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Transformation of Three-Connected Silicon Nets in $CaSi_2$

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Up to 40 kbar and 1100°C, $CaSi_2$ is dimorphic. Trigonal/rhombohedral $CaSi_2I$ ($CaSi_2$-type structure) with corrugated layers of three-connected Si atoms can be transformed by a high pressure–high temperature treatment into tetragonal $CaSi_2II$ ($\alpha-ThSi_2$-type structure) with a three-dimensional net of three-connected Si atoms. The silicon net of $CaSi_2II$ is slightly distorted from the topologically simplest tetragonal three-dimensional three-connected net derived on a geometrical basis. In order to correlate crystal chemical with thermochemical data the transformation between both polymorphs of $CaSi_2$ has been studied at equilibrium and nonequilibrium conditions. The pressure–temperature phase diagram of $CaSi_2$ has been investigated by X-ray technique in quenched samples. From the slope of the equilibrium line and the change in molar volume the approximate values of the entropy and energy of transformation $CaSi_2$(I–II) have been determined $\Delta S = 3.2$ e.u., $\Delta U = 4.9$ kcal/mole. Under nonequilibrium conditions the transformation $CaSi_2$(II–I) yielded $\Delta H = -4.2$ kcal/mole at 500°C and ambient pressure in a DTA apparatus. Complete transformation of metastable $CaSi_2II$ can be achieved within 5 min at a heating rate of 20°C/min. Due to the relatively high speed of transformation simple structural relations between both polymorphs of $CaSi_2$ are discussed.

Introduction

Corrugated layers of three-connected metalloid atoms in divalent metal disilicides and digermanides MSi_2 and MGe_2 (M = Yb, Ca, Eu, Sr, Ba) are reported to be stacked in three different arrangements. In trigonal $EuGe_2$ (*1*), space group D_{3d}^3–$P\bar{3}m1$, the simplest stacking is found. In the [001] direction the structure is repeated after only one corrugated layer of three-connected Ge atoms. However, different stacking can be obtained from this structure if the layers are shifted to each other by $(a/3)3^{1/2}$ in the trigonal [110] direction and/or the layers are rotated by 180° around the layer normal. In the TR3 modification of trigonal/rhombohedral $CaSi_2$ (*2, 3*), space group D_{3d}^5–$R\bar{3}m$, corrugated layers of three-connected Si atoms are shifted without rotation and achieve periodicity in the [001] direction after three layers. In addition to shifting of corrugated layers in the TR6 modification of trigonal/rhombohedral $CaSi_2I$ (*4*), space group D_{3d}^5–$R\bar{3}m$, every second layer is here rotated by 180° around layer normal. In this case the structure is repeated after six layers in the [001] direction. Different stacking in both modifications of $CaSi_2$ seems to be effected by purity and stoichiometry.

By a high pressure–high temperature (HPHT) treatment (e.g., 40 kbar, 1000°C) trigonal/rhombohedral $CaSi_2I$ ($CaSi_2$-type structure) with corrugated layers of three-connected Si atoms can be transformed into tetragonal $CaSi_2II$ (*5–9*) (α-$ThSi_2$-type structure) (*10*) with a three-dimensional net of three-connected Si atoms. This net is slightly distorted from the topologically

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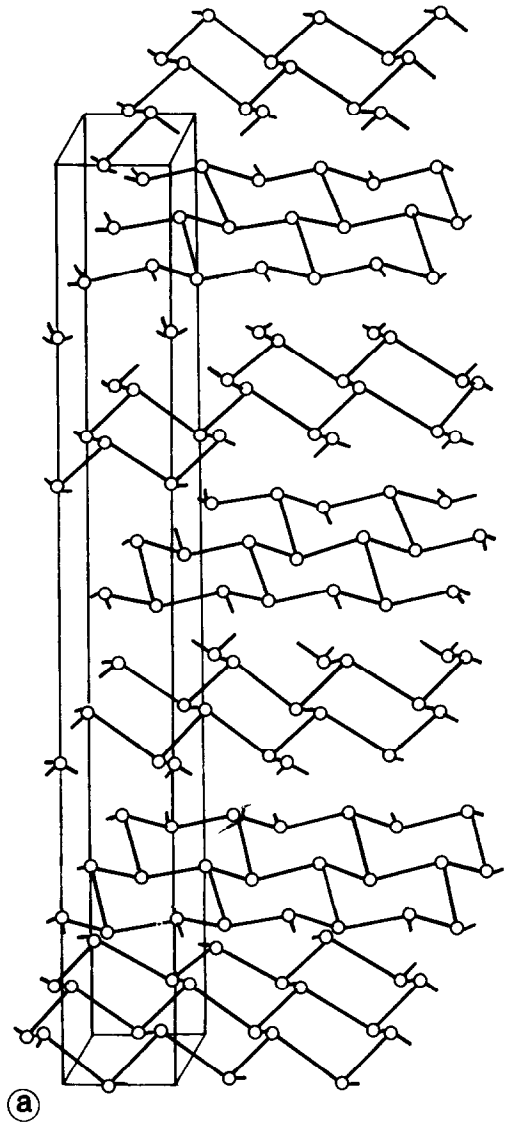

FIG. 1. (a) Corrugated layers of three-connected silicon atoms in trigonal/rhombohedral $CaSi_2I$ (TR6 modification). (b) Three-dimensional three-connected silicon net in tetragonal $CaSi_2II$.

simplest tetragonal three-dimensional three-connected (3D 3C) net which has been derived on a geometrical basis by Wells (*11–16*). Instead of a coplanar group of four equidistant Si atoms with equal bond angles of 120° the repeat unit in the distorted 3D 3C net of $CaSi_2II$ is coplanar, but not equidistant (2.3_4 Å (1×), 2.3_8 Å (2×)) and not with equal bond angles (128° (1×), 116° (2×)) (*9*). This distorted tetragonal 3D 3C net is for divalent metal disilicides and digermanides found also in $EuSi_2$ (*17*) at ambient pressure and in $SrSi_2$ (*7-9*) and $BaGe_2$ (*18*) at high pressure. In Fig. 1a corrugated Si layers of $CaSi_2I$ (TR6 modification) are shown; in Fig. 1b the tetragonal 3D 3C Si net of $CaSi_2II$.

In addition to crystal chemical characterization of the transformation $CaSi_2$(I–II) thermochemical data seem to be very informative. In order to obtain a first insight into changes of entropy and energy during this transformation the pressure–temperature phase diagram of $CaSi_2$ was studied, with the fact that the required data could be obtained via the Clausius–Clapeyron equation borne in mind. As is well known, the slope of the equilibrium line $\Delta P/\Delta T$ is related to changes in entropy and actual molar volume. From P–T equilibrium conditions in connection with entropy change the transformation energy can be calculated.

Tetragonal $CaSi_2II$ is quenchable and can be stored at room temperature and pressure for long periods without showing any change. However, when this phase is heated to 450°C at ambient pressure complete retransformation into $CaSi_2I$ is achieved. Therefore, the change in energy during this exothermic process can be easily measured in a cali-

brated DTA apparatus, although one obtains no equilibrium data of transformation. Nevertheless, transformation of metastable (at 500°C and ambient pressure) tetragonal $SrSi_2$II (α-$ThSi_2$-type structure) into stable cubic $SrSi_2$I in a DTA apparatus yielded a 20% lower value of the transformation energy than that for equilibrium conditions obtained via the Clausius–Clapeyron equation (nonequilibrium $SrSi_2$(II–I) $\Delta H = -1.6 \pm 0.3$ kcal/mole; equilibrium $SrSi_2$(I–II) $\Delta U = 1.9 \pm 0.4$ kcal/mole) (*19, 20*). Therefore, the nonequilibrium value of the transformation $CaSi_2$(II–I) at ambient pressure can be considered as a rough test for the equilibrium value of the transformation $CaSi_2$(I–II). In addition, a first insight into the speed of transformation can be derived from the nonequilibrium experiment. This must be very informative for better understanding the transformation of corrugated layers of three-connected Si atoms into the tetragonal 3D 3C Si net in $CaSi_2$.

Experimental

Sample preparation. High-purity $CaSi_2$I was prepared by inductive heating of high-ohmic silicon with ultrahigh-vacuum-distilled calcium (*21*) in a high-vacuum tight cold copper boat. Additional details have been given elsewhere (*9, 19*).

High-pressure–high-temperature treatment. High pressure up to 40 kbar was generated in a belt-type apparatus (*22*). Calibration of pressure was performed measuring the discontinuities of resistance at ambient temperature in the transformations of Ce(I–II), Bi(I–II), and Tl(I–III) with alternating current. Calibration of temperature was obtained via wattages against chromel–alumel thermocouples. More details of pressure and temperature calibration are quoted elsewhere (*20*). In the P–T diagram pressure is believed to be correct within ±2 kbar and temperatures (via wattages) within ±25°C. For the phase diagram studies defined P–T conditions were maintained for 15 min. After quenching to room temperature pressure was released.

X-Ray characterization. Phase analyses in quenched samples were performed by the Debye–Scherrer technique in a Straumanis arrangement (Ni-filtered copper K_α, 114.6 mm Seifert camera).

Differential thermal analysis. Nonequilibrium transformation $CaSi_2$(II–I) at ambient pressure was investigated in a high-vacuum tight Linseis-DTA apparatus under dynamic flow of argon (20 cm^3/min) at a heating rate of 20°C/min in tantalum crucibles with Pt90Rh10–Pt thermocouples. Typical weights of $CaSi_2$II for DTA runs were in the range 27–30 mg. Additional details and calibration have been quoted elsewhere (*19*).

Results

In Table I the structural data for trigonal/rhombohedral $CaSi_2$I (TR6 modification) (*2–4*) and tetragonal $CaSi_2$II (*9*) are presented.

In Fig. 2 the pressure-temperature phase diagram of $CaSi_2$ up to 40 kbar and 1100°C derived from 17 different P–T experiments is shown. No attempt was made to resolve curvature of the phase boundary. In a quasiunary approach the slope of the equilibrium line is $\Delta P/\Delta T = -60$ bar/deg. For example, at approximately 32 kbar and 1000°K $CaSi_2$I and $CaSi_2$II coexist.

The equilibrium entropy change $CaSi_2$(I–II) is obtained if $\Delta P/\Delta T$ is multiplied by the actual change in molar volume ΔV_T^P under HPHT conditions (e.g., 32 kbar, 1000°K). However, ΔV_T^P can be obtained from the change in molar volume at ambient conditions ΔV_{298} ($= -2.19 \approx -2.2$ cm^3/mole; Table I) if the coefficients of isobaric thermal expansion α and isothermal compressibility χ are known. Since α and χ are proportional to each other (Grüneisen parameter) (*23*) the influence of χ values on ΔV_T^P can be

TABLE I

STRUCTURAL DATA FOR TRIGONAL/RHOMBOHEDRAL AND FOR TETRAGONAL $CaSi_2$

Phase	Normal pressure[a]	High pressure
Crystal class	Trigonal/rhombohedral	Tetragonal
Space group	D_{3d}^5–$R\bar{3}m$	D_{4h}^{19}–$I4_1/amd$
Lattice parameters (Å)	$a = 3.855 \pm 0.005$	$a = 4.283 \pm 0.003$
	$c = 30.6 \pm 0.1$	$c = 13.52 \pm 0.01$
Cell volume (Å^3)	393.8	248.0
Density (g/cm^3)		
Observed	2.46	2.5_5
X-Ray	2.44	2.578
Molar volume (cm^3/mole)	39.53	37.34
Formula units	6	4
Positions	6 Ca in 6*c*	4 Ca in 4*a*
	$(0, 0, z)(0, 0, \bar{z})$	$(0, 0, 0,)(0, \frac{1}{2}, \frac{1}{4})$
	$(\frac{1}{3}, \frac{2}{3}, \frac{2}{3}+z)(\frac{1}{3}, \frac{2}{3}, \frac{2}{3}-z)$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})(\frac{1}{2}, 0, \frac{3}{4})$
	$(\frac{2}{3}, \frac{1}{3}, \frac{1}{3}+z)(\frac{2}{3}, \frac{1}{3}, \frac{1}{3}-z)$	
	$z = 0.083$	
	6 Si_I in 6*c*	8 Si in 8*e*
	$z = 0.183$	$(0, 0, z)(0, 0, \bar{z})$
	6 Si_{II} in 6*c*	$(0, \frac{1}{2}, \frac{1}{4}+z)(0, \frac{1}{2}, \frac{1}{4}-z)$
	$z = 0.350$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+z)(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-z)$
		$(\frac{1}{2}, 0, \frac{3}{4}+z)(\frac{1}{2}, 0, \frac{3}{4}-z)$
		$z = 0.413_5$

[a] TR6 modification

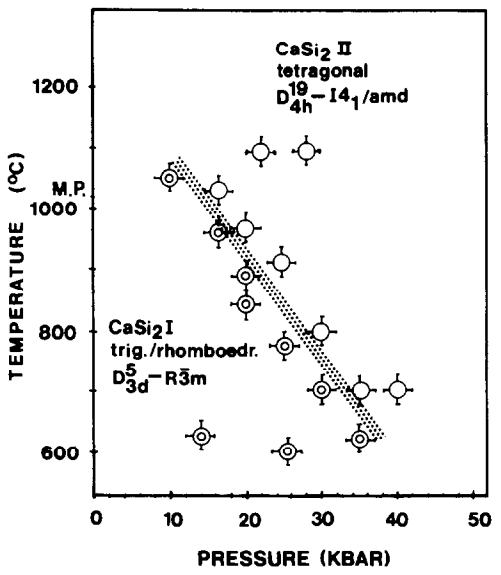

FIG. 2. Pressure–temperature phase diagram of $CaSi_2$.

estimated if α values are known. Measurement of thermal expansion of $CaSi_2$I and II at ambient pressure showed only a small difference. Therefore, differences between χ values must also be small so that ΔV_T^P can be identified with ΔV_{298} (to a good approximation). With $\Delta V_{298} = -2.2$ cm^3/mole one calculates the entropy change $CaSi_2$(I–II), $\Delta S = 3.2 \pm 0.6$ e.u. and the energy change $\Delta U = 4.9 \pm 1.0$ kcal/mole.

Table II shows the thermochemical data derived from two different DTA runs under nonequilibrium conditions. A typical first heating run is presented in Fig. 3a and a second one after transformation in Fig. 3b. The significant feature of these figures is that the transformation $CaSi_2$(II–I) at 500°C and ambient pressure is exothermic and irreversible. The average value of the energy of this transformation $\Delta H = -4.2 \pm 0.8$ kcal/mole has been determined. Complete trans-

TABLE II

THERMOCHEMICAL DATA OF THE PHASE TRANSFORMATION TETRAGONAL INTO TRIGONAL/RHOMBOHEDRAL $CaSi_2$ AT AMBIENT PRESSURE

Transformation character	Exothermic irreversible	
Heating rate	20°C/min	
Sample weight (mg)	27.95	30.07
Transformation peak (°C)		
Start	482	478
Medium	533	528
End	578	573
Energy of transformation at ambient pressure (cal/mole)	-4165 ± 833	-4286 ± 857
Average value of the transformation energy at ambient pressure (kcal/mole)	-4.2 ± 0.8	

formation $CaSi_2$(II–I) at ambient pressure is achieved within 5 min at a heating rate of 20°C/min (Fig. 3a, Table 1).

Discussion

By inspection of Table III it is clear that coordination numbers are increased by HPHT treatment of $CaSi_2$I, in agreement with general experience. Trigonal/rhombohedral $CaSi_2$I (TR6 modification) shows 7:3.5 coordination (Ca has seven Si neighbors; Si_I has four Ca and Si_{II} three Ca neighbors), whereas 12:6 coordination is found for tetragonal $CaSi_2$II. Interestingly, three-connection of silicon atoms is retained in tetragonal $CaSi_2$II. Both phases of $CaSi_2$ and also all investigated polymorphs of divalent metal disilicides and digermanides at ambient and at high pressure satisfy the generalized $8-N$ rule derived for polyanionic compounds (*24–26*).

The transformation of the tetragonal 3D 3C Si-net of $CaSi_2$II into corrugated Si-layers is relatively rapid. Under nonequilibrium conditions complete transformation $CaSi_2$(II–I) is achieved within 5 min (Table II, Fig. 3). Under comparable experimental conditions the nonequilibrium transformation speed for $SrSi_2$(II–I) (*19*) is the same. Nevertheless, from these observations no quantitative conclusions can be drawn

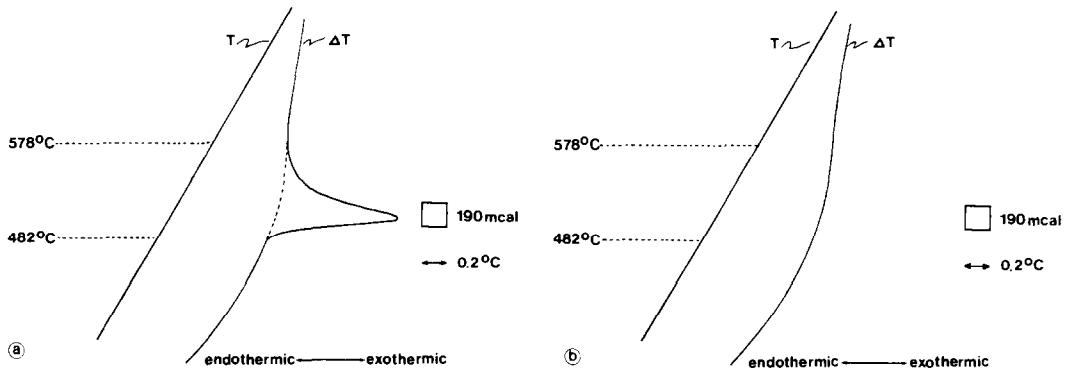

FIG. 3. (a) Thermogram of first heating cycle of 27.95 mg tetragonal $CaSi_2$II at ambient pressure. (b) Thermogram of second heating cycle.

TABLE III

NUMBER OF NEIGHBORS AND BOND DISTANCES FOR TRIGONAL/RHOMBOHEDRAL AND TETRAGONAL $CaSi_2$

Phase	Trigonal/ rhombohedral[a] (Å)	Tetragonal (Å)
Calcium neighbors	6 Ca 3.86	4 Ca 4.00
	6 Si 3.03	4 Si 3.08
	1 Si 3.06	8 Si 3.25
Silicon neighbors	3 Si 2.45	1 Si 2.3_4
		2 Si 2.3_8
	3 Ca 3.03	2 Ca 3.08
	(1 Ca 3.06)[b]	4 Ca 3.25

[a] TR6 modification after Böhm and Hassel (*4*) (1927).

[b] There are two different Si atoms; Si_I with 3 Ca 3.03 Å and 1 Ca 3.06 Å and Si_{II} with 3 Ca 3.03 Å.

since equilibrium conditions are missing. It is also known that crystal order and impurities influence transformation kinetics. However, the transformation of at ambient pressure quenchable α-$ThSi_2$ (high-temperature phase) with a nearly ideal tetragonal 3D 3C Si net into stable β-$ThSi_2$ (low-temperature phase) with planar Si layers is not as rapid as in $CaSi_2$(II–I) or in $SrSi_2$(II–I) (*27*).

If one looks for crystal chemical relations between $CaSi_2$I and II it must be considered that total breakdown of the old lattice in order to build up the new one is avoided. Otherwise such a total reconstructive transformation (*29, 30*) will proceed sluggishly. A projection of two unit cells (lying above) of the Si net I down the orthohexagonal b axis ($= a_{trig} \cdot 3^{1/2}$) is shown in Fig. 4a. Since one orthohexagonal cell of $CaSi_2$I contains twice the number of formula units than the trigonal one, 48 ($= 2 \cdot 2 \cdot 12$) silicon atoms are found here in corrugated layers. The silicon atoms in three pairs of the six layers are at different heights $n \cdot a_{trig} \cdot 3^{1/2}$. Due to the geometry of equilateral triangles accepted values for n are $\frac{1}{6}$, $\frac{2}{6}$, $\frac{4}{6}$, and $\frac{5}{6}$. Corrugated (cyclohexane chair-like) Si hexagons in one layer can be considered as built up by flat distorted "helices" which repeat after four atoms (Fig. 5a). Besides the different "diameters" (1.93 and 1.01 Å, Fig. 5a) the "helices" are not true 4_3- or 4_1-helices since there is no constant sense in screw motion (Fig. 5a). This is a consequence of corrugating the layers. In two orthohexagonal unit cells of the TR6 modification of $CaSi_2$I there exist six different distorted flat "helices."

In Fig. 4b a projection of six unit cells of the tetragonal 3D 3C Si net II down the c_{tetr} axis is shown. These six unit cells also contain 48 ($= 6 \cdot 8$) silicon atoms. The tetragonal 3D 3C net can be built up by true 4_1-helices (Fig. 5b). Further details are discussed in (*19*).

Comparing Figs. 4a, b and 5a, b one sees the striking difference between the two Si nets. For two of the three axes of the cells considered with equal number of silicon atoms, good agreement is found: $a_{trig} = 3.86$ Å $\approx a_{tetr} = 4.28$ Å and $2 \cdot 3^{1/2} a_{trig} = 13.37$ Å $\approx c_{tetr} = 13.52$ Å. However, the third relation, $\frac{1}{6} \cdot c_{trig} = 5.10$ Å $\approx a_{tetr} = 4.28$ Å, shows the greatest difference. For transformation $CaSi_2$(I–II) one-third of bonds between the three-connected Si atoms in the corrugated layers have to be broken, and the "diameter" of the distorted helices must increase in one direction (Figs. 5a, b) (1.01 Å → 2.14 Å). After additional minor changes in "helix" dimensions (1.93 Å → 2.14 Å and 13.37 Å → 13.52 Å), Si atoms have to rearrange in the helices and reconstruct the third Si–Si bond within the tetragonal 3D 3C net. Therefore this transformation must be considered as a reconstructive one (*28, 29*), as also observed for $SrSi_2$ (*19*).

Although both nonequilibrium transformations $CaSi_2$(II–I) and $SrSi_2$(II–I) can be performed within the same time, crystal chemical differences between $CaSi_2$I and $CaSi_2$II are greater than those between $SrSi_2$I and $SrSi_2$II. These differences are reflected in the thermochemical data of both

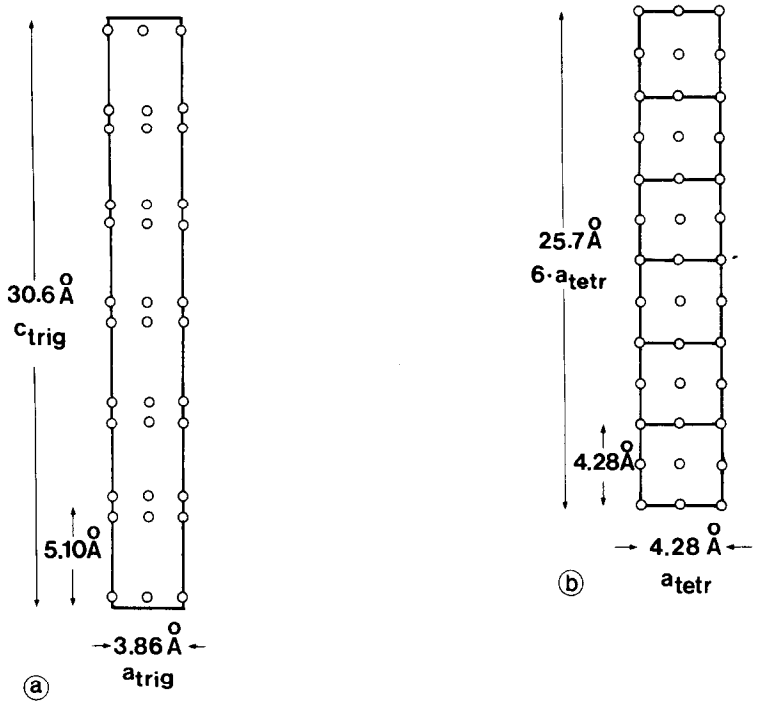

FIG. 4. (a) Projection of two unit cells with corrugated layers of $CaSi_2I$ (TR6 modification) down orthohexagonal *b* axis. (b) Projection of six unit cells of tetragonal 3D 3C Si net down tetragonal *c* axis.

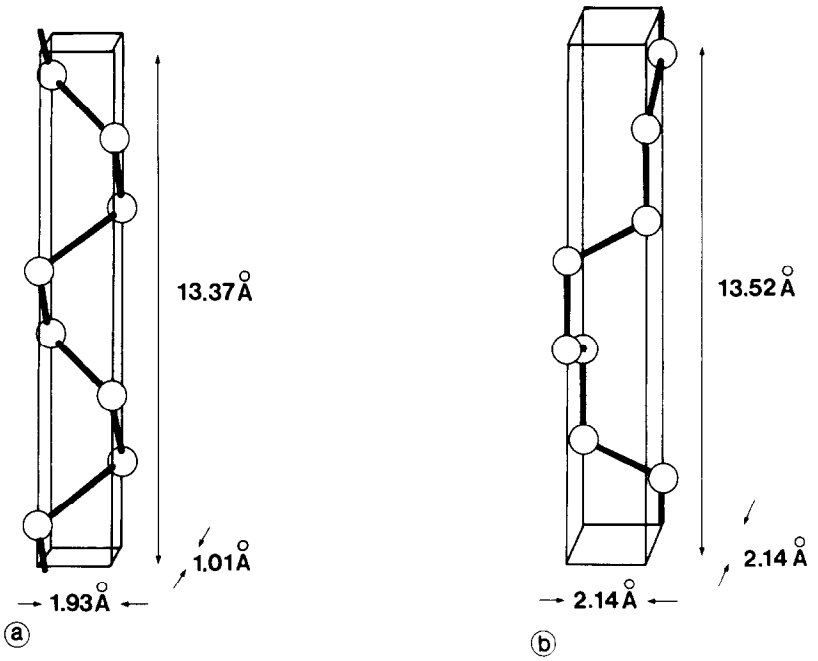

FIG. 5. (a) Flat distorted "helices" which repeat after four atoms in Si net of $CaSi_2I$ (TR6 modification). (b) 4_1-Helix of the tetragonal 3D 3C Si Net of $CaSi_2II$.

transformations. Since the slope of the equilibrium line of $CaSi_2$(I–II) $\Delta P/\Delta T = -60$ bar/deg and also the change in molar volume is greater, $\Delta V = -2.2$ cm^3/mole ($SrSi_2$(I–II): $\Delta P/\Delta T = -47$ bar/deg, $\Delta V = -1.0$ cm^3/mole), one calculates both a higher entropy change $\Delta S = 3.2 \pm 0.6$ e.u. and energy change $\Delta U = 4.9 \pm 1.0$ kcal/mole ($SrSi_2$(I–II): $\Delta S = 1.1 \pm 0.2$ e.u., $\Delta U = 1.9 \pm 0.4$ kcal/mole) (*19, 20*). Higher energy change is also found in the thermograms of the DTA runs for which one finds nonequilibrium $CaSi_2$(II–I) $\Delta H = -4.2 \pm 0.8$ kcal/mole, with a well-pronounced peak instead of a flat one for nonequilibrium $SrSi_2$(II–I) (*19*).

Tetragonal $CaSi_2$II is not high-temperature phase at ambient pressure. At the melting point of $CaSi_2$I (1020°C = 1293°K) one calculates approximately 0.8 kcal/mole (=16% of the total change) to be missing. Since $CaSi_2$II is the more densely packed phase ($\Delta V = -2.2$ cm^3/mole) small pressures are sufficient near the melting point of $CaSi_2$I to generate the missing stabilization energy.

The different features between the structure types of $CaSi_2$I and II ($CaSi_2$ and α-$ThSi_2$ types of structure, respectively) are shown if one lists the number of binary examples of the structure types found for divalent metal disilicides and digermanides at ambient and at HPHT conditions (Table IV). Ytterbium compounds have not been considered, due to the unsolved problem of stoichiometry. The greatest dependence of a structure type on the metallic radius is found for the $CaSi_2$ type because here only two compounds with the same metal (Ca) exist. On the other hand, present knowledge of the α-$ThSi_2$ type with a tetragonal 3D 3C net indicates that it is the most variable one since it is found in MSi_2 or MGe_2 compounds with four different divalent metals M (M = Ca, Eu, Sr, Ba). Also sensitive to changes of metallic radius is the $SrSi_2$ type with a cubic 3D 3C net known for $SrSi_2$I and $BaSi_2$III (*33*). From the dependence of lattice parameters on the metallic radius in solid solutions $M_{1-x}M'_xSi_2$ (M, M' = Ca, Eu, Sr, Ba) with $SrSi_2$-type lattic parameters for hypothetical $EuSi_2$ and $CaSi_2$ with this structure type have been extrapolated (*38*). From these data it seems that the structure types observed up to now at ambient pressure are more densely packed than those with a cubic 3D 3C net ($SrSi_2$ type). The cavities in this net seem too large for europium and calcium to stabilize this structure type. From geometrical relations between the ideal cubic and tetragonal 3D 3C nets it has been calculated that for a constant Si–Si bond distance of 2.39 Å the unit-cell volume of the cubic 3D 3C net is much larger (308.9 Å^3) than that of the tetragonal one (245.8 Å^3) (*19*). This is in agreement with the experimental fact that for strontium (r_{Sr} = 2.151 Å CN 12) and thorium (r_{Th} = 1.798 Å) nearly the same Si–Si bond distance of 2.39 Å is achieved in the cubic and tetragonal 3D 3C nets, respectively (V_{SrSi_2I} = 279.1 Å^3, V_{ThSi_2II} = 245.8 Å^3 for four formula units each).

Also in agreement with the interpretation that for $CaSi_2$ with $SrSi_2$-type structure the metallic radius of Ca (r_{Ca} = 1.974 Å) seems

TABLE IV

BINARY EXAMPLES OF STRUCTURE TYPES KNOWN FOR DIVALENT METAL DISILICIDES AND DIGERMANIDES[a]

$CaSi_2$	$CaSi_2$I (*2-4*), $CaGe_2$I (*30*)
$SrSi_2$	$SrSi_2$I (*31, 3, 32*), $BaSi_2$III (*33*)
$EuGe_2$	$EuGe_2$I (*1*), $SrGe_2$II (*34*), $BaSi_2$II (*7, 8, 35*)
$BaSi_2$	$SrGe_2$I (*37*), $BaSi_2$I (*36, 3*), $BaGe_2$I (*37*)
α-$ThSi_2$	$CaSi_2$II (*5–9*), $EuSi_2$I (*17*), $SrSi_2$II (*7–9, 19, 20*), $BaGe_2$II (*18*)

[a] Due to the unsolved problem of stoichiometry Yb compounds are not considered here..

to be too small is that for large barium (r_{Ba} = 2.243 Å) transformation of corrugated layers in $BaSi_2$II with $EuGe_2$-type structure into the cubic 3D 3C net was successful (*33*). Investigation of the pressure–temperature phase diagram of trimorphic $BaSi_2$ is still in progress (*39*).

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