structure was refined with a full-matrix least-squares program using atomic scattering factors for neutral atoms (Cromer & Liberman, 1970). Weights were assigned according to $w = 1/(\sigma^2 + kF_o^2)$, where k is a parameter in the refinement. An isotropic extinction parameter $x = 5.5 \times 10^{-7}$ was applied, where F_o is multiplied by $(1 - xF_o^2/\sin \theta)$. The final conventional R is 0.023 for 443 unique structure factors excluding the seven strong reflections most severely affected by extinction and the 37 reflections with $F_o < 6\sigma$, some of which were judged to be affected by double diffraction. For all 487 reflections the R value is 0.055.

To test the possible deviations from full occupancy of the La positions, several least-squares cycles were calculated where the occupancy of this position was allowed to vary. It refined to a value of 1.020 ± 0.006 and thus it can be assumed that this position is fully occupied.

A final difference Fourier map for the $\text{La}_6\text{Ni}_6\text{P}_{17}$ data shows only unextended ripples with values between -2.5 and $+2.3 \text{ e } \text{\AA}^{-3}$. Most of these are associated with the positions of the atomic nuclei. In particular there are no significant features in the space around position 6(b) $(0, \frac{1}{2}, \frac{1}{2})$ which is surrounded by La and Ni atoms as closest 'neighbors'. The highest electron density value in that cavity – except for positions very close to the nuclei of La and Ni – is $+1.3 \text{ e } \text{\AA}^{-3}$. This value is found within 0.2 \AA of the position $0, \frac{1}{2}, \frac{1}{2}$. However, since negative values are also close by, the integration over one cube with an edge of 1 \AA centered at that position resulted in a value of less than 0.05 e within that cube. Thus we could not find any evidence

Table 3. *Interatomic distances (Å) and selected interatomic angles (°) in $\text{La}_6\text{Ni}_6\text{P}_{17}$ and $\text{Ce}_6\text{Ni}_6\text{P}_{17}$*

All metal–metal and metal–P distances shorter than 3.5 \AA are listed. Non-bonding P–P distances are all greater than 3.1 \AA . Standard deviations are all less than 0.002 \AA and 0.1° for $\text{La}_6\text{Ni}_6\text{P}_{17}$, and less than 0.004 \AA and 0.2° for $\text{Ce}_6\text{Ni}_6\text{P}_{17}$.

	$\text{La}_6\text{Ni}_6\text{P}_{17}$	$\text{Ce}_6\text{Ni}_6\text{P}_{17}$		$\text{La}_6\text{Ni}_6\text{P}_{17}$	$\text{Ce}_6\text{Ni}_6\text{P}_{17}$	
Ln–1 P(3)	2.949	2.927	P(1)–Ni–P(1)	92.8	92.8	(4×)
4 P(1)	3.113	3.092	P(1)–Ni–P(1)	154.3	154.7	(2×)
2 P(2)	3.182	3.163	Ni–P(1)–Ni	108.3	108.0	(1×)
2 P(1)	3.239	3.233	Ni–P(1)–P(2)	110.6	110.5	(2×)
4 Ni	3.320	3.307	P(1)–P(2)–P(1)	96.8	96.4	(3×)
Ni–4 P(1)	2.217	2.210	Ln–P(2)–Ln	81.9	81.7	(3×)
4 Ln	3.320	3.307	Ln–P(2)–P(1)	71.1	71.5	(3×)
P(1)–2 Ni	2.217	2.210	Ln–P(2)–P(1)	131.0	131.2	(6×)
1 P(2)	2.220	2.208	Ln–P(3)–Ln	90.0	90.0	(12×)
2 Ln	3.113	3.092	Ln–P(3)–Ln	180.0	180.0	(3×)
1 Ln	3.239	3.233				
P(2)–3 P(1)	2.220	2.208				
3 Ln	3.182	3.163				
P(3)–6 Ln	2.949	2.927				

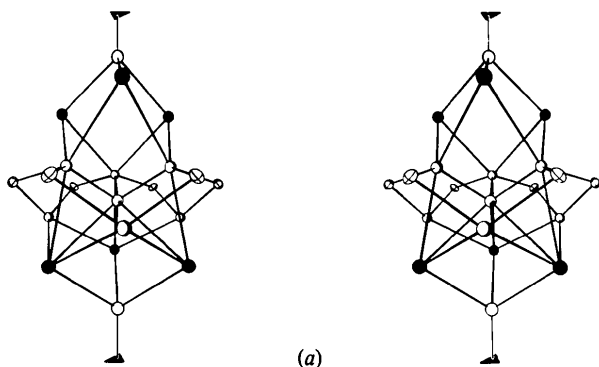


Fig. 2. Stereoplots of partial structures in $\text{La}_6\text{Ni}_6\text{P}_{17}$. (a) The atomic arrangement around a threefold axis.

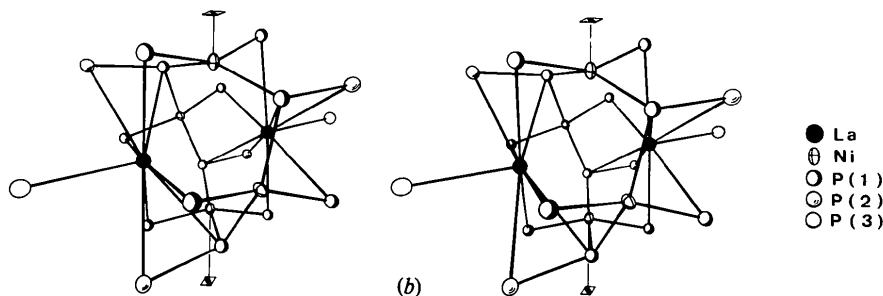


Fig. 2 (cont.). (b) The environment of the vacant site at $(0, \frac{1}{2}, \frac{1}{2})$.

for scattering matter in the cavity formed by this octahedral arrangement of four Ni and two La atoms.

The structure refinement of $\text{Ce}_6\text{Ni}_6\text{P}_{17}$ was carried out in a similar way to the refinement of $\text{La}_6\text{Ni}_6\text{P}_{17}$. The final conventional R is 0.046 for 419 reflections* excluding the four reflections most strongly affected by secondary extinction and the seven reflections with $F_o < 3\sigma$.

Final positional and thermal parameters are listed in Table 2. Drawings of the structure and near-neighbor environments are given in Figs. 1, 2 and 3, and Table 3.

Discussion

Formally the structure of $\text{La}_6\text{Ni}_6\text{P}_{17}$ may be considered as isotypic with binnite, $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ (Pauling & Neuman, 1934; Wuensch, Takéuchi & Nowacki, 1966), and tetrahedrite, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ (Wuensch, 1964), with an ordered distribution of La and Ni atoms on the two Cu sites, and P atoms at the As(Sb) and S

positions. Due to the differing space and bonding requirements, however, the positional parameters of $\text{La}_6\text{Ni}_6\text{P}_{17}$ differ greatly from those of $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$. Thus, while the structure of the copper compounds can be described as a superstructure of sphalerite with a doubled cell edge, due to ordering, vacancy formation, and filling of sites not occupied in sphalerite, the $\text{La}_6\text{Ni}_6\text{P}_{17}$ structure has no resemblance to a tetrahedral structure. In fact, all positional parameters are equal or close to 0, $\frac{1}{4}$, $\frac{1}{2}$, or $\frac{3}{4}$, and therefore the structure can be derived from a primitive cubic lattice with a fourfold cell edge, where all atoms are located on or close to 58 of the 64 cube corners. The six unoccupied corners correspond to positions 6(b) at $0, \frac{1}{2}, \frac{1}{2}$ etc. of space group $I43m$. The 'ideal'

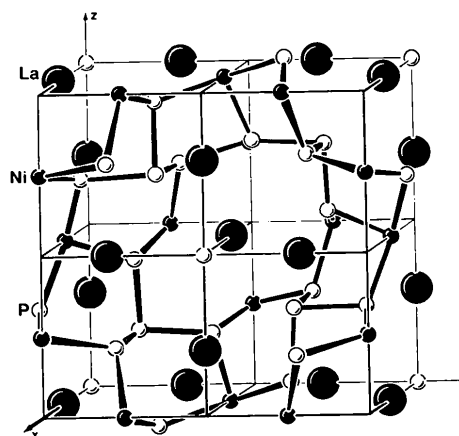


Fig. 3. Crystal structure of $\text{La}_6\text{Ni}_6\text{P}_{17}$. Four octants of the body-centered-cubic cell are shown. Heavy lines correspond to two-electron bonds in conventional bonding models.

structure with all positional parameters equal to 0, $\frac{1}{4}$, $\frac{1}{2}$, or $\frac{3}{4}$ has symmetry $Im3m$.

The large differences between the structure of $\text{La}_6\text{Ni}_6\text{P}_{17}$ and the structures of tetrahedrite and related minerals are best seen in the differing coordinations of the metal atoms. Thus, while the Cu(2) atoms in

* Lists of structure factors and anisotropic thermal parameters for $\text{La}_6\text{Ni}_6\text{P}_{17}$ and $\text{Ce}_6\text{Ni}_6\text{P}_{17}$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33409 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$\text{Cu}_{12}\text{As}_4\text{S}_{13}$ (and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$), which correspond to the La atoms in $\text{La}_6\text{Ni}_6\text{P}_{17}$, have only three S atoms as close neighbors, the coordination of the La atoms in $\text{La}_6\text{Ni}_6\text{P}_{17}$ is quite different and unusual in that La has nine P neighbors as one side of its coordination shell. The four Ni at 3.32 Å and the one La at 4.27 Å, at the other side, completing the shell, are somewhat further away than the sum of their metallic radii for CN 12 (3.12 and 3.75 Å respectively) and thus at least to a first approximation can be considered as not bonded to the La atom. The La–P distances cover the range from 2.95 to 3.24 Å and are similar to those in LaP_2 , LaP_5 , and LaP_7 (von Schnering, Wichelhaus & Schulze-Nahrup, 1975; Wichelhaus & von Schnering, 1975, 1976).

The other Cu atoms in $\text{Cu}_{12}\text{As}_4\text{S}_{13}$, which correspond to Ni in $\text{La}_6\text{Ni}_6\text{P}_{17}$, are coordinated by four S atoms forming an almost perfect tetrahedron. In contrast, the P atoms surrounding Ni in $\text{La}_6\text{Ni}_6\text{P}_{17}$ form a tetrahedrally distorted square. A square-planar environment is very common for Ni^{II} ; however, examples of tetrahedral and square-planar coordination are known for both Ni^I and Ni^{II} (Fergusson, 1974). In NiP_2 , where Ni^{II} has square-planar P coordination, the Ni–P distances are 2.205 and 2.208 Å (Larsson, 1965) and are thus only slightly shorter than the distances of 2.217 Å in $\text{La}_6\text{Ni}_6\text{P}_{17}$.

The P(1) and P(2) atoms are linked together to form P_4 groups with P(2) at the apex of a trigonal pyramid and three P(1) atoms at the base. The P(1)–P(2) distances of 2.22 Å are within the range of 2.21 ± 0.02 Å which is typical for two-electron P–P bonds (Jeitschko, 1974; Jeitschko & Donohue, 1975, and references therein). In addition to the bond to P(2), the P(1) atoms form two bonds to Ni. Therefore, to a first approximation both the P(1) and P(2) atoms can be assumed to be sp^3 hybridized with three short neighbors and a lone pair of electrons as the fourth 'ligand'. In both coordinations the lone pairs point at least approximately towards other P atoms which, however, are all further away than 3.1 Å. The P(3) atoms do not have close P neighbors and are coordinated octahedrally by six La. In view of the large electronegativity difference between La and P, the P(3) atoms may be regarded as P^{3-} anions.

Assigning formal oxidation numbers in the usual manner by counting the bonding electrons of the Ni–P bonds as belonging to P, the P_4 groups become $[\text{P}_4]^{6-}$ polyanions. In this way, in the formula $\text{La}_6\text{Ni}_6\text{P}_{17}$ a total of 27 negative charges could be counted as belonging to the P atoms. The formula can then be written as $\text{La}_6^{3+}\text{Ni}_3^{2+}\text{Ni}_3^{1+}[\text{P}_4]_4^{6-}\text{P}^{3-}$ or $\text{La}_6^{3+}\text{Ni}_6^{1.5+}[\text{P}_4]_4^{6-}\text{P}^{3-}$, indicating that roughly the Ni atoms, although all with equal environments, are either in two different oxidation states (d^8 and d^9 configuration) or have a fractional oxidation number. The latter could be achieved by partial filling of Ni–P–Ni bonding states or

through metal–metal interactions. Without further physical data any discussion of this point remains speculative.

In this context it is interesting that a similar account of bonding electrons in $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ (and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) also leads to mixed or fractional oxidation numbers for the Cu atoms, and the formula can be written $\text{Cu}_{10}^{1+}\text{Cu}_2^{2+}[\text{SbS}_3]_4^{3-}\text{S}^{2-}$. Naturally occurring specimens contain impurities of divalent metals *M*, like Zn^{2+} or Fe^{2+} , and the average formula is better represented by $\text{Cu}_{10}\text{M}_2\text{Sb}_4\text{S}_{13}$ (Machatschki, 1928; Pauling & Neuman, 1934). Accordingly, synthetic $\text{Cu}_{12}\text{As}_4\text{S}_{12.7}$ and $\text{Cu}_{12}\text{Sb}_4\text{S}_{12.7}$ are paramagnetic while $\text{Cu}_{10}\text{Zn}_2\text{Sb}_4\text{S}_{13}$ is diamagnetic (Kiriyama, 1977). Large thermal amplitudes of the Cu atoms in these compounds indicate good ionic conductivity (Makovicky & Skinner, 1976). This property is not expected for the $\text{La}_6\text{Ni}_6\text{P}_{17}$ type compounds.

A somewhat unusual feature in the structure of $\text{La}_6\text{Ni}_6\text{P}_{17}$ is the 'hole' centered at position 6(*b*) ($0, \frac{1}{2}, \frac{1}{2}$). This site is 'coordinated' by a square of Ni atoms at 2.54 Å and two La atoms at 2.14 Å completing a compressed octahedron. In view of the fractional oxidation number of Ni, we considered the possibility that small impurity atoms might occupy this position. If this site were half-filled with O, the oxidation number of Ni would increase to +2. Since this would raise the density by only 1.4%, it is difficult to prove or disprove the filling of this site by density measurements. Interatomic distances, however, are not favorable for the placement of O in this position. Commonly-found La–O distances are 2.5 to 2.6 Å depending on the coordination number (Shannon, 1976), and thus are considerably greater than the distances of 2.14 Å available in the structure. Even if the O atoms were placed somewhat off-center, closer to the Ni atoms, optimal bonding distances cannot be obtained. As was emphasized in the previous section, the difference Fourier map also failed to give any indication for impurity atoms in this cavity. Nevertheless, small amounts (in our estimate up to at most 15% occupancy for O) cannot be excluded by our experimental data.

Even though the octahedral void formed by the two La and four Ni atoms is unusual, it can be rationalized as being filled by the non-bonding d_{z^2} electrons of the (nearly) square-planar coordinated Ni atoms. In this way the four 'lone pairs' of electrons of the four Ni atoms reduce the repulsion of the two La^{3+} ions in much the same way as an oxygen ion placed in that cavity. The large space requirements of non-bonding (inert, lone) electron pairs are well known for the main-group elements in their lower oxidation state (Andersson & Åström, 1972).

The refinement of $\text{Ce}_6\text{Ni}_6\text{P}_{17}$ led to positional parameters very similar to those of $\text{La}_6\text{Ni}_6\text{P}_{17}$. Slight differences in the thermal parameters probably result from errors in the intensity data due to absorption

effects. The Ce—P distances are only slightly shorter than the corresponding distances in $\text{La}_6\text{Ni}_6\text{P}_{17}$, which indicates that Ce is in its trivalent state.

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The O—H vs O...O Distance Correlation, the Geometric Isotope Effect in OHO Bonds, and Its Application to Symmetric Bonds

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On the basis of recent accurate crystal-structure data, the correlation between O—H and O...O distances and the geometric isotope effect in OHO bonds have been investigated. The average correlation curve of asymmetric bonds appears to coincide with that of symmetric bonds only at the shortest limit of O...O length, around 2.4 Å. On deuteration an expansion can be seen in the O...O distance range 2.44–2.64 Å, with a maximum value of 0.027 Å. Factors smearing the correlation are discussed. The equilibrium position of H in symmetric bonds is considered using the correlation curve of O—H vs O...O distance and the geometric isotope effect as an empirical basis, under the assumption that the potential curve can be expressed as the superposition of two asymmetric bonds. The isotope effect on the distance between the two equilibrium positions is discussed in connexion with an anomalous isotope effect on the transition temperature of hydrogen-bonded crystals which undergo ferro-, antiferroelectric, and other structural phase transitions.

Introduction

It is well known that there exist some correlations between hydrogen-bond parameters; as Nakamoto, Margoshes & Rundle (1955) have pointed out, the

O—H bond length decreases with increasing O...O distance (Iwasaki, Iwasaki & Saito, 1967; Hamilton & Ibers, 1968; Pimentel & McClellan, 1971; Speakman, 1972). However, it seems that the details of the correlation remain uncertain in the short and very short