

## RPtSi Phases ( $R = \text{La, Ce, Pr, Nd, Sm and Gd}$ ) with an Ordered $\text{ThSi}_2$ Derivative Structure

BY K. KLEPP AND E. PARTHÉ

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

(Received 11 August 1981; accepted 29 October 1981)

### Abstract

The ternary equiatomic platinum silicides of the early rare-earth metals crystallize with a new structure type which was refined for LaPtSi:  $a = 4.2490$  (3),  $c = 14.539$  (2) Å,  $I4_1md$ ,  $Z = 4$ ,  $D_x = 9.16 \text{ Mg m}^{-3}$ ,  $\mu(\text{Mo } K\alpha) = 72.34 \text{ mm}^{-1}$ ;  $R = 0.052$  for 80 observed reflections. Isotypic RPtSi compounds are formed with  $R = \text{Ce, Pr, Nd, Sm and Gd}$ . The LaPtSi structure is a lattice-equivalent ternary derivative of the  $\text{ThSi}_2$  structure type and has a maximal subgroup symmetry of the latter.

### Introduction

For many years a Ukrainian research group in Lvov under the guidance of Gladyshevskii (1971) and the late Kripyakevich (1977) has undertaken great efforts to study systematically the crystal structures of ternary compounds containing rare-earth elements ( $R$ ), transition metals and Group  $B$  elements. The recent discovery of superconductivity with  $R$ -(Fe,Co,Rh,Os,Ir)-(Si,Ge) alloys (Braun, 1980; Braun & Segre, 1980, 1981) has revitalized interest in the crystal structures and the crystal chemistry of these compounds. A number of different laboratories are now working along these lines. In the course of our structure studies we have investigated, beside others, the ternary equiatomic compounds which crystallize with three structure types: the tetragonal PbFCl type, the hexagonal  $\text{ZrAlNi}$  type and the orthorhombic  $\text{TiNiSi}$  type (Hovestreydt, Engel, Klepp, Chabot & Parthé, 1982). With RPtSi compounds the  $\text{TiNiSi}$  type occurs when  $R = \text{Tb, Dy, Ho, Er, Tm or Lu}$ , whereas with the early light rare-earth elements from La to Gd a new structure type appears which is described in this paper.

### Experimental

The title compounds were obtained from high-purity elements (rare-earth metals 99.9%, Pt 99.99%, Si

99.999%) by melting together appropriate amounts of the components in an arc furnace under a purified Ar atmosphere ( $\sim 0.8 \text{ g}$  per sample). Two series of alloys were prepared. The first was studied as obtained from melting in the arc furnace ('as quenched' samples) whereas the ingots of the second series were subjected to annealing (1050 K, 2 weeks). The crushed samples were investigated by powder techniques (Guinier-de Wolff camera, Cu  $K\alpha$  radiation,  $\lambda = 1.54178 \text{ Å}$ ). The powder diagrams of the quenched alloys indicated a series of isotypic compounds; a study of the annealed alloys showed that the crystal structure was retained at 1050 K with the exception of GdPtSi, which had undergone a phase transformation to an unknown structure. The powder diagrams could be indexed unambiguously assuming the compounds to be of the  $\text{ThSi}_2$  structure type. The lattice dimensions, given in Table 1, were obtained by least-squares refinement of the Guinier patterns using Si ( $a = 5.4301 \text{ Å}$ ) as an internal standard. Model calculations with the *LAZY PULVERIX* program (Yvon, Jeitschko & Parthé, 1977), however, revealed discrepancies of the relative intensities in the powder patterns. To ensure that this was not just a texture effect a single-crystal study was undertaken.

A small single crystal of LaPtSi ( $40 \times 60 \times 60 \mu\text{m}$ ) was isolated from the quenched alloy and mounted on a computer-controlled four-circle diffractometer (Philips PW 1100, graphite-monochromated Mo  $K\alpha$  radiation). Preliminary investigations performed on the

Table 1. Unit-cell dimensions for RPtSi phases with the LaPtSi structure type

E.s.d.'s are given in parentheses.

	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )
LaPtSi	4.2490 (3)	14.539 (2)	262.49 (4)
CePtSi	4.1982 (7)	14.488 (3)	255.35 (8)
PrPtSi	4.1797 (7)	14.458 (3)	252.58 (8)
NdPtSi	4.1630 (8)	14.415 (4)	249.82 (10)
SmPtSi	4.1300 (9)	14.376 (4)	245.21 (10)
GdPtSi	4.0996 (3)	14.329 (2)	240.82 (4)

diffractometer confirmed the centered cell with Laue symmetry  $4/mmm$ , which was assumed from the powder photographs. The systematic extinctions  $hkl$ :  $h + k + l \neq 2n$ ,  $hk0$ :  $h, (k) \neq 2n$ , and  $hhl$ :  $2h + l \neq 4n$  and the special extinctions for  $hkl$ :  $2k + l \neq 2n + 1$  or  $4n$  were consistent with the ThSi<sub>2</sub> structure type which belongs to space group  $I4_1/amd$ . Intensity data were collected within one octant of reciprocal space ( $6^\circ \leq 2\theta \leq 54^\circ$ ) using the  $\omega$ - $2\theta$  scan mode. The usual background, Lorentz and polarization corrections were applied. Absorption was accounted for by assuming a spherical crystal ( $\mu R = 1.9$ ). Averaging equivalent reflections yielded a unique set of 80 observed reflections with  $I > 3\sigma(I)$ .

### Structure refinement

A preliminary least-squares refinement in the centrosymmetric space group  $I4_1/amd$  on the basis of the ThSi<sub>2</sub> structure type with mixed occupation of the eightfold Si site  $8(e)$  by Pt and Si resulted in a rather high  $R$  value of 0.32. Moreover, the statistics of the normalized structure factors revealed the absence of a symmetry center. From the diamond-sphalerite analogy this was taken as an indication that the Pt-Si partial structure was ordered. On the assumption that the ordering would lead exclusively to Pt-Si hetero contacts a model structure was found which could be described in the non-centrosymmetric space group  $I4_1md$ , with La, Pt, Si in the special positions  $4(a)$ . The general extinctions of space group  $I4_1md$  differ from those for  $I4_1/amd$  by the absence of a condition for the  $hk0$  reflections. However, since all atoms occupy the point set  $4(a)$  in  $I4_1md$ , the special extinction condition  $hkl$ :  $2k + l \neq 2n + 1$  or  $4n$  has as a consequence that all  $hk0$  reflections are extinct when  $h(k) \neq 2n$ . Thus both ThSi<sub>2</sub> and LaPtSi types have the same extinctions.

Least-squares refinement of this model with isotropic temperature factors converged after a few cycles

Table 2. Point positions for LaPtSi (space group  $I4_1md$ ) and interatomic distances up to 4 Å

Isotropic temperature factors are expressed as  $T = \exp[-2\pi^2 U(2 \sin \theta/\lambda)^2]$ . E.s.d.'s are given in parentheses. It is assumed that  $2 \pm 1\%$  of the Si and Pt sites are occupied by Pt and Si atoms, respectively.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å <sup>2</sup> )
La in 4( <i>a</i> )	0	0	0.0*	0.006 (2)
Si in 4( <i>a</i> )	0	0	0.419 (2)	0.008 (6)
Pt in 4( <i>a</i> )	0	0	0.5850 (4)	0.007 (1)
La-Pt 3.204 (4)	Pt-Si 2.41 (3)	Si-Pt 2.41 (3)		
4Pt 3.249 (2)	2Si 2.45 (1)	2Pt 2.45 (1)		
4Si 3.23 (1)	2La 3.204 (4)	4La 3.23 (1)		
2Si 3.25 (2)	4La 3.249 (2)	2La 3.25 (2)		

\* Fixed arbitrarily.

to  $R = 0.054$  but resulted in slightly negative temperature factors for Si, indicating that the ordering of Pt and Si was not perfect. This was taken into account in a subsequent refinement, where the population parameters of Pt and Si were varied under the constraint that the overall stoichiometry should be maintained. The refinement showed that occupations of  $2 \pm 1\%$  of Pt and Si were on the mainly Si and Pt sites respectively. This appears fairly small for an intermetallic compound if one takes into account the fact that the sample was obtained directly from the melt. A final refinement resulted in  $R = \sum |AF|/\sum |F_o| = 0.052$  [ $R_w = 0.057$ ,  $w = 1/\sigma^2(F_o)$ ] for 80 observed reflections and 6 variables.\* Refinement of the enantiomorph led to a higher  $R$  value of 0.062. All calculations were performed with the XRAY system (1976). The final structural parameters and the interatomic distances are given in Table 2.

### Isotypic compounds

The compounds RPtSi with  $R = \text{Ce, Pr, Nd, Sm and Gd}$  are isotypic with LaPtSi. This was verified by comparing observed powder diagram intensities with calculated intensities using the LAZY PULVERIX program (Yvon, Jeitschko & Parthé, 1977).

Bodak, Miskiv, Tyvanchuk, Kharchenko & Gladyshevskii (1973) reported the existence of a CeNiSi compound with the ThSi<sub>2</sub> structure type ( $I4_1/amd$ ,  $a = 4.055$  and  $c = 14.539$  Å), where the Ni and Si atoms are supposed to occupy the Si sites of ThSi<sub>2</sub> at random. According to their phase-diagram studies this phase has practically no homogeneity range. It seems probable that this phase also crystallizes with the LaPtSi structure type. As will be demonstrated below, there are only small intensity differences which distinguish the LaPtSi type from the ThSi<sub>2</sub> type.

### Discussion

As shown in Fig. 1 the LaPtSi type is a lattice-equivalent ternary derivative of the ThSi<sub>2</sub> structure type. Pt and Si atoms are arranged in an ordered fashion on the Si sites in ThSi<sub>2</sub>, such that each Pt has three Si close neighbors and *vice versa*. The space group  $I4_1md$  of LaPtSi is lattice-equivalent to  $I4_1/amd$ , the space group of the ThSi<sub>2</sub> type.

Since ThSi<sub>2</sub> and LaPtSi types have the same extinctions, a distinction is possible only by a careful

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36527 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

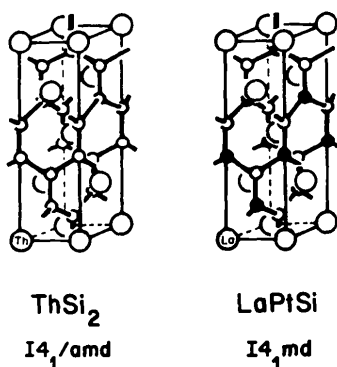


Fig. 1. Structures of ThSi<sub>2</sub> (*I*4<sub>1</sub>/*amd*) and LaPtSi (*I*4<sub>1</sub>*md*). Large circles correspond to Th or La atoms, small open ones to Si atoms and the filled ones to Pt atoms.

study of the intensities. Model calculations of the ratio  $F_{\text{LaPtSi type}}^2/F_{\text{ThSi}_2 \text{ type}}^2$  were performed which showed that the value of the relative intensity depends only on  $l$ . In particular, we obtain the following equation, assuming  $z(\text{La}) = 0$ ,  $z(\text{Si}) = \frac{1}{2}$  and  $z(\text{Pt}) = -\frac{1}{2}$ :

$$F_{\text{LaPtSi type}}^2/F_{\text{ThSi}_2 \text{ type}}^2 = 1 + a_1 \Delta^2 / (f_{\text{La}} + a_2 \Sigma)^2$$

where  $\Delta = f_{\text{Pt}} - f_{\text{Si}}$  and  $\Sigma = f_{\text{Pt}} + f_{\text{Si}}$ . The coefficients  $a_1$  and  $a_2$  have the following values for  $l = 12n + i$ :

$i$	0	$\pm 1$	$\pm 2$	$\pm 3$	$\pm 4$	$\pm 5$	6
$a_1$	0	$\frac{1}{4}$	$\frac{3}{4}$	1	$\frac{3}{4}$	$\frac{1}{4}$	0
$a_2$	0	$+\sqrt{\frac{3}{2}}$	$+\frac{1}{2}$	0	$-\frac{1}{2}$	$-\sqrt{\frac{3}{2}}$	0.

For all  $hk6n$  reflections, the ratio is always unity, while all other  $hkl$  reflections have increased intensity if the atoms are ordered. Further, independent of the values of  $f_{\text{La}}$ ,  $f_{\text{Pt}}$  and  $f_{\text{Si}}$  the relative intensity increase must be larger for the  $hk1$  compared to the  $hk5$  and larger for  $hk4$  compared to the  $hk2$ . This should serve as a useful guide in the search for ordering in the ternary ThSi<sub>2</sub>-type structures.

It should be mentioned that in  $\text{RSi}_x\text{Ge}_{2-x}$  phases with the ThSi<sub>2</sub> structure there is an indication for a different (partial) ordering (Mayer & Eshdat, 1968). Here an orthorhombic deformation of the ThSi<sub>2</sub> structure is observed which has been explained by the formation of Ge-Ge contacts.

It has been shown before that the ThSi<sub>2</sub> type can be considered a stacking variation of the AlB<sub>2</sub> type (Parthé, 1967). The AlB<sub>2</sub> type has also been reported for equiatomic ternary phases like, for example, LuCuGe (Dwight, 1968) or GdCuSi and TbCuSi (W. Rieger, 1969, unpublished, cited by Parthé, 1970). In the pseudobinary sections Gd(Cu,Si)<sub>2</sub> and Tb(Cu,Si)<sub>2</sub>, in fact, two AlB<sub>2</sub>-type phases are formed. The AlB<sub>2</sub>I-type phase is silicon rich and has a homogeneity range with a continuous variation of the lattice parameters. The AlB<sub>2</sub>II-type phase, however, occurs at

the equiatomic composition and is distinguished from the AlB<sub>2</sub>I phase by a smaller  $c/a$  ratio. It is not unreasonable to expect that in the AlB<sub>2</sub>II-type phases the Cu and Si atoms should be ordered with each Cu surrounded by three Si and *vice versa*, as shown in Fig. 2. The detection of the ordering of the atoms on the boron sites in the AlB<sub>2</sub>-type structures is a problem similar to the experimental differentiation between the ThSi<sub>2</sub> and the LaPtSi types. The space group of the AlB<sub>2</sub> type is *P*6/*mmm* and that of a ternary lattice-equivalent AlB<sub>2</sub> type with order on the boron sites is *P*6̄*m*2, which again has maximal subgroup symmetry. In both types there are no extinctions. A model calculation shows that the ratio  $F_{\text{AlBB}'}^2/F_{\text{AlB}_2}^2$  is unity for reflections where  $h - k = 3n$  and depends on the parity of  $l$  for  $h - k \neq 3n$  according to:

$$F_{\text{AlBB}'}^2/F_{\text{AlB}_2}^2 = 1 + \frac{\frac{3}{4}\Delta^2}{(f_{\text{Al}} + \frac{1}{2}s\Sigma)^2}$$

where  $s = 1$  for  $l = 2n$ ,  $s = -1$  for  $l \neq 2n$ , and  $\Delta = f_{\text{B}} - f_{\text{B}'}$ , and  $\Sigma = f_{\text{B}} + f_{\text{B}'}$ .

A maximum intensity increase will therefore be observed for  $hkl$  reflections where  $h - k \neq 3n$  and  $l = 2n$ .

Thus, with ternary ThSi<sub>2</sub>- and AlB<sub>2</sub>-type compounds the intensities have to be compared very carefully in order to find a possible ordering of the atoms. No examples of a translation-equivalent ternary AlB<sub>2</sub> type with order on the boron sites has been found in the literature. It might be worthwhile reinvestigating the reported 'disordered' ternary AlB<sub>2</sub>-type compounds for their possible ordering of atoms on the boron sites. The only known AlB<sub>2</sub>-related ordered ternary phases are MnFeGe (Suzuoka, Adelson & Austin, 1968), MnCoGe (Jeitschko, 1975) and MnNiGe (Castelliz, 1953) which crystallize, however, with a ternary Ni<sub>2</sub>In type (not lattice-equivalent to AlB<sub>2</sub> because  $c_{\text{Ni}_2\text{In}} = 2c_{\text{AlB}_2}$ , but class-equivalent) and which can be distinguished from the AlB<sub>2</sub> type by the appearance of superstructure lines.

In Fig. 3 is plotted for  $\text{RPtSi}$  compounds the single-atom-cube length ( $\sqrt[3]{V/n}$ , where  $n$  is the number of atoms per unit cell) as a function of the ionic radii of the trivalent rare-earth atoms after Templeton &

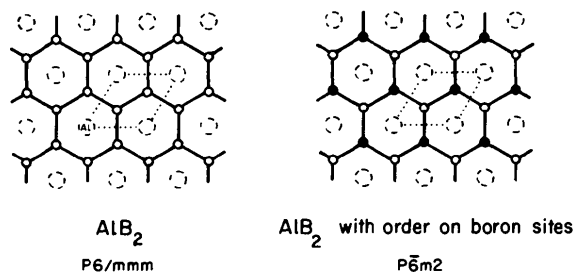


Fig. 2. Projection along the  $c$  axis for AlB<sub>2</sub> and a ternary AlB<sub>2</sub> derivative structure with atom order on the boron sites.

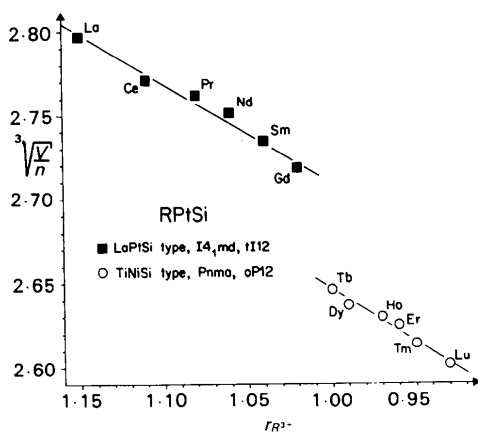


Fig. 3. A plot of  $(V/n)^{1/3}$  versus  $r^{3+}$  for RPtSi compounds with tetragonal LaPtSi and orthorhombic TiNiSi structure types.

Dauben (1954). In this diagram are indicated not only the six LaPtSi-type compounds, but also the six new TiNiSi-type compounds from TbPtSi to LuPtSi which are described in detail elsewhere (Hovestreydt, Engel, Klepp, Chabot & Parthé, 1982). The change from the LaPtSi to the TiNiSi structure type is accompanied by an unexpected volume decrease which is difficult to explain as an electronic transition. In both structures, Si atoms are at the centers of trigonal prisms; however, the Pt atoms change their surroundings from a trigonal prism to a strongly deformed cube whilst the rare-earth atoms increase their coordination. The better space filling of the TiNiSi type as compared to LaPtSi type is the reason for the volume change.

*Acta Cryst.* (1982). B38, 1108–1112

## The Structure of Deuterated Lithium Uranyl Arsenate Tetrahydrate $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$ by Powder Neutron Diffraction

BY A. N. FITCH, B. E. F. FENDER AND A. F. WRIGHT

*Institut Laue–Langevin, 156 X, Centre de Tri, 38042 Grenoble, France*

(Received 27 August 1981; accepted 6 November 1981)

### Abstract

The structure of  $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$  has been determined in space group  $P4/n$  with  $a = 7.0969$  (1),  $c = 9.1903$  (2) Å and  $Z = 2$  from a powder neutron

0567-7408/82/041108-05\$01.00

This study was supported by the Swiss National Science Foundation under contract No. 2.001-0.81.

### References

- BODAK, O. I., MISKIV, M. G., TYVANCHUK, A. T., KHARCHENKO, O. I. & GLADYSHEVSKII, E. I. (1973). *Inorg. Mater. (USSR)*, **9**, 777–779.
- BRAUN, H. F. (1980). *Phys. Lett. A*, **75**, 386–388.
- BRAUN, H. F. & SEGRE, C. U. (1980). *Solid State Commun.* **35**, 735–738.
- BRAUN, H. F. & SEGRE, C. U. (1981). *Ternary Superconductors*, edited by G. K. SHENOY, B. D. DUNLAP & F. Y. FRADIN, pp. 239–242. Amsterdam: Elsevier–North-Holland.
- CASTELLIZ, L. (1953). *Monatsh. Chem.* **84**, 765–776.
- DWIGHT, A. E. (1968). Proceedings of the Seventh Rare-Earth Research Conference, Coronado, California.
- GLADYSHEVSKII, E. I. (1971). *Crystal Chemistry of Silicides and Germanides* (in Russian). Moscow: Metallurgia.
- HOVESTREYDT, E., ENGEL, N., KLEPP, K., CHABOT, B. & PARTHÉ, E. (1982). *J. Less-Common Met.* In the press.
- JEITSCHKO, W. (1975). *Acta Cryst.* B31, 1187–1190.
- KRIPYAKEVICH, P. I. (1977). *Structure Types of Intermetallic Compounds* (in Russian). Moscow: Nauka.
- MAYER, I. & ESHDAT, Y. (1968). *Inorg. Chem.* **7**, 1904–1908.
- PARTHÉ, E. (1967). *Colloq. Int. CNRS*, **157**, 195–205.
- PARTHÉ, E. (1970). *Colloq. Int. CNRS*, **180**, 61–79.
- SUZUOKA, T., ADELSON, E. & AUSTIN, A. E. (1968). *Acta Cryst.* A24, 513–517.
- TEMPLETON, D. H. & DAUBEN, C. H. (1954). *J. Am. Chem. Soc.* **76**, 5237–5239.
- XRAY system (1976). Edited by J. M. STEWART. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1977). *J. Appl. Cryst.* **10**, 73–74.

diffraction study at 294 K. 258 reflections were refined to an  $R$  factor on intensities of 3.8%. The water molecules are arranged in a two-dimensional array alternating with  $\text{UO}_2^{2+}$  and  $\text{AsO}_4^{3-}$  ions. The  $\text{Li}^+$  ions are tetrahedrally coordinated to the O atoms of the

© 1982 International Union of Crystallography