

## Ternary Phases $MPtSi$ ( $M = Ca, Eu, Sr, Ba$ ) with the $LaIrSi$ -Type Structure

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Four ternary phases  $MPtSi$  ( $M = Ca, Eu, Sr, Ba$ ) have been shown to crystallize in the  $LaIrSi$ -type structure (space group  $P2_13$ ). This ternary structure is a derivative structure of the binary  $SrSi_2$ -type structure (space group  $P4_332$  or  $P4_132$ ). In the  $MPtSi$  series the  $LaIrSi$ -type structure has a stability range for metals with radii from  $r_{Ca} = 1.973 \text{ \AA}$  to  $r_{Ba} = 2.243 \text{ \AA}$  in contrast to  $MSi_2$  compounds which exist with the  $SrSi_2$ -type structure only from  $r_{Sr} = 2.151 \text{ \AA}$  to  $r_{Ba} = 2.243 \text{ \AA}$ . From a single-crystal investigation on  $CaPtSi$  remarkably short Pt–Si distances of  $2.30 \text{ \AA}$  ( $3x$ ) are obtained. Structural relations are discussed. © 1986 Academic Press, Inc.

### Introduction

Dimorphic  $SrSi_2$  is the only compound for which the two simplest three-dimensional three-connected (3D3C) nets are observed in its polymorphs, although in slightly distorted arrangements (1–7). The cubic 3D3C net is found in the silicon sublattice of the normal-pressure (NP) phase of  $SrSi_2$  I ( $SrSi_2$ -type structure, space group  $P4_332$  or  $P4_132$ ) (8), the tetragonal 3D3C net, in that of the high-pressure (HP) phase  $SrSi_2$  II ( $\alpha$ - $ThSi_2$ -type structure, space group  $I4_1/amd$ ) (9, 10). The tetragonal phase is quenchable from high-pressure–high-temperature conditions (e.g., 4 GPa,  $1000^\circ\text{C}$ , belt-type apparatus).

Recently, Parthé and Klepp observed both 3D3C nets in the ternary compounds  $LaIrSi$  and  $LaPtSi$  (11, 12). In cubic  $LaIrSi$  the Ir and the Si atoms are found in an ordered arrangement which leads to a lowering of the symmetry (space group  $P2_13$ )

(11). In tetragonal  $LaPtSi$  the Pt and the Si atoms are also distributed in an ordered arrangement of two different sites leading to a lowered symmetry (space group  $I4_1md$ ) (12).

It is the purpose of this paper to study whether the 3D3C nets can be obtained in ternary compounds  $MPtSi$  ( $M = Ca, Eu, Sr, Ba$ ). In these ternary compounds the metallic radius of the four electropositive metals is varied from  $r_{Ca} = 1.973 \text{ \AA}$  (for coordination number 12) to  $r_{Ba} = 2.243 \text{ \AA}$  bearing in mind that for the four binary disilicides up to 4 GPa five different structure types are known contrary to the four binary diplatinites which are isotypic at normal pressure and crystallize in the  $MgCu_2$ -type structure.

To check if the Si and the Pt atoms have an ordered arrangement in the  $MPtSi$  compounds a single-crystal investigation of  $CaPtSi$  has been performed on a four-circle X-ray diffractometer.

## Experimental

Samples of the ternary compounds were prepared by inductively heating the elements in a water-cooled copper boat under argon. For X-ray powder investigations the Debye-Scherrer method ( $\text{CuK}\alpha$ -radiation, 114.6-mm camera diameter) was used without further annealing of the as-cast samples. The powder diagrams showed that the MPtSi compounds are isotypic.

A single crystal of CaPtSi ( $0.03 \times 0.03 \times 0.03 \text{ mm}^3$ ) was measured on a Siemens four-circle diffractometer and showed Laue symmetry  $m\bar{3}$  with systematic absences for  $\{h00\}$  reflections with  $h \neq 2n$ . This leads to space group  $P2_13$ , recently found for LaIrSi by Parthé and Klepp (11). The structural investigation (633 reflections with  $\bar{6} \leq h \leq 6$ ,  $0 \leq k, l \leq 6$  measured with Zr-filtered  $\text{MoK}\alpha$ -radiation; 191 reflections unique with internal consistency of 8.04%;  $R = 5.03\%$  for anisotropic thermal parameters) shows that the Si and the Pt atoms have the ordered arrangement of the LaIrSi-type structure (11). For statistical occupation for the Si and Pt positions one finds  $R = 32\%$ .

In Table I the lattice parameters for the ternary MPtSi ( $M = \text{Ca, Eu, Sr, Ba}$ ) compounds are presented; in Table II the positional and thermal parameters for CaPtSi.

TABLE I

LATTICE PARAMETERS FOR CUBIC MPtSi ( $M = \text{Ca, Eu, Sr, Ba}$ ) PHASES WITH THE LaIrSi-TYPE STRUCTURE

Compound	$a$ -axis <sup>a</sup> (Å)
CaPtSi	6.320(5)
EuPtSi	6.420(5)
SrPtSi	6.485(5)
BaPtSi	6.633(5)

<sup>a</sup> Estimated standard deviations (ESDs) are given in parentheses.

TABLE II

POSITIONAL AND THERMAL PARAMETERS ( $\text{Å}^2 \times 10^3$ ) FOR CaPtSi WITH THE LaIrSi-TYPE STRUCTURE<sup>a</sup>

	$x$	$U_{11}$	$U_{12}$
Ca	0.1276(6)	0.86(8)	0.09(8)
Pt	0.4189(1)	1.53(2)	-0.14(2)
Si	0.8345(9)	0.93(13)	0.03(15)

<sup>a</sup> Space group  $P2_13$ , all atoms in equipoint  $4a(x = y = z; U_{11} = U_{22} = U_{33}; U_{12} = U_{13} = U_{23})$ ; ESDs in parentheses.

## Discussion

Four ternary phases MPtSi ( $M = \text{Ca, Eu, Sr, Ba}$ ) have been shown to be isotypic with LaIrSi (11). The lattice parameters of these compounds (Table I) increase as the metallic radii of the electropositive metals increase. For EuPtSi this value ( $a = 6.420 \text{ Å}$ , Table I) is slightly higher than the average of the lattice parameters of CaPtSi and SrPtSi ( $a = 6.320 \text{ Å}$ ,  $a = 6.485 \text{ Å}$ , respectively). Since the metallic radius of divalent europium is nearly the average of those values of calcium and strontium it seems that in EuPtSi the europium atoms are divalent.

The cubic 3D3C net is known up to now only for two binary compounds: NP-phase  $\text{SrSi}_2$  I with lattice parameter  $a = 6.535 \text{ Å}$  (7) and HP-phase  $\text{BaSi}_2$  III with  $a = 6.715 \text{ Å}$  (13).  $\text{BaSi}_2$  III is quenchable from 4 GPa and  $800^\circ\text{C}$ . In comparison to the lattice parameters of the ternary compounds SrPtSi and BaPtSi, one finds an increase for the binary phases. The cubic 3D3C net ( $\text{SrSi}_2$ -type structure (8)) has not been observed for  $\text{CaSi}_2$  and  $\text{EuSi}_2$  although ternary cubic compounds CaPtSi and EuPtSi with the LaIrSi-type structure exist (Table I).

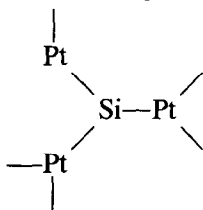
The interatomic distances for CaPtSi (Table III) are of special interest. The Pt-Si distances within the cubic 3D3C net are remarkably short ( $2.30 \text{ Å}$ ,  $3x$ ). These results are in line with the observation of Parthé and Klepp who found short Ir-Si distances of  $2.32 \text{ Å}$  in LaIrSi (11). On the other hand,

TABLE III  
INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°)  
FOR CaPtSi<sup>a</sup>

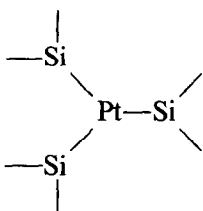
Ca-6 Ca 3.871(3)	Pt-3 Ca 3.169(6)	Si-2 Ca 3.208(11)
-3 Pt 3.169(6)	-1 Ca 3.188(6)	-3 Ca 3.650(13)
-1 Pt 3.188(6)	-3 Ca 3.708(7)	-3 Pt 2.297(5)
-3 Pt 3.708(7)	-3 Si 2.297(5)	-6 Si 3.937(3)
-4 Si 3.208(11)	-6 Pt 3.949(3)	
-3 Si 3.650(13)	$\angle$ Pt <sup>Si</sup> Pt 118.5(1)	$\angle$ Si <sup>Pt</sup> Si 117.9(1)

<sup>a</sup> ESDs are given in parentheses.

the shortest Ca-Si distances (3.21 Å, 4x, Table III) in CaPtSi are slightly longer than the shortest Ca-Pt distances (3.17 Å, 3x; 3.19 Å, 1x). The analogous relation holds for LaIrSi where the La-Si distances are longer than the La-Ir distances (11). Although the interbond angles in the



and the



groups are only slightly different (118.5, 117.9°, respectively, Table III) the positions in the 3D3C net cannot be interchanged. Doing this raises the *R* value of the single-crystal investigation to 42% for CaPtSi and to 40% for LaIrSi (11). The slightly asymmetric distribution of the three-connected atoms in the ternary LaIrSi-type structure is perhaps one reason for the large stability range in the MPtSi series with metallic radii from  $r_{\text{Ca}} = 1.973$  Å to  $r_{\text{Ba}} = 2.243$  Å. The binary SrSi<sub>2</sub>-type structure exists in the MSi<sub>2</sub> series only from  $r_{\text{Sr}} = 2.151$  Å to  $r_{\text{Ba}} = 2.243$  Å.

The hypothetical ideal cubic 3D3C net represents the three-connected analogon of four-connected cubic diamond (5). In group-theoretical description (14) a change of the ideal 3D3C net with space group *I*4<sub>1</sub>32 to the 3D3C net really observed in the SrSi<sub>2</sub>-type structure with space group *P*4<sub>3</sub>32 (or *P*4<sub>1</sub>32) corresponds to a class-equivalent ("klassengleich") maximal subgroup of index 2. The space group of the LaIrSi-type structure (*P*2<sub>1</sub>3) is a maximal lattice-equivalent ("translationengleich") subgroup of *P*4<sub>3</sub>32 (or *P*4<sub>1</sub>32). However, in the LaIrSi-type structure the twofold axis in the [110] direction is lost so that the index of the subgroup is 2. The symmetry reduction going from the ideal 3D3C net to the two distorted versions is given schematically in Fig. 1 together with comments.

For cubic CaSi<sub>2</sub> with the 3D3C net (SrSi<sub>2</sub>-type structure) one can expect from the remarkable short Pt-Si distances in CaPtSi (2.30 Å, 3x, Table III) also three short Si-Si distances. However, silicides containing more than one Si-Si distance shorter than that in silicon itself (2.35 Å) have not been characterized by modern single-crystal diffraction techniques so far. In tetragonal CaSi<sub>2</sub>, EuSi<sub>2</sub>, and SrSi<sub>2</sub> with the 3D3C net ( $\alpha$ -ThSi<sub>2</sub>-type structure) only one Si-Si distance is shorter than 2.35 Å (2.30, 2.31, 2.33 Å, respectively) (15-17). The two other Si-Si distances are longer.

The MSi<sub>2</sub> phases (*M* = Ca, Eu, Sr, Ba) are classified as Zintl phases because their Si atoms are three-connected (even up to high pressures of 4 GPa). Commonly, this behavior can be interpreted by an ionic formulation  $M^{2+}(\text{Si}^-)_2$  in which the Si atoms become isoelectronic with phosphorus and have, due to the 8-*N*-rule, three next neighbors. However, the radii and the electronegativity of Si and Pt are nearly the same, only half the Si atoms in MSi<sub>2</sub> must be replaced in order to get MPtSi phases in which the Si and the Pt atoms remain three-connected. Replacing all the Si at-

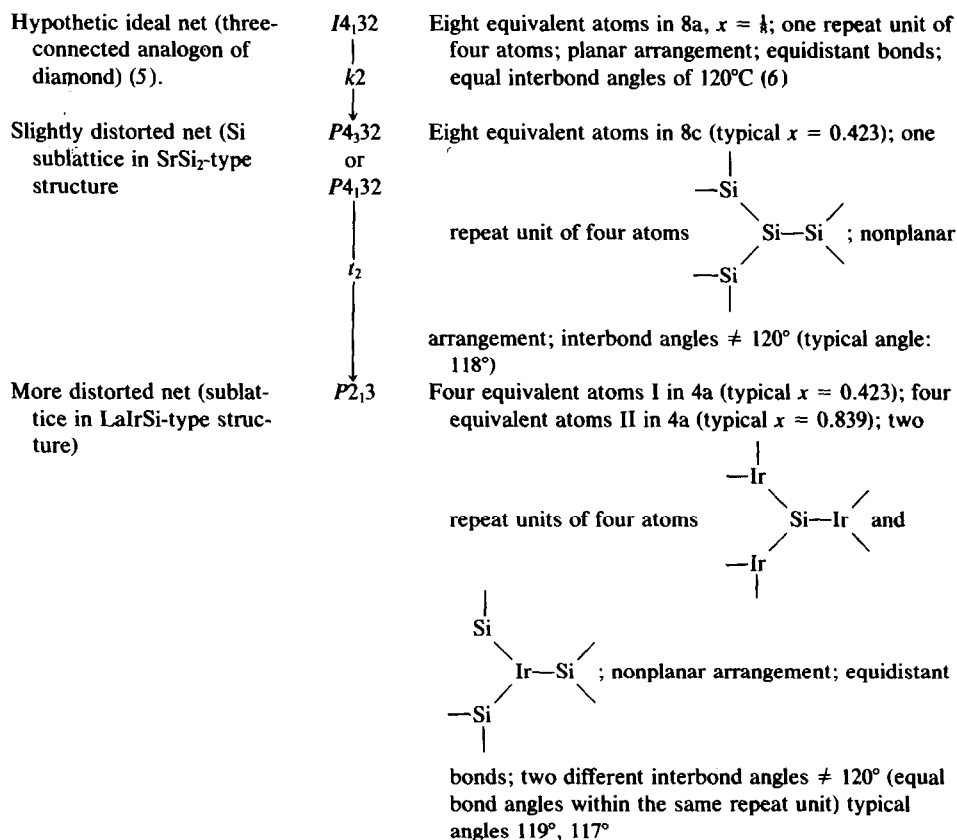


FIG. 1. Symmetry relations between cubic 3D3C nets.

oms in  $MSi_2$  to get  $MPt_2$  phases one obtains the  $MgCu_2$ -type structure already known for Laves phases.  $CaPt_2$ ,  $EuPt_2$ ,  $SrPt_2$ ,  $BaPt_2$  are all isotypic at NP (18–19). The Zintl-phase character which is represented by the three-connected bonds is lost in the  $MPt_2$  compounds since the Pt atoms have now six nearest Pt neighbors.

Therefore the interesting question arises if it is possible to transform even the disilicides  $MSi_2$  at very much higher pressures than 4 GPa with loss of Zintl-phase character into phases with  $MgCu_2$ -type structure with Laves-phase character. It would be a great success of high-pressure chemistry if one could change the bond character between Zintl and Laves phases for  $MSi_2$  compounds. Investigation of ternary

phases with compositions between  $MPtSi$  and  $MPt_2$  ( $M = Ca, Eu, Sr, Ba$ ) will give some information to this problem and is under way now.

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