

## SHORT STRUCTURAL PAPERS

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LaIrSi with an Ordered SrSi<sub>2</sub> Derivative Structure

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**Abstract.** LaIrSi, *cP*12, *P*2<sub>1</sub>3, *a* = 6.363 (3) Å, *Z* = 4, *D<sub>x</sub>* = 9.26 Mg m<sup>-3</sup>, *μ*(Mo *Kα*) = 71.38 mm<sup>-1</sup>, *F*(000) = 592. The crystal structure was determined from single-crystal diffractometer data and refined to a conventional *R* factor of 0.056 for 108 observed reflections and 10 variables. LaIrSi is the first example of a ternary SrSi<sub>2</sub>-type derivative structure formed by an ordered occupation of the Si sites by Ir and Si. The LaIrSi structure is compared with the LaPtSi structure, an ordered ThSi<sub>2</sub> derivative structure.

**Introduction.** For the ternary equiatomic rare-earth-transition-metal silicides (*RTSi*), three ternary ordered structure types are known from the literature which are all ordered derivatives of binary structure types: the tetragonal PbFCl type, an Fe<sub>2</sub>As-type derivative; the hexagonal ZrNiAl type, an Fe<sub>2</sub>P-type derivative; and the orthorhombic TiNiSi type, a PbCl<sub>2</sub>- or CeCu<sub>2</sub>-type derivative. In the course of a new extensive study of *RTSi* compounds (Hovestreydt, Engel, Klepp, Chabot & Parthé, 1982) two new types were found: LaPtSi and LaIrSi. The LaPtSi type was recognized to be a ternary ordered derivative of the ThSi<sub>2</sub> type (Klepp & Parthé, 1982). This paper deals with the second new structure type, the LaIrSi type.

**Experimental.** LaIrSi was prepared by arc melting high-purity elements (La, Ir: 99.9%; Si: 99.999%) under a purified Ar atmosphere. Small single crystals could be isolated from the crushed ingot. Preliminary X-ray investigations indicated a primitive cubic cell with Laue symmetry *m*3. Systematic absences were observed for *h*00: *h* ≠ 2*n* thus leading uniquely to the noncentrosymmetric space group *P*2<sub>1</sub>3.

A well developed single crystal of prismatic shape (~40 × 50 × 60 μm) was selected and mounted on a computer-controlled four-circle diffractometer (Philips PW 1100) equipped with graphite-monochromated Mo *Kα* radiation. The lattice constant given in the *Abstract* was obtained by least-squares refinement of the 2θ values of 24 reflections using Mo *Kα*<sub>1</sub> radiation (λ = 0.7093 Å). Intensity data were collected in one octant of reciprocal space using the ω–2θ scan mode (6° ≤ 2θ ≤ 54°). The usual background, Lorentz and polarization corrections were applied. Absorption effects were accounted for by a spherical absorption correction (*μR* = 1.8). Symmetry-equivalent reflections were averaged (internal consistency factor 0.05). The unique set consisted of 123 reflections from which 108 with *I* > 3σ(*I*) were considered as significant.

Composition, cell size and space group led to the assumption that the structure of LaIrSi could be an ordered ternary derivative of the SrSi<sub>2</sub> type. The SrSi<sub>2</sub> structure determined by Janzon, Schäfer & Weiss (1965), Kripyakevich & Gladyshevskii (1966) and Pringle (1972) has been described with space group *P*4<sub>3</sub>2 with Sr in 4(*a*) with *x* = 1/8 and Si in 8(*c*) with *x* ≈ 0.42 (0.428 or 0.412 or 0.4231 respectively for coordinates transformed to the same axial system). The space group of LaIrSi, *P*2<sub>1</sub>3, is a maximal lattice-equivalent subgroup of *P*4<sub>3</sub>2. Space group *P*2<sub>1</sub>3 as compared to *P*4<sub>3</sub>2 differs in the extinction law for the *h*00 reflections. The presence of *h*00 reflections for *h* = 4*n* + 2 was taken as proof that the Ir and Si atoms are ordered. As a starting model it was assumed that the site set 8(*c*) in *P*4<sub>3</sub>2 is split in *P*2<sub>1</sub>3 into two fourfold sets 4(*a*) *xxx* with *x*<sub>1</sub> = 0.42 and *x*<sub>2</sub> = 3/4 – 0.42 occupied by Ir and Si atoms respectively. This model

Table 1. Atomic positions and thermal parameters ( $\text{\AA}^2 \times 10^2$ ) for LaIrSi (space group  $P2_13$ )

All atoms are in equipoint  $4(a)$ .  $U_{11} = U_{22} = U_{33}$ ;  $U_{12} = U_{13} = U_{23}$ . E.s.d.'s are given in parentheses.

	$x$	$y$	$z$	$U_{11}$	$U_{12}$
La	0.1325 (3)	0.1325 (3)	0.1325 (3)	1.43 (10)	0.06 (9)
Ir	0.4230 (2)	0.4230 (2)	0.4230 (2)	1.73 (9)	-0.17 (7)
Si	0.839 (2)	0.839 (2)	0.839 (2)	2.0 (5)	-0.6 (5)

Table 2. Interatomic distances ( $\text{\AA}$ ) for LaIrSi up to 4  $\text{\AA}$

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

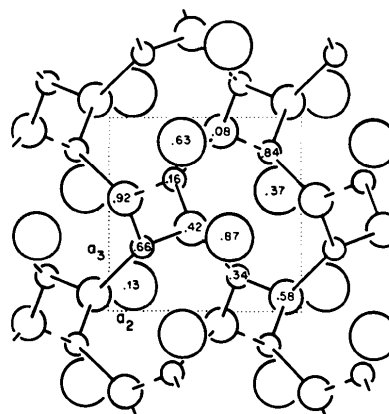
La-6La	3.899 (2)	Ir-3La	3.147 (2)	Si-La	3.237 (7)
-3Ir	3.147 (2)	-La	3.202 (2)	-La	3.279 (6)
-Ir	3.202 (2)	-3La	3.794 (2)	-3La	3.616 (6)
-3Ir	3.794 (3)	-3Si	2.315 (7)	-3Ir	2.315 (7)
-Si	3.237 (7)	-6Ir	3.991 (2)	-6Si	3.951 (9)
-3Si	3.279 (6)				
-3Si	3.616 (6)				

converged after a few cycles of refinement to an  $R$  factor of 0.06. At this stage of refinement anisotropic temperature factors were introduced and the weights were assigned according to counting statistics. The final refinement resulted in  $R = \sum |\Delta F| / \sum |F_o| = 0.056$  [ $R_w = 0.055$ ,  $w = 1/\sigma^2(F_o)$ ] for 108 observed reflections and 10 variables.\* The atomic coordinates and anisotropic temperature factors are given in Table 1 and a list of interatomic distances is in Table 2. A test was made interchanging the arrangement of the Ir and Si atoms and this led to  $R = 0.40$  and physically unreasonable temperature factors.

All calculations were performed with programs of the XRAY system (1976). Scattering factors for neutral atoms were taken from Cromer & Mann (1968), and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

**Discussion.** A projection of the LaIrSi structure along the  $a_1$  axis is shown in Fig. 1 and a spatial presentation of four unit cells in Fig. 2. All short Ir-Si distances have been indicated by connecting lines. Each Ir has three Si and each Si three close Ir neighbours. The La atoms have a complicated environment of 20 atoms, comprising 7 Ir, 7 Si and 6 La atoms (Fig. 3a). The simple crystal-chemical formula is thus  $\text{La}^{[\sim 14]}\text{Ir}^{[3]}\text{Si}^{[3]}\text{Ir}^{[3]}\text{Ir}^{[1]}$ .

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36611 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



LaIrSi  
LaIrSi type  $\equiv$   $\text{SrSi}_2$  type derivative ( $\text{SrSiSi}$ )  
cP12,  $P2_13$   
 $a = 6.363 \text{\AA}$

Fig. 1. Projection of the LaIrSi structure along the  $a_1$  axis. Large circles: La; medium circles: Ir; small circles: Si.

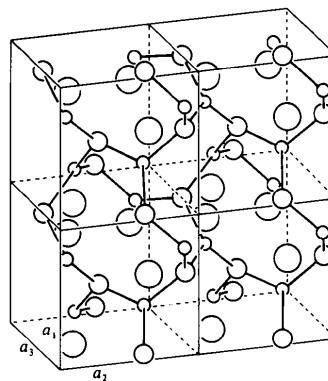


Fig. 2. Four unit cells of LaIrSi. Large circles: La; medium circles: Ir; small circles: Si. The closest Ir-Si neighbours are connected by lines. The structure corresponds to  $\text{SrSi}_2$  if the sites of the Ir-Si framework are occupied by Si atoms only.

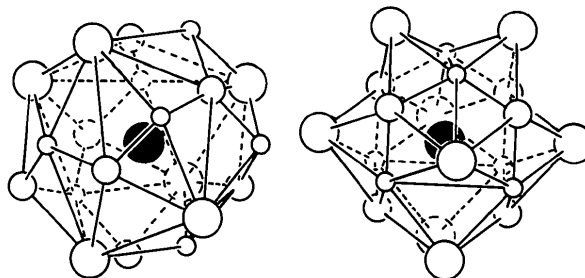


Fig. 3. The coordination polyhedra of the La atoms in (a) LaIrSi and (b) LaPtSi. Large circles: La; medium circles: Ir or Pt; small circles: Si.

Table 3. Geometric relations for idealized SrSi<sub>2</sub>- and ThSi<sub>2</sub>-type structures

## Idealized structure data

SrSi <sub>2</sub> , P4 <sub>3</sub> 32	ThSi <sub>2</sub> , I4 <sub>1</sub> /amd, c/a = 2√3
Sr in 4(a) $\frac{1}{2}\frac{1}{2}\frac{1}{2}$	Th in 4(a) 000
Si in 8(c) xxx with x = $\frac{1}{2}$	Si in 8(e) 00z with z = $\frac{1}{2}$ (Origin away from symmetry centre)

## Interatomic distances related to unit-cell parameters

$$\begin{aligned}
 6 \ d_{\text{Sr-Sr}} &= \frac{\sqrt{3}}{2\sqrt{2}} a_{\text{SrSi}_2} & 8 \ d_{\text{Th-Th}} &= a_{\text{ThSi}_2} \\
 2 \ d_{\text{Sr-Si}} &= \frac{\sqrt{3}}{4} a_{\text{SrSi}_2} & 12 \ d_{\text{Th-Si}} &= \frac{\sqrt{7}}{2\sqrt{3}} a_{\text{ThSi}_2} \\
 12 \ d_{\text{Sr-Si}} &= \frac{\sqrt{5}}{4} a_{\text{SrSi}_2} \\
 3 \ d_{\text{Si-Si}} &= \frac{\sqrt{2}}{4} a_{\text{SrSi}_2} & 3 \ d_{\text{Si-Si}} &= \frac{1}{\sqrt{3}} a_{\text{ThSi}_2}
 \end{aligned}$$

## Interatomic distances, unit-cell parameters and cell volume related to Si-Si distances s

$$\begin{aligned}
 6 \ d_{\text{Sr-Sr}} &= \sqrt{3} s & 8 \ d_{\text{Th-Th}} &= \sqrt{3} s \\
 2 \ d_{\text{Sr-Si}} &= \frac{\sqrt{3}}{\sqrt{2}} s = 1.225s & 12 \ d_{\text{Th-Si}} &= \frac{\sqrt{7}}{2} s = 1.323s \\
 12 \ d_{\text{Sr-Si}} &= \frac{\sqrt{5}}{\sqrt{2}} s = 1.581s \\
 3 \ d_{\text{Si-Si}} &= s & 3 \ d_{\text{Si-Si}} &= s \\
 a_{\text{SrSi}_2} &= 2\sqrt{2}s & a_{\text{ThSi}_2} &= \sqrt{3}s \\
 & & c_{\text{ThSi}_2} &= 6s \\
 V_{\text{SrSi}_2} &= 16\sqrt{2}s^3 = 22.63s^3 & V_{\text{ThSi}_2} &= 18s^3
 \end{aligned}$$

A comparison of the LaIrSi with the LaPtSi structure, which is a ThSi<sub>2</sub>-type derivative (Klepp & Parthé, 1982), indicates that, in both, each Si has 3*T* (*T* = Pt or Ir) and each *T* has 3 close Si neighbours. Further, the *T*-Si framework is three-dimensional, whereas the spatial arrangement is different. As seen in Fig. 3(b), La in LaPtSi also has 20 neighbours but they consist now of 6 Pt, 6 Si and 8 La atoms. The simple crystal-chemical formula La<sup>[12]</sup>Pt<sup>[3 Si]</sup>Si<sup>[3 Pt]</sup> differs from the one given for LaIrSi only in the value for the La-atom coordination.

In both the SrSi<sub>2</sub> and ThSi<sub>2</sub> types, the Si nets are three-connected and three-dimensional, and the shortest closed loop consists of 10 Si atoms. Using the notation of Wells (1977) they are both uniform (10,3) nets with the net in SrSi<sub>2</sub> occupying a unique position because of its high symmetry.

In the idealized SrSi<sub>2</sub>- and ThSi<sub>2</sub>-type structures all nearest Si-Si distances are equal and the angles between the Si-Si bonds are exactly 120°. There are thus no adjustable parameters and axial ratios and consequently all interatomic distances can be expressed

in terms of the unit-cell parameters or in terms of the Si-Si distance *s* as given in Table 3. For the idealized structures we note that for a given *s* there are no differences in the Sr-Sr or Th-Th distances; however, two Sr-Si distances are shorter and 12 longer than the Th-Si distances. The volume of the idealized SrSi<sub>2</sub> structure is larger than that of the idealized ThSi<sub>2</sub> structure.

As far as the real structures are concerned, SrSi<sub>2</sub> and LaIrSi have *x* parameters for the Si (or Ir) atoms which deviate by about 0.04 from the idealized values. It can be demonstrated that with increasing deviation from the ideal *x* value of  $\frac{3}{8}$ :

– the corresponding unit-cell volume decreases according to

$$V = s^3 \left( \frac{1}{8} + 4\Delta^2 \right)^{-3/2} \quad (1)$$

where  $\Delta = x - \frac{3}{8}$ ;

– the two shortest Sr-Si distances increase according to

$$d_{\text{Sr-Si}} = \frac{\sqrt{3} \left( \frac{1}{4} + \Delta \right)}{\left( \frac{1}{8} + 4\Delta^2 \right)^{1/2}} s \quad (2)$$

when  $0 < \Delta \leq 0.125$ . After insertion of the experimentally obtained *x* value in (1) the relation between *V* and *s* given in Table 3 is  $V = 20.84s^3$ . With the observed *s* value of 2.315 Å (Table 2) the calculated volume  $V_{P2,3} = 258.55 \text{ \AA}^3$  is in good agreement with the observed volume  $V_{\text{obs}} = 257.62 \text{ \AA}^3$ . A theoretical volume for a hypothetical LaIrSi with LaPtSi-type structure (space group *I4<sub>1</sub>md*) – after taking into consideration the 0.03 Å smaller radius of Ir as compared to Pt – has a surprisingly close numerical value of  $V_{I4,md} = 256.7 \text{ \AA}^3$ . These data may be represented as follows:

$$V_{\text{obs}} \simeq V_{P2,3} (\equiv 20.84s_{P2,3}^3) \simeq V_{I4,md} (\equiv 18s_{I4,md}^3). \quad (3)$$

$s_{I4,md}$ , calculated from the observed unit-cell volume, gives 2.43 Å which corresponds roughly to the sum of the covalent Si and metallic Ir radii (1.36 + 1.11 = 2.47 Å).  $s_{P2,3}$  is, however, much smaller at 2.31 Å (see Table 2). We note that LaIrSi could have adopted the tetragonal LaPtSi type without any stretching or shortening of Ir-Si distances (with respect to the sum of the radii) but chooses instead the LaIrSi type with shortened Ir-Si distances.

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## Ammonium-hexahydroxoplatinat(IV) und Strukturverfeinerung für Kalium-hexahydroxoplatinat(IV)

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**Abstract.**  $(\text{NH}_4)_2[\text{Pt}(\text{OH})_6]$ , rhombohedral,  $a = 5.668(2) \text{ \AA}$ ,  $\alpha = 77.01(2)^\circ$  [trigonal axes:  $a = 7.057(2)$ ,  $c = 11.820(3) \text{ \AA}$ ],  $R\bar{3}$ ,  $Z = 1$ ,  $D_x = 3.259(3) \text{ Mg m}^{-3}$ . Two-circle diffractometer data, least-squares refinement,  $R(F) = 0.033$ , 316 observed reflections.  $\text{K}_2[\text{Pt}(\text{OH})_6]$ , rhombohedral,  $a = 5.658(2) \text{ \AA}$ ,  $\alpha = 69.04(2)^\circ$  [trigonal axes:  $a = 6.413(3)$ ,  $c = 12.836(3) \text{ \AA}$ ],  $R\bar{3}$ ,  $Z = 1$ ,  $D_x = 4.109(3) \text{ Mg m}^{-3}$ . Two-circle diffractometer data, least-squares refinement,  $R(F) = 0.038$ , 275 observed reflections. The structures of the ammonium and potassium salt contain similar arrangements of  $\text{Pt}(\text{OH})_6$  octahedra [Pt–O distances of 2.017(7) and 2.016(8)  $\text{ \AA}$ ]. In contrast to the (3 + 3 + 3)-coordination of potassium, the ammonium ion has only three oxygen neighbours [O–N distance = 2.758(7)  $\text{ \AA}$ ] due to the formation of hydrogen bonds.

**Einleitung.** Das Ammoniumsalz der Hydroxoplatin(IV)-säure wurde im Rahmen von Untersuchungen über Platinsäure und Hydroxoplatinate(IV) in Form von Einkristallen dargestellt (Bandel, Platte & Trömel, 1981). Wenige kleine gelbe plättchenförmige Kristalle wurden erhalten, indem eine Lösung von Platinsäure in etwa 20%igem Ammoniak im Exsikkator über KOH eingeengt wurde. Die Kristalle zerfielen an der Luft rasch unter Ammoniakabspaltung. Sie wurden deshalb zur Untersuchung in Markröhrchen eingeschmolzen. Die röntgenographische Untersuchung zeigte grosse Ähnlichkeit zu  $\text{K}_2[\text{Pt}(\text{OH})_6]$ , so dass eine eng verwandte Struktur angenommen werden konnte. Da die Strukturdaten von  $\text{K}_2[\text{Pt}(\text{OH})_6]$  (Björling, 1941) gegenüber den anderen

bisher bekannten Hydroxoplatinaten (Trömel & Lupprich, 1975a; Bandel, Müllner & Trömel, 1979) verhältnismässig kurze Platin–Sauerstoff-Abstände ergeben, wurden auch diese Struktur neu verfeinert. Plättchenförmige gelbe Einkristalle von  $\text{K}_2[\text{Pt}(\text{OH})_6]$  wurden durch Einengen einer Lösung von Platinsäure in 2MKOH über Silikagel im Exsikkator erhalten.

Die Gitterkonstanten von  $(\text{NH}_4)_2[\text{Pt}(\text{OH})_6]$  wurden aus Weissenberg- und Präzessionsaufnahmen bestimmt und ebenso wie die von  $\text{K}_2[\text{Pt}(\text{OH})_6]$  nach Zählrohr-Guinier-Aufnahmen [Huber System 600, Cu  $K\alpha_1$ -Strahlung,  $\lambda = 1.54051 \text{ \AA}$ , Quarzmonochromator, mit  $\text{Pb}(\text{NO}_3)_2$ ,  $a = 7.8562 \text{ \AA}$ , als externem Standard] verfeinert. Bei rhomboedrischer Indizierung zeigten sich keine Auslöschungen, so dass als Raumgruppen  $R\bar{3}$ ,  $R\bar{3}m$  und ihre nichtzentrosymmetrischen Untergruppen  $R3$ ,  $R3m$  und  $R32$  in Betracht kamen. Reflexintensitäten der rhomboederförmigen Kristalle {Abmessungen in Richtung der  $a$ -,  $b$ - und  $c$ -Achsen bei  $(\text{NH}_4)_2[\text{Pt}(\text{OH})_6]$ : 0,090 (5), 0,096 (5) und 0,062 (5) mm; bei  $\text{K}_2[\text{Pt}(\text{OH})_6]$ : 0,100 (5), 0,140 (5) und 0,180 (5) mm} wurden mit einem automatischen Zweikreisdiffraktometer Huber RHD 402 aufgenommen (Mo  $K\alpha$ -Strahlung, Graphitmonochromator,  $\lambda = 0.71069 \text{ \AA}$ ,  $\omega$ - $2\theta$ -Abtastung, Abtastbreite in  $\omega$  2,4°, in  $\theta$  1,2°, Drehung um die rhomboedrische  $a$ -Achse). Im Winkelbereich bis  $\theta = 30^\circ$  wurden bei  $(\text{NH}_4)_2[\text{Pt}(\text{OH})_6]$  831 Reflexe und bei  $\text{K}_2[\text{Pt}(\text{OH})_6]$  608 Reflexe gemessen. Zwischen den symmetrisch äquivalenten Reflexen wurde ohne Absorptionskorrektur gemittelt. Die resultierenden Datensätze umfassten bei  $(\text{NH}_4)_2[\text{Pt}(\text{OH})_6]$  316, bei  $\text{K}_2[\text{Pt}(\text{OH})_6]$  275 Reflexe. Die Auswertung erfolgte mit