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The Rare Earth Silicon Phosphides $LnSi_2P_6$ (Ln = La, Ce, Pr, and Nd)

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The title compounds were prepared in well-crystallized form from a tin flux and their crystal structure was determined from single-crystal diffractometer data of $LaSi_2P_6$: $Cmc2_1$, a = 1012.9(3) pm, b = 2817.5(7) pm, c = 1037.4(5) pm, Z = 16, R = 0.034 for 3303 structure factors and 181 variable parameters. The structure of the isotypic compound $CeSi_2P_6$ was also refined from single-crystal X-ray data: a = 1011.8(4) pm, b = 2803.1(8) pm, c = 1031.1(4) pm, R = 0.035 for 2132 F values and 181 variables. The silicon and the phosphorus atoms could be distinguished by comparing their occupancy parameters obtained from both structure refinements. The assignments agree with those deduced by structure-chemical arguments. These atoms form a three-dimensionally infinite framework polyanion, which accommodates four different kinds of rare earth atoms: three with nine and one with ten phosphorus neighbors. The silicon atoms are all in tetrahedral phosphorus coordination. There are phosphorus atoms which have only two rare earth and two silicon neighbors, but most phosphorus atoms have—in addition to the rare earth and silicon atoms—phosphorus neighbors, thus forming P_3, P_4, P_5, and P_6 units. Using oxidation numbers, the compounds can be rationalized with the formulas $Ln^{3+}(Si_2P_6)^{3-}$ and $Ln^{3+}(Si^{4+})_2(P_6)^{11-}$, where the octet rule is obeyed for the silicon and phosphorus atoms and two electrons are counted for each Si-P and P-P interaction. © 1996 Academic Press, Inc.

INTRODUCTION

Ternary compounds of the rare earth elements with silicon and phosphorus were first prepared some years ago. Three series of compounds are recognized (1–3), the isotypic series $LnSiP_3$ (Ln = Ce, Pr, Nd, and Sm) being the best-characterized. Their crystal structure has been determined for $CeSiP_3$ (3). The compounds of the other two series have been characterized by their X-ray powder patterns, and the lattice constants of several have been communicated. In the course of our investigations of ternary metal silicon phosphides we have recently reported on $NiSi_2P_3$ (4) and Cu_4SiP_8 (5). In $NiSi_2P_3$ the nickel and silicon atoms have only phosphorus neighbors, and there are no phosphorus–phosphorus bonds. In contrast, the structure of Cu_4SiP_8 contains Cu_2 pairs and a three-dimensionally infinite silicon phosphorus polyanion. In $CeSiP_3$ (3) the cerium atoms are coordinated by nine phosphorus atoms, the silicon atoms have tetrahedral phosphorus coordination, and some phosphorus atoms have—in addition to cerium and silicon neighbors—also phosphorus neighbors, thus forming infinite phosphorus chains.

Ono *et al.* (2) have reported on the preparation of the compounds $LnSi_2P_6$ (Ln = La, Ce, Pr). Their X-ray powder patterns were indexed on the basis of a C centered orthorhombic cell. We have been successful in growing single crystals of the lanthanum and cerium compounds of these series from a tin flux, and we now report their structure, which is notable for the presence of four different phosphorus polyanions. In addition, we have prepared the new isotypic compound $NdSi_2P_6$.

SAMPLE PREPARATION AND LATTICE CONSTANTS

The samples were prepared by the tin flux technique. Starting materials were filings of the rare earth metals (Kelpin, 99.9 %), silicon powder (≥99.9%), red phosphorus (Hoechst, "ultrapure"), and granules of tin (Merck, 99.9%). The elements, in the atomic ratio Ln : Si : P : Sn = 1 : 2 : 15 : 36, were sealed in evacuated silica tubes and annealed for 1 day at 450°C, 1 day at 700°C, and finally 2 weeks at 800°C. After quenching in air, the tin-rich matrix was dissolved in diluted (1 : 1) hydrochloric acid, which leaves the crystals of the ternary compounds nearly unattacked.

Well-crystallized samples of the ternary lanthanoid silicon phosphides are shiny gray, like crystals of silicon; the powders are black. They are stable in air for long periods of time. Energy-dispersive X-ray fluorescence analyses of the ternary compounds in a scanning electron microscope showed the average atomic ratio Ln : Si : P = 1 : 2.1 : 6.1 (Ln = La, and Ce) and no impurity elements heavier than sodium.

The earlier reported C centered orthorhombic lattice of these compounds (2) was confirmed. To ensure proper indexing the observed X-ray powder patterns were com-

TABLE 1
Lattice Constants of the Compounds *Ln*Si$_2$P$_6$ (*Ln* = La, Ce, Pr, and Nd)[a]

Compound	*a* (pm)	*b* (pm)	*c* (pm)	*V*(nm^3)
LaSiP$_6$	1012.9(3)	2817.5(7)	1037.4(5)	2.961
CeSi$_2$P$_6$	1011.8(4)	2803.1(8)	1031.1(4)	2.924
PrSi$_2$P$_6$	1008.8(5)	2794.9(8)	1026.7(4)	2.895
NdSi$_2$P$_6$	1003.1(3)	2780.5(8)	1024.5(5)	2.857

[a] Standard deviations in the values of the last listed digits are given in parentheses throughout this paper.

pared with those calculated (6), the latter having been generated using the positional parameters of the refined structures. The orthorhombic lattice constants (Table 1) were refined by least-squares fits of the Guinier powder data using α-quartz (a = 491.30 pm, c = 540.46 pm) as an internal standard. They are slightly smaller than those reported earlier (Fig. 1).

STRUCTURE DETERMINATION

Single crystals of LaSi$_2$P$_6$ and CeSi$_2$P$_6$ were investigated with a precession camera to establish their symmetry and suitability for the data collection. Intensity data were collected on an Enraf–Nonius CAD-4 single-crystal diffractometer with graphite-monochromated Mo$K\alpha$ radiation, a scintillation counter with a pulse-height discriminator, and background counts at both sides of each $\theta/2\theta$ scan. An absorption correction was applied on the basis of psi scan data. The intensity distribution suggested the crystal class *mm*2 and the space group extinctions led to the non-centrosymmetric space group *Cmc*2$_1$ (No. 36). The other two space groups with these extinctions—*Cmcm* (No. 63) and *C*2*cm* (a nonstandard setting of *Ama*2)—could definitely be ruled out during the structure refinements.

The stucture was solved from Patterson and difference Fourier syntheses (7) and refined by a full-matrix least-squares program (8) using atomic scattering factors (9), corrected for anomalous dispersion (10). The weighting scheme was based on the counting statistics, and a parameter correcting for secondary extinction was optimized during the least-squares refinements. The crystallographic data of LaSi$_2$P$_6$ and CeSi$_2$P$_6$ and some results are summarized in Table 2.

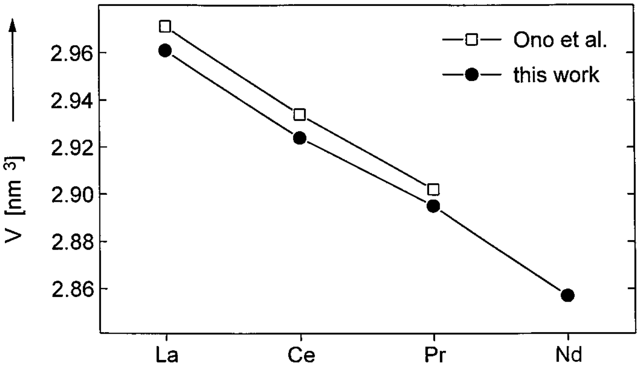

FIG. 1. Cell volumes of LaSi$_2$P$_6$ type compounds. The presently found values are compared to those reported by Ono *et al.* (2).

We have recently reported on the compounds NiSi$_2$P$_3$ (4) and Cu$_4$SiP$_8$ (5), where the correct atom distribution for the silicon and phosphorus atoms was initially based on chemical arguments. Nevertheless, somewhat to our surprise, it was also possible to distinguish the silicon and phosphorus atoms on the basis of their scattering factors, even though these elements differ by only one electron. This was also the case for the structure refinements of LaSi$_2$P$_6$ and CeSi$_2$P$_6$, especially if one assumes that the atom distribution in both compounds should be analogous. In Fig. 2 we show the results of the refinements of the occupancy parameters of the silicon and phosphorus positions. For the atom distributions that were deduced from chemical arguments, we obtained occupancy parameters between 96.0(9) and 101.1(9)% for the silicon atoms of both compounds, and between 97.5(8) and 102.7(6)% for the phosphorus atoms. In contrast, for the inverse occupancies (P on Si positions and Si on P positions) the occupancy values varied between 91.0(9) and 96.1(9)% for the silicon positions, and between 102.5(8) and 108.1(7)% for the phosphorus positions. These results were obtained by simultaneous refinements of occupancy and anisotropic thermal parameters. This was possible because both data sets were collected up to the relatively high 2θ value of 65°.

For the final refinements the ideal occupancy parameters were assumed. The final conventional residuals (on F values) are 0.034 and 0.035 for the lanthanum and the cerium compounds, respectively. These values were obtained for the correct polarity of the acentric structures. For the wrong polarity the R values were 0.046 for both compounds. The atomic positions of the crystals used for the structure refinements of the two compounds had opposite handedness. The positional parameters for LaSi$_2$P$_6$ listed in Table 3 were standardized by the program STRUCTURE TIDY (11). Those obtained from the refinement of the CeSi$_2$P$_6$ structure were converted to the other polarity to make them comparable to those of the lanthanum compound. The interatomic distances are listed in Table 4 and a stereoplot of the LaSi$_2$P$_6$ structure is shown in Fig. 3.

DISCUSSION

The four compounds *Ln*Si$_2$P$_6$ (*Ln* = La–Nd) crystallize in a new structure type. The silicon and phosphorus atoms form a three-dimensionally infinite framework polyanion

TABLE 2
Crystal Data for $LaSi_2P_6$ and $CeSi_2P_6$

	$LaSi_2P_6$	$CeSi_2P_6$
Lattice constants	see Table 1	see Table 1
Space group	$Cmc2_1$	$Cmc2_1$
Formula units/cell	$Z = 16$	$Z = 16$
Formula weight	380.9	382.1
Calculated density (g/cm^3)	3.42	3.47
Crystal dimensions (μm)	70 × 50 × 30	60 × 20 × 10
$\theta/2\theta$ scans up to	$2\theta = 65°$	$2\theta = 65°$
Range in h, k, l	±14, 0–42, ±15	±14, 0–39, ±15
Total no. of reflections	10931	9927
Unique reflections	5696	5139
Inner residual	$R_i = 0.048$	$R_i = 0.049$
Reflections with $I_0 > 3\sigma(I_0)$	3303	2132
Number of variables	181	181
Highest residual electron density (e/Å^3)	1.41	1.18
Conventional residual	$R = 0.034$	$R = 0.035$
Weighted residual	$R_w = 0.034$	$R_w = 0.035$

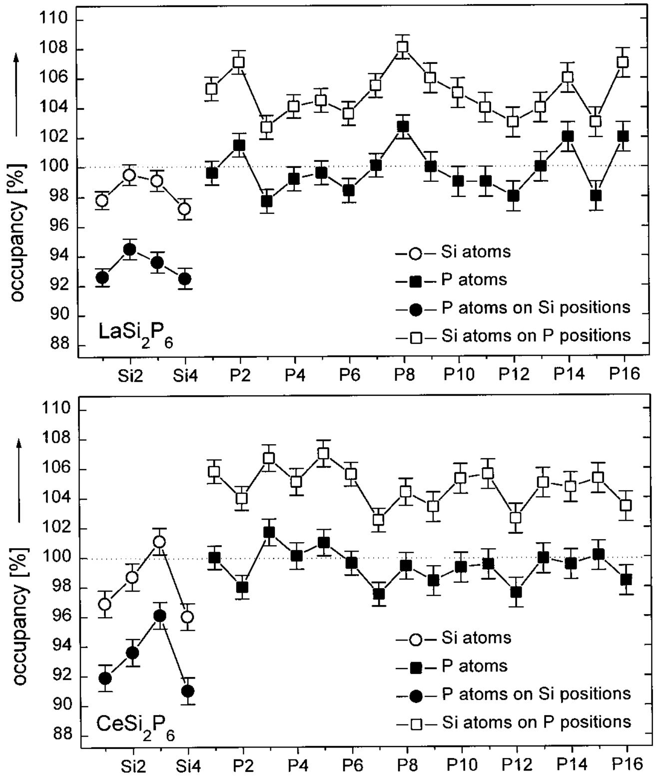

FIG. 2. Occupancy parameters for the silicon and phosphorus positions. The choice for the placement of silicon and phosphorus atoms on the respective sites was made from chemical considerations. It can be seen that the assignments conform well with the occupancies as obtained by the least-squares refinements.

(Fig. 4), which accommodates the rare earth atoms. The silicon atoms are all in tetrahedral phosphorus coordination. The SiP_4 tetrahedra may be regarded as analogs of the SiO_4 groups found in silicates and could therefore be considered as phosphidosilicate groups. There is, however, an important difference between our present compounds and the usual (oxo)silicates, in that the present compounds contain numerous phosphorus–phosphorus bonds. Thus, the SiP_4 tetrahedra are not only linked via common phosphorus corners, but also by phosphorus polyanions (Fig. 5).

To some extent the present compounds are also related to recently characterized nitridosilicates, *e.g.*, $Sr_2Si_5N_8$ (12) and $Sm_3Si_6N_{11}$ (13). These nitridosilicates contain nitrogen atoms, which belong to three SiN_4 tetrahedra. Similarly, the phosphidosilicates $NiSi_3P_4$ (14) and $NiSi_2P_3$ (4) have phosphorus atoms belonging to three SiP_4 tetrahedra. In contrast, in the present phosphidosilicates the phosphorus atoms are never bonded to more than two silicon atoms. In this respect they resemble the oxosilicates, where an oxygen atom never has more than two silicon neighbors (15).

The structure of $LaSi_2P_6$ has some layer character. As can be seen from Fig. 4 these layers consist of corner-shared SiP_4 tetrahedra and extend two-dimensionally infinite along the a and c axes. Four such (double) layers are needed to complete one translation period along the b axis. They are connected to each other via P–P bridges and by rare earth atoms. The latter are shown in Fig. 3, but are omitted in Fig. 4 for clarity. Phosphorus bridges together with SiP_4 tetrahedra are also found in $ZnSiP_2$ (16), $CeSiP_3$ (3), $AlSiP_3$ (17), and Cu_4SiP_8 (5).

The rare earth-phosphorus distances (Table 4) reflect the different coordination numbers of the rare earth (Ln)

TABLE 3
Atomic Parameters of $LaSi_2P_6$ and $CeSi_2P_6$[a]

		$LaSi_2P_6$				$CeSi_2P_6$			
Atom	$Cmc2_1$	x	y	z	B_{eq}	x	y	z	B_{eq}
*Ln*1[b]	4*a*	0	0.08105(3)	0	0.49(1)	0	0.08062(4)	0	0.50(2)
*Ln*2	4*a*	0	0.18935(3)	0.59396(7)	0.61(1)	0	0.18938(4)	0.5927(1)	0.56(2)
*Ln*3	4*a*	0	0.26606(3)	0.11367(7)	0.55(1)	0	0.26601(4)	0.1133(1)	0.57(2)
*Ln*4	4*a*	0	0.54141(3)	0.07564(7)	0.48(1)	0	0.54124(4)	0.0758(1)	0.45(2)
Si1	8*b*	0.1602(3)	0.41951(9)	0.1775(2)	0.56(4)	0.1602(4)	0.4197(1)	0.1768(4)	0.59(6)
Si2	8*b*	0.1705(3)	0.06651(8)	0.3590(2)	0.53(4)	0.1704(4)	0.0667(1)	0.3577(5)	0.59(6)
Si3	8*b*	0.1715(3)	0.32170(9)	0.3849(2)	0.59(4)	0.1713(4)	0.3216(1)	0.3833(3)	0.45(6)
Si4	8*b*	0.3231(3)	0.16501(9)	0.2186(2)	0.56(4)	0.3234(4)	0.1651(1)	0.2182(3)	0.58(7)
P1	8*b*	0.1555(3)	0.14594(8)	0.3537(2)	0.68(4)	0.1549(4)	0.1466(2)	0.3534(3)	0.64(6)
P2	8*b*	0.1993(3)	0.02919(8)	0.1722(2)	0.57(4)	0.1996(4)	0.0294(1)	0.1703(3)	0.55(6)
P3	8*b*	0.2037(3)	0.34375(8)	0.1769(2)	0.65(4)	0.2031(4)	0.3434(1)	0.1748(3)	0.68(6)
P4	8*b*	0.2929(3)	0.24203(8)	0.1879(2)	0.68(4)	0.2927(4)	0.2425(1)	0.1865(3)	0.53(6)
P5	8*b*	0.2940(3)	0.12247(8)	0.0363(2)	0.69(4)	0.2950(4)	0.1217(1)	0.0354(3)	0.66(6)
P6	8*b*	0.3342(3)	0.26667(8)	0.3863(2)	0.63(4)	0.3356(4)	0.2674(1)	0.3867(3)	0.59(6)
P7	8*b*	0.3397(3)	0.45769(8)	0.2539(2)	0.57(3)	0.3404(4)	0.4573(1)	0.2543(3)	0.61(5)
P8	8*b*	0.3463(3)	0.04710(8)	0.4782(2)	0.50(4)	0.3471(4)	0.0463(1)	0.4776(3)	0.58(6)
P9	4*a*	0	0.0312(1)	0.4630(3)	0.51(6)	0	0.0312(2)	0.4623(5)	0.51(9)
P10	4*a*	0	0.0748(1)	0.6391(3)	0.52(6)	0	0.0753(2)	0.6367(5)	0.64(9)
P11	4*a*	0	0.1549(1)	0.2080(3)	0.60(6)	0	0.1551(2)	0.2053(5)	0.51(9)
P12	4*a*	0	0.1822(1)	0.8792(3)	0.79(6)	0	0.1808(2)	0.8752(5)	0.9(1)
P13	4*a*	0	0.2734(1)	0.4030(3)	0.71(6)	0	0.2728(2)	0.4018(5)	0.7(1)
P14	4*a*	0	0.4575(1)	0.2785(3)	0.58(5)	0	0.4583(2)	0.2801(5)	0.69(9)
P15	4*a*	0	0.5776(1)	0.3565(3)	0.46(5)	0	0.5781(2)	0.3532(5)	0.59(9)
P16	4*a*	0	0.3436(1)	0.8540(3)	0.56(6)	0	0.3438(2)	0.8546(5)	0.69(9)

[a] The structures were refined with ellipsoidal displacement parameters for all atoms; only the equivalent isotropic displacement parameters B_{eq} are listed ($\times 10^{-4}$ in pm^2).

[b] The parameter z of the *Ln*1 atoms was fixed at $z = 0$ to define the origin of the cell.

atoms. The atoms *Ln*1 (with average La–P and Ce–P distances of 313.3 and 311.1 pm, respectively), *Ln*2 (313.0 and 310.3 pm), and *Ln*4 (313.1 and 310.0 pm) have 9 phosphorus neighbors and therefore their average *Ln*-P distances are shorter than the corresponding distances of the *Ln*3 atoms (320.1 and 318.5 pm), which have 10 phosphorus neighbors.

The average Si–P distances of the SiP_4 tetrahedra show the same pattern for both compounds, with 222.0, 224.2, 224.9, and 225.2 pm for, respectively, the Si1–P, Si2–P, Si3–P, and Si4–P distances in $LaSi_2P_6$, and with 223.0, 224.3, 224.5, and 225.7 pm as the analogous values in $CeSi_2P_6$. In view of the good agreement between the corresponding distances of both compounds, it is not surprising that the overall average Si–P (224.1 and 224.4 pm) and P–P distances (220.7 and 220.8 pm) are practically the same in both compounds ($LaSi_2P_6$ and $CeSi_2P_6$, respectively). The average Si–P distances of 224.1 and 224.4 pm mentioned above compare well with the average Si–P distances of 225.9 pm in $NiSi_3P_4$ (14), 225.1 pm in $NiSi_2P_3$ (4), 223.0 pm in $CeSiP_3$ (3), 225.4 pm in $ZnSiP_2$ (16), and 227.2 pm in K_2SiP_2 (18). They are all shorter than the average

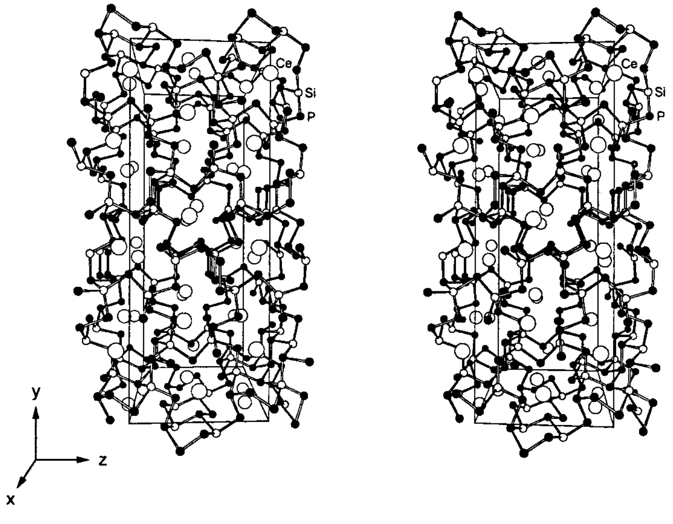

FIG. 3. Stereoplot of the $LaSi_2P_6$ structure.

TABLE 4
Interatomic Distances in $LaSi_2P_6$ and $CeSi_2P_6$[a]

		$LaSi_2P_6$	$CeSi_2P_6$			$LaSi_2P_6$	$CeSi_2P_6$
*Ln*1:	1P11	299.7	297.4	P3:	1Si1	218.0	218.4
	2P2	306.6	303.8		1Si3	226.9	226.0
	1P12	311.3	309.0		1*Ln*3	307.9	305.4
	1P9	318.6	315.9		1*Ln*2	325.9	325.4
	2P7	321.7	318.6	P4:	1P6	221.2	222.2
	2P5	322.1	322.1		1Si4	221.4	221.6
*Ln*2:	1P12	296.6	291.1		1*Ln*2	301.4	299.6
	2P4	301.4	299.6		1*Ln*3	313.9	312.7
	1P13	308.8	305.8	P5:	1Si3	225.1	225.9
	2P1	319.2	315.9		1Si4	225.8	226.1
	2P3	325.9	325.4		1*Ln*4	312.0	309.4
	1P10	326.2	323.1		1*Ln*1	322.1	322.1
*Ln*3:	1P13	300.9	298.1	P6:	1P4	221.2	222.2
	2P6	303.9	301.6		1P12	221.4	221.1
	2P3	307.9	305.4		1Si3	226.3	225.0
	2P4	313.9	312.7		1*Ln*3	303.9	301.6
	1P11	328.2	325.0	P7:	1P10	221.1	221.4
	1P12	339.1	342.6		1P2	222.1	223.8
	1P16	346.9	344.4		1Si1	225.7	225.1
*Ln*4:	1P14	308.3	305.0		1*Ln*1	321.7	318.6
	1P15	308.6	304.0	P8:	1P15	218.1	219.8
	2P8	310.9	307.2		1Si2	223.6	224.7
	2P5	312.0	309.4		1Si1	227.2	226.5
	1P14	316.4	313.6		1*Ln*4	310.9	307.2
	2P2	322.5	320.9	P9:	1P10	220.1	218.3
Si1:	1P3	218.0	218.4		2Si2	226.7	226.3
	1P14	220.9	222.1		1*Ln*1	318.6	315.9
	1P7	225.7	225.1	P10:	1P9	220.1	218.3
	1P8	227.2	226.5		2P7	221.1	221.4
Si2:	1P2	222.4	221.6		1*Ln*2	326.2	323.1
	1P8	223.6	224.7	P11:	2P1	219.8	220.2
	1P1	224.4	224.7		1*Ln*1	299.7	297.4
	1P9	226.7	226.3		1*Ln*3	328.2	325.0
Si3:	1P13	221.5	221.2	P12:	2P6	221.4	221.1
	1P5	225.1	225.9		1*Ln*2	296.6	292.1
	1P6	226.3	225.0		1*Ln*1	311.3	309.0
	1P3	226.9	226.0		1*Ln*3	339.1	342.6
Si4:	1P4	221.4	221.6	P13:	2Si3	221.5	221.2
	1P5	225.8	226.1		1*Ln*3	300.9	298.1
	1P1	226.6	226.3		1*Ln*2	308.8	305.8
	1P16	229.0	228.7	P14:	2Si1	220.9	222.1
P1:	1P11	219.8	220.2		1*Ln*4	308.3	305.0
	1Si2	224.4	224.7		1*Ln*4	316.4	313.6
	1Si4	226.6	226.3	P15:	2P8	218.1	219.8
	1*Ln*2	319.2	315.9		1P16	222.0	219.2
P2:	1P7	222.1	223.8		1*Ln*4	308.6	304.1
	1Si2	222.4	221.6	P16:	1P15	222.0	219.2
	1*Ln*1	306.6	303.8		2Si4	229.0	228.7
	1*Ln*4	322.5	320.9		1*Ln*3	346.9	344.4

[a] All distances shorter than 400 pm (*Ln*–*Ln*), 350 pm (*Ln*–Si, *Ln*–P), and 295 pm (all others) are listed. Standard deviations, calculated from those of the lattice constants and those of the positional parameters, are all equal to or less than 0.4 pm for *Ln*–P distances and 0.6 pm for Si–P and P–P distances.

Si–P distances of 229.4 pm in $Na_{10}Si_2P_6$ (19), where the SiP_4 tetrahedra share an edge; the other compounds contain only corner-sharing SiP_4 tetrahedra.

By counting two electrons for each Si–P and each P–P bond, and assuming the octet rule to be obeyed by the silicon and phosphorus atoms, the phosphorus atoms may be assigned oxidation numbers (formal charges), where the electrons of the Si–P interactions are counted as belonging to the phosphorus atoms. In this way the P3, P5, P13, and P14 atoms, which form no P–P bonds, attain the oxidation number −3. The P1, P2, P4, P8, P9, and P16 atoms, which form one P–P bond each, are assigned the formal charge −2. The P6, P7, P11, and P12 atoms have two phosphorus neighbors and therefore are characterized by the oxidation number −1. Finally, the phosphorus atoms with three phosphorus neighbors (P10 and P15) have the oxidation number 0, like the phosphorus atoms in the various modifications of the element phosphorus, where each phosphorus atom also forms three P–P bonds. Accordingly, the rare earth and silicon atoms attain the oxidation numbers +3 and +4, respectively, and the cell content of the compound may be expressed by the formula $(Ln^{+3})_{16}(\mathrm{Si}^{+4})_{32}(\mathrm{P}^{-3})_{24}(\mathrm{P}^{-2})_{40}(\mathrm{P}^{-1})_{24}(\mathrm{P}^{0})_{8}$. Dividing by $Z = 16$, the formula becomes simply $Ln^{+3}(\mathrm{Si}^{+4})_2(\mathrm{P}_6)^{-11}$, or in de-emphasizing the (weakly) ionic character of the Si–P interactions, we may prefer the formula $Ln^{+3}(\mathrm{Si}_2\mathrm{P}_6)^{-3}$. In agreement with this formulation, the volume plot (Fig. 1) indicates the cerium atoms in $\mathrm{CeSi_2P_6}$ to be trivalent (a much smaller cell volume would be expected for $\mathrm{CeSi_2P_6}$ if cerium were tetravalent). We expect these compounds to be semiconducting with a small band gap, which is in agreement with their grey color.

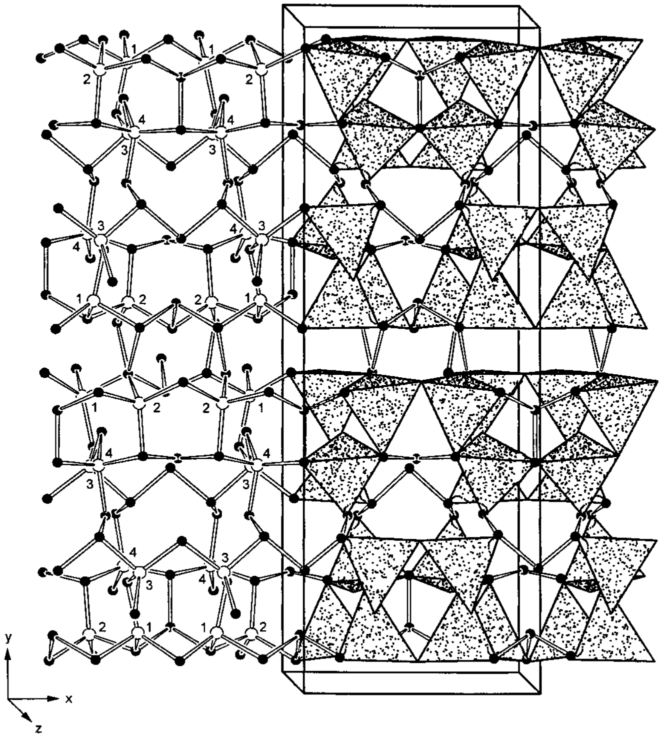

FIG. 4. The three-dimensionally infinite silicon–phosphorus polyanion. In the left-hand part of the drawing the network of the silicon (open circles) and phosphorus atoms is shown. The numbers correspond to the atom designations of the silicon atoms. On the right-hand side the linking of the $\mathrm{SiP_4}$ tetrahedra by corner-sharing and by additional phosphorus atoms is emphasized.

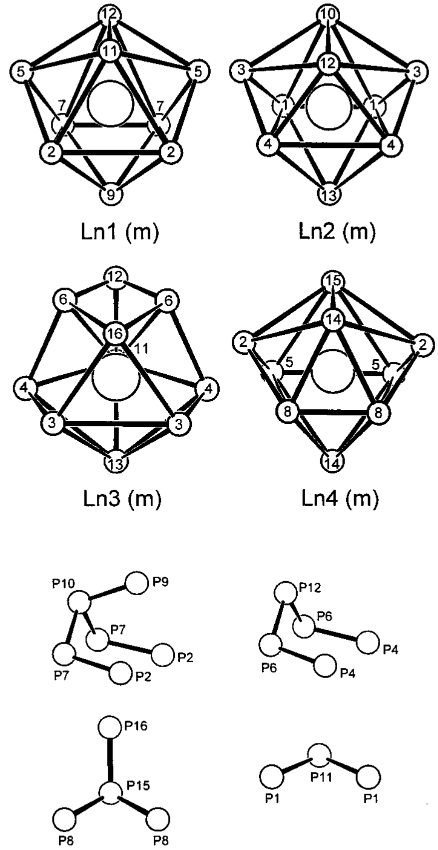

FIG. 5. Phosphorus coordination of the lanthanum atoms and the phosphorus polyanions in the structure of $\mathrm{LaSi_2P_6}$.

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