JOURNAL OF SOLID STATE CHEMISTRY 20, 173–181 (1977)

Effect of Pressure on the Structures of Divalent Metal Disilicides MSi_2 (M = Ca, Eu, Sr)

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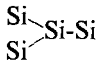
Received July 29, 1976

After high-pressure/high-temperature treatment (40 kbar at 1000–1500°C) and quenching to ambient conditions $CaSi_2$, $EuSi_2$, and $SrSi_2$ crystallize in the α-$ThSi_2$ type of structure. Lattice constants and positional parameters have been determined by X-ray powder technique. Structural relations are discussed.

Introduction

The alkaline earth metals calcium and strontium and the divalent rare earth metal europium have two outer *s*-electrons in their atomic ground state. Obviously, in many of their compounds similar properties and isotypic structures are found. At ambient pressure, however, their disilicides crystallize in three structure types which differ characteristically in their silicon sublattices. The purpose of this paper is to show that the disilicides $CaSi_2$, $SrSi_2$, and $EuSi_2$ become isotypic after high-pressure/high-temperature treatment.

In $CaSi_2$ ($CaSi_2$ type of structure) (*1*, *2*) the Si sublattice consists of corrugated layers in which each silicon has three equidistant neighbors. In $SrSi_2$ ($SrSi_2$ type of structure) (*3–5*) the silicon atoms form a cubic three-dimensional network. Again all Si atoms have three equidistant neighbors in flat trigonal pyramids, but twisted against each other. In $EuSi_2$ (α-$ThSi_2$ type of structure) (*6*) another type of Si network is found. Each silicon atom also has three neighbors, but here they are in a planar arrangement. These



$$\begin{array}{l}\mathrm{Si}\diagdown \\ \qquad \mathrm{Si{-}Si} \\ \mathrm{Si}\diagup \end{array}$$

groups are twisted alternatively by 90° in the direction of the tetragonal *c* axis.

All of these Si sublattices satisfy the (8-N) rule (*7*) which requires a formal transfer of the valence electrons of the divalent metal to silicon. The Si atoms then become isoelectronic with Group V elements.

High-pressure transformations frequently lead to an increase in the number of nearest neighbors. It seemed of general interest to check whether such an increase is also found in the Si sublattices of the disilicides or if the validity of the (8-N) rule persists. In addition, only three binary representatives are known for both $CaSi_2$ and $SrSi_2$ type of structures contrary to some 20 for α-$ThSi_2$. Therefore, the question arose of whether or not it might be possible to transform the quite unusual connection of Si atoms in $CaSi_2$ and $SrSi_2$ into a more common array by high-pressure/high-temperature treatment.

A survey of the literature data shows that at least for $CaSi_2$ a high-pressure polymorph does exist (*8*, *9*). For this phase the α-$ThSi_2$ type of structure was determined from tetragonal indexing of the X-ray powder pattern.

Experimental

Synthesis of normal pressure phases. Synthesis of these compounds was aimed toward stoichiometric samples of high purity in order to get the maximum information

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ISSN 0022-4596

regarding the measurement of physical properties after high-pressure/high-temperature treatment. Difficulties arise from three problems. The commercially available metals calcium and strontium are very impure. Hot alkaline earth and rare earth metals and silicon are quite reactive against crucible materials and atmosphere applied during melting. Another problem is connected with the high vapor pressure of divalent metals at melting conditions. Therefore, the alkaline earth metals calcium and strontium were purified by "reactive" ultrahigh vacuum distillation. Experimental details have been given elsewhere (*10*, *11*). In order to lower the contamination rate by crucible material and atmosphere the syntheses were performed in a high-vacuum tight cold copper boat under argon. The apparatus has been described previously (*12*). Samples were heated inductively. Evaporation losses of the divalent metals during melting were determined in preliminary experiments by weighing final samples. Typical purities were in the range between 99.92 and 99.98 wt% (*13*). Cu impurity from the metal boat was introduced between 1 and 5 wt ppm (*14*). Starting materials were $CaSi_2$ in the TR 6 modification ($a = 3.855$ Å, $c = 30.6$ Å). $EuSi_2$ ($a = 4.304$ Å, $c = 13.65$ Å), and cubic $SrSi_2$ ($a = 6.535$ Å). The lattice constant of the $SrSi_2$ samples in this work is higher than the value in the redetermination of the structure by Pringle (*5*) ($a = 6.515$ Å) and closer to the value of the earlier structure determination (*3*, *4*) ($a = 6.540$ Å).[1]

High-pressure/high-temperature treatment. The treatment was performed in a belt-type apparatus in boron nitride crucibles. Experimental data are quoted elsewhere (*15*). Typical conditions were 40 kbar, 1000–1500°C, 15–30 min, and decompression after quenching to room temperature. Samples of normal and of high-pressure phases were manipulated in a glove box under argon atmosphere which was continuously regenerated with liquid sodium–potassium alloy.

X-ray characterization. X-ray characterization was performed by the Debye–Scherrer technique (114.6 mm camera diameter, filtered Cu and Mo radiation). Lattice constants were determined with samples to which germanium was admixed as an internal standard. Intensities were measured via optical densities of exposed films obtained on a Joyce and Loibl Autodensidater (*16*). The data were corrected for absorption.

Results

Metastable high-pressure modifications up to 40 kbar only were found for $CaSi_2$ and $SrSi_2$. Samples of these showed a reddish-brown color which cannot be attributed to oxidation. No phase transition was observed for $EuSi_2$ under our experimental conditions. Powder patterns of $EuSi_2$ and of high pressure polymorphs of $CaSi_2$ and $SrSi_2$ showed sharp reflections and could be indexed with a tetragonal lattice. The best agreement of observed and calculated intensities was achieved with the α-$ThSi_2$ type of structure (space group D_{4h}^{19}, 4 M in 4a, 8 Si in 8e) (*17*) with parameters z of 0.413–0.414. The residual values (defined as $\sum |I_0 - I_c| / \sum I_0$) were in the range of 0.07–0.08. No experimental hint was found for nonstoichiometry in these phases. In agreement with the analytical data the lowest residual value for $CaSi_2$ was obtained for a $1._0:2._0$ composition. Among all known compounds with α-$ThSi_2$-type structures the high pressure polymorph of $CaSi_2$ is most favorable for the determination of the positional parameter z. The number of electrons Z which contribute to X-ray intensity is comparable to the value of silicon (Si: $Z = 14$, Ca: $Z = 20$). The response of the X-ray reflections to variations of the positional parameter is less intense the heavier the metal is.

Experimental data are listed in Table I and observed and calculated d values and intensities are shown in Tables II–IV. Good agreement is obtained between the results of tetragonal axes of $CaSi_2$ of this work and data quoted by McWhan *et al.* (*9*). The c axis of

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[1] Redetermination of the structure led to a parameter change of −0.005 ($z = 0.173$, derived from 235 planes by complete crystallographic examination instead of 0.178 from 105 planes without correction for absorption and thermal vibrations, as determined earlier (*3*, *4*). With $a = 6.535$ Å this results in changes of nearest spacings: Sr–Sr 0.00 Å, Si–Si −0.02 Å, Sr–Si + 0.04 Å.

TABLE I

CRYSTALLOGRAPHIC DATA

Compound	$CaSi_2$	$EuSi_2$	$SrSi_2$
a-axis ± 0.003 (Å)	4.283	4.304	4.438
c-axis ± 0.01 (Å)	13.52	13.65	13.83
Unit cell volume (Å^3)	248.0	252.9	272.4
Axial ratio c/a	3.16	3.17	3.12
Space group	D_{4h}^{19}-$I4_1/amd$	D_{4h}^{19}-$I4_1/amd$	D_{4h}^{19}-$I4_1/amd$
Metal positions	4 M in 4a	$(0, 0, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(0, \frac{1}{2}, \frac{1}{4})$ $(\frac{1}{2}, 0, \frac{3}{4})$
Silicon positions	8 Si in 8e	$(0, 0, z)$ $(0, \frac{1}{2}, \frac{1}{4} + z)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z)$ $(\frac{1}{2}, 0, \frac{3}{4} + z)$	$(0, 0, \bar{z})$ $(0, \frac{1}{2}, \frac{1}{4} - z)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + \bar{z})$ $(\frac{1}{2}, 0, \frac{3}{4} - z)$
Positional parameter of Si atoms in 8e	0.413_5	0.414	0.414

the present work is slightly shorter (13.52 Å as compared with 13.541 Å). This may be due to differences in stoichiometry. A still higher change with stoichiometry is observed in $SrSi_2$ ($c = 13.83$ Å in stoichiometric high-pressure polymorphs and $c = 13.92$ Å in defect $SrSi_{2-x}$, where $x = 0.25$. (*18*)

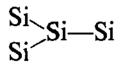
At low scattering angles very weak reflections appeared in high-pressure polymorphs of $CaSi_2$, $SrSi_2$, and $EuSi_2$, which hints at the existence of superstructures. Details of these will be published in a separate paper.

The metastable phases of $CaSi_2$ and $SrSi_2$ can be stored at room temperature at normal pressure for several months without retransformation into the stable normal pressure phases. However, heating to 350°C leads to retransformation of $CaSi_2$. $SrSi_2$ remains stable even at 650°C.

Discussion

Generally, coordination number and space filling are increased by high-pressure treatment of solids. In normal pressure phases the volume contraction in comparison with the additive volume of the elements (Table V) is higher in $EuSi_2$ (nominal 20:9 coordination) and in $SrSi_2$ (14:7 coordination) than in $CaSi_2$ (13:6.5 coordination). The volume contraction in these phases can be compared with experimental conditions of high-pressure/high-temperature treatment. $CaSi_2$ is easily transformed, $SrSi_2$ requires stronger treatment, and $EuSi_2$ cannot be transformed under our conditions. Accordingly, the rearrangement of the metastable high pressure polymorph into the normal pressure phase is faster with $CaSi_2$ than with $SrSi_2$ and needs less activation energy. Raising the coordination for $CaSi_2$ and $SrSi_2$ to 20:9 in their high pressure polymorphs leads to a decrease of the unit cell volume of 6.9 and 1.9%, respectively. The large decrease in $CaSi_2$ is connected with a change of Si layers into a three-dimensional network while in $SrSi_2$ only a rearrangement in the network takes place. Formal increase of bond distances in the high pressure polymorphs is overcompensated by higher coordination, thus lowering the unit cell volume.

The Zintl–Klemm–Busmann concept (*19*) (= (8-N) rule) can also be applied to the high-pressure phases of $CaSi_2$ and $SrSi_2$, but in a limited way. The silicon atoms are still three-coordinated, but in coplanar



groups. In addition, the bond distances of the three neighbors are slightly different (Table VI). Contrary to the normal pressure phase of

TABLE II

Observed and Calculated d Values (Å) and Intensities[a] for Tetragonal $CaSi_2$

$h\,k\,l$	d_{obs}	d_{calc}	I^{b}_{obs}	I_{calc}
1 0 1	—	4.0825	0.0	0.7
0 0 4	—	3.3795	0.0	1.0
1 0 3	3.0890	3.1042	27.8	27.0
1 1 2	2.7503	2.7635	100.0	91.0
1 0 5	2.2774	2.2861	49.4	48.3
2 0 0	2.1447	2.1413	44.3	44.6
2 1 1	—	1.8963	0.0	0.3
2 0 4	1.8051	1.8088	1.3	0.5
1 1 6		1.8076		1.2
2 1 3	1.7563	1.7626	29.8	10.5
1 0 7		1.7604		19.6
0 0 8	—	1.6898	0.0	0.6
2 1 5	1.5591	1.5628	27.3	30.9
2 2 0	1.5105	1.5141	14.8	15.5
3 0 1	—	1.4196	0.0	0.1
1 0 9	—	1.4174	0.0	1.0
2 2 4	—	1.3818	0.0	0.1
3 0 3	1.3579	1.3608	18.7	1.9
2 1 7		1.3598		14.9
3 1 2	1.3253	1.3279	19.0	17.1
2 0 8		1.3265		0.7
3 0 5	1.2601	1.2623	6.8	7.0
1 1 10	1.2324	1.2344	8.7	10.4
3 2 1	1.1804	1.1832	1.7	0.1
2 1 9		1.1819		1.4
1 0 11		1.1812		0.3
3 1 6	—	1.1607	0.0	0.8
3 2 3	1.1460	1.1485	5.9	2.5
3 0 7		1.1479		5.0
2 2 8	1.1257	1.1276	3.2	0.5
0 0 12		1.1265		2.9
3 2 5	1.0872	1.0874	w[c]	9.6
4 0 0	1.0706	1.0706	w	5.1
4 1 1	—	1.0356	—	0.1
3 0 9		1.0347		0.4
2 1 11		1.0343		0.2
4 0 4	—	1.0206	—	0.1
4 1 3	1.0112	1.0121	w	1.6
3 2 7		1.0117		6.3
1 0 13		1.0105		0.0
3 3 2	0.9966	0.9983	w	3.4
2 0 12		0.9970		7.0
4 1 5	0.9693	0.9696	w	5.9
4 2 0	0.9560	0.9576	w	6.3
3 1 10		0.9567		8.0

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[a] Mo radiation.

[b] At high d values additional reflections ($I_{obs} < 1$) appeared. Intensities of reflections with d values <1.12 Å could not be measured with high accuracy due to line broadening.

[c] w = weak.

TABLE III

OBSERVED AND CALCULATED *d* VALUES (Å) AND INTENSITIES[a] FOR $EuSi_2$

h k l	d_{obs}	d_{calc}	I_{obs}	I_{calc}
1 0 1	4.0791	4.1048	46.2	43.5
0 0 4	3.4040	3.4130	17.9	19.5
1 0 3	3.1129	3.1270	52.3	52.0
1 1 2	2.7692	2.7796	100.0	104.7
1 0 5	2.3002	2.3056	43.4	40.5
2 0 0	2.1432	2.1530	37.1	35.7
2 1 1	1.9024	1.9060	9.7	12.7
1 1 6	1.8185	1.8223	69.8	15.2
2 0 4		1.8204		9.7
1 0 7	1.7725	1.7764		23.0
2 1 3		1.7728		18.7
0 0 8	1.7065	1.7065	4.7	3.7
2 1 5	1.5723	1.5732	23.4	27.5
2 2 0	1.5195	1.5217	11.6	13.2
1 0 9	1.4303	1.4306	7.6	5.2
3 0 1		1.4268		2.5
2 2 4	1.3889	1.3898	29.9	6.2
2 1 7	1.3701	1.3700		15.3
3 0 3		1.3683		4.8
2 0 8	1.3335	1.3371	29.3	6.5
3 1 2		1.3348		23.7
3 0 5	1.2694	1.2700	8.8	6.7
1 1 10	1.2459	1.2456	11.5	11.7
1 0 11	1.1912	1.1925	11.1	1.5
2 1 9		1.1914		6.0
3 2 1		1.1892		3.2
3 1 6	1.1701	1.1680	5.2	5.3
3 0 7	1.1537	1.1557	10.4	5.2
3 2 3		1.1546		6.3
0 0 12	1.1372	1.1377	6.8	2.7
2 2 8		1.1357		4.3
3 2 5	1.0937	1.0938	w[b]	9.0
4 0 0	1.0768	1.0760	w	4.5
2 1 11	1.0435	1.0431	w	2.0
3 0 9		1.0423		2.0
4 1 1		1.0408		2.1
4 0 4	1.0243	1.0262	vw[c]	2.7
1 0 13		1.0202		1.1
3 2 7	1.0187	1.0181	w	6.7
4 1 3		1.0174		4.2
2 0 12	1.0059	1.0058	w	7.0
3 3 2		1.0034		5.2
4 1 5	0.9758	0.9750	w	5.8
3 1 10	0.9641	0.9639	w	9.7

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[a] Mo radiation. Intensities of reflections with *d* values <1.13 Å could not be measured with high accuracy due to line broadening.

[b] w: weak.

[c] vw: very weak.

TABLE IV

OBSERVED AND CALCULATED d VALUES (Å) AND INTENSITIES[a] FOR TETRAGONAL $SrSi_2$

$h\,k\,l$	d_{obs}	d_{calc}	I_{obs}	I_{calc}
1 0 1	4.2128	4.2259	14.3	15.3
0 0 4	3.4586	3.4585	10.0	9.7
1 0 3	3.1895	3.1977	37.6	39.9
1 1 2	2.8513	2.8578	100.0	95.4
1 0 5	2.3460	2.3479	39.1	38.5
2 0 0	2.2135	2.2190	30.3	35.4
2 1 1	1.9623	1.9646	4.7	3.7
2 0 4	1.8637	1.8676	7.2	6.3
1 1 6		1.8581		2.0
2 1 3	1.8218	1.8230	31.6	15.2
1 0 7	1.8016	1.8054		15.8
0 0 8	1.7254	1.7293	2.2	1.7
2 1 5	1.6140	1.6127	23.0	23.2
2 2 0	1.5661	1.5691	13.4	11.5
3 0 1	—	1.4709	0.0	0.7
1 0 9	1.4499	1.4525	2.7	2.6
2 2 4	1.4264	1.4289	2.7	2.5
3 0 3	1.4054	1.4086	14.2	2.8
2 1 7	1.3980	1.4004		11.7
3 1 2	1.3744	1.3754	18.0	16.5
2 0 8	1.3621	1.3640		2.8
3 0 5	1.3031	1.3046	7.1	5.3
1 1 10	1.2635	1.2659	8.3	7.5
3 2 1	—	1.2260	0.0	0.7
2 1 9	1.2145	1.2153	3.7	3.0
1 0 11		1.2100		0.2
3 1 6	1.1992	1.1988	1.8	1.0
3 2 3	1.1892	1.1892	6.5	3.7
3 0 7	1.1843	1.1843		3.9
2 2 8	1.1620	1.1620	2.1	1.9
0 0 12	1.1541	1.1528	2.2	2.2
3 2 5	1.1239	1.1246	w[b]	7.7
4 0 0	1.1094	1.1095	w	4.0
4 1 1	—	1.0731	—	0.6
3 0 9	1.0636	1.0659	vw[c]	1.1
2 1 11		1.0623		0.4
4 0 4	1.0558	1.0565	vw	1.1
4 1 3	1.0443	1.0482	w	2.8
3 2 7		1.0448		6.0
1 0 13	1.0336	1.0348	w	0.4
3 3 2		1.0343		4.4
2 0 12	1.0225	1.0230	w	6.7
4 1 5	1.0028	1.0031	w	6.2
4 2 0	0.9921	0.9924	w	6.3
3 1 10	0.9851	0.9852	w	9.3

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[a] Cu radiation. Intensities of reflections with d values < 1.15 Å could not be measured with high accuracy due to line broadening.

[b] w: weak.

[c] vw: very weak.

TABLE V

Volume Contraction

Compound	Volume contraction[a] $-\Delta V/V$ (%) Normal pressure phase	High pressure phase
$CaSi_2$	12.0	18.9
$EuSi_2$	20.1	20.1
$SrSi_2$	20.1	22.0

[a] $V_{Ca} = 43.6$, $V_{Eu} = 48.1$, $V_{Sr} = 56.3$, $V_{Si} = 15.5$ (in Å^3).

$CaSi_2$ in which the Si sublattice consists of arsenic-like corrugated layers, no structural analog of a Group V element exists for the α-$ThSi_2$-type structure of the high-pressure phases of $CaSi_2$ and $SrSi_2$. This is due to the fact that an element structure of this Si-sublattice type would comprise large holes. In the case of disilicides the holes can be filled with metal atoms. The same argument may be used for the normal pressure phase of $SrSi_2$ for which also no structural analog in the Group V series is known.

According to Wells (*20*) the silicon networks in the cubic phase of $SrSi_2$ and in α-$ThSi_2$ represent the two simplest three-connected networks. The ideal cubic network can be considered as the three-connected analog of the diamond. To the knowledge of the authors $SrSi_2$ is the first example in which both three-connected networks are observed in the polymorphs of one compound. By only a few translation steps with breaking and linking bonds the networks can be transformed into each other, However, more activation energy is needed for retransformation of the α-$ThSi_2$ network into the cubic one in $SrSi_2$ than is needed for its retransformation into corrugated layers in $CaSi_2$.

As mentioned above in the α-$ThSi_2$-type structure of $CaSi_2$, $EuSi_2$, and $SrSi_2$, quite unequal Si–Si spacings appear (Table 6). This is a consequence of the axial ratio *c/a* which deviates from the ideal value of 3.46 ($=2(3^{1/2})$) by approximately 10%. For an ideal *c/a* ratio and a parameter *z* of 5/12—as nearly observed in α-$ThSi_2$—equal Si–Si,

TABLE VI

Bond Distances, Coordination Numbers, and Bond Angles

Compound	$CaSi_2$		$EuSi_2$	$SrSi_2$	
Phase	Normal pressure	High pressure	Normal and high pressure	Normal pressure	High pressure
Metal neighbors	6Ca 3.86 Å	4Ca 4.00 Å	4Eu 4.03 Å	6Sr 4.00 Å	4Sr 4.11 Å
		4Ca 4.28 Å	4Eu 4.30 Å		4Sr 4.44 Å
	6Si 3.03 Å	4Si 3.08 Å	4Si 3.11 Å	6Si 3.25 Å	4Si 3.17 Å
	1Si 3.06 Å	8Si 3.25 Å	8Si 3.26 Å	2Si 3.37Å	8Si 3.36 Å
Coordination number	13	20	20	14	20
Silicon neighbors	3Si 2.45 Å	1Si 2.3_4 Å	1Si 2.3_5 Å	3Si 2.39 Å	1Si 2.3_8 Å
		2Si 2.3_8 Å	2Si 2.4_0 Å		2Si 2.4_7 Å
	3Ca 3.03 Å	2Ca 3.08 Å	2Eu 3.11 Å	3Sr 3.25 Å	2Sr 3.17 Å
	(1Ca 3.06 Å)[a]	4Ca 3.25 Å	4Eu 3.26 Å	1Sr 3.37 Å	4Sr 3.36 Å
Coordination number	6.5[a]	9	9	7	9
$Si^{Si}Si$ Bond angle	104.2^0 (3x)	$115._{90}$ (2x)	$116._{30}$ (2x)	117.8^0 (3x)	$115._{90}$ (2x)
		$128._{20}$ (1x)	$127._{30}$ (1x)		$128._{10}$ (1x)

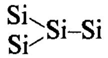
[a] There are two different Si atoms, one with 6 neighbors (3Si 2.45 Å, 3Ca 3.03 Å), the second with 7 neighbors (3Si 2.45 Å, 3Ca 3.03 Å, 1Ca 3.06 Å).

TABLE VII

VARIATION OF BOND DISTANCES AND ANGLES WITH PARAMETER z FOR TETRAGONAL $SrSi_2$

	Bond distances (Å)		Bond angles (°)	
Parameter z	$Si–Si_{(1)}$	$Si–Si_{(2)}$	$Si^{Si}Si_{(1)}$	$Si^{Si}Si_{(2)}$
0.412	2.43	2.44	130.5	114.8
0.415	2.35	2.48	127.0	116.5
0.418	2.27	2.52	123.6	118.2
0.421	2.19	2.56	120.3	119.8

equal M–M, and equal M–Si spacings and $Si^{Si}Si$ bond angles of 120° can exist. However, these bond characteristics cannot be fulfilled with a c/a ratio of 3.1–3.2. In Table VII calculated Si–Si spacings and $Si^{Si}Si$ bond angles for the high-pressure polymorph of $SrSi_2$ are shown as a function of the positional parameter z. Extremes of z have been chosen to give equal Si–Si spacings on the top and bond angles of 120° at the bottom. For planar



$$\begin{matrix}Si\searrow \\ Si\nearrow\end{matrix}Si–Si$$

groups equal Si–Si bond length would demand bond angles of 130.5° (1x) and 114.8° (2x) while bond angles of 120° would result in Si–Si spacings of 2.19 (Å) (1x) and 2.56 Å (2x). The value of 2.19 Å is unusually short.

Also, in the cubic phase of $SrSi_2$ the three-dimensional Si network shows a distortion from the ideal configuration. Equal Si–Si spacings and bond angles of 120° would lead to two very short M–Si bonds (2.8 Å). By distortion of the bond angle to 117.7°, however, the six nearly equatorial M–Si bonds (3.25 Å) and the two axial ones (3.37 Å) are of comparable length.

It seems that besides other influences the ratio of radii plays an important role for the deviation from ideal configuration in both three-connected networks. In order to get more information about this influence investigations of the effect of pressure on the structures of the remaining disilicides and of all digermanides in the series of the reactive divalent metals ytterbium, calcium, europium, strontium, and barium are under way now (*21*).

Acknowledgment

One of the authors (J. E.) is especially grateful to Prof. Dr. G. Busch and PD Dr. E. Kaldis, ETH Zürich, for the permission to use various facilities of the Laboratorium für Festkörperphysik, Hönggerberg. J. E. also thanks Prof. Dr. K.-J. Range, Universität Regensburg, for putting the high-pressure equipment at his disposal.

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