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Transformation of Three-Dimensional Three-Connected Silicon Nets in $SrSi_2$

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Dimorphic $SrSi_2$ is the first compound for which the two simplest three-dimensional three-connected nets are found in its polymorphs. The cubic net of three-connected silicon atoms ($SrSi_2$ type of structure) can be transformed into the tetragonal one (α-$ThSi_2$ type of structure) by a high-pressure–high-temperature treatment. The tetragonal phase is quenchable. Heating of this phase to 600–700°C at ambient pressure results in transformation into the cubic one. At a heating rate of 20°C/min complete transformation can be achieved within 5 min in a DTA apparatus. The energy of transformation has been obtained from the peak areas of the DTA curves to -1.6 ± 0.3 kcal/mole. Although the transformation between the three-dimensional three-connected sets in $SrSi_2$ must be formally classified as a reconstructive one, a relatively small entropy change ($\Delta S = 1 \cdot_1$ cal/deg · mole) has been calculated from the change in molar volume and *p*–T equilibrium conditions. Therefore, structural relations between the cubic and the tetragonal nets are discussed.

Introduction

It is very well known that in a large class of solids, e.g., borides, silicides, and phosphides, directed bonds extend indefinitely in one, two, or three dimensions just building up chains, layers, and frameworks, respectively. Some years ago, an attempt was made by Wells (*1–6*) to derive systematically periodic three-dimensional nets in which each point is connected to three others. The two simplest three-dimensional three-connected (3D 3C) nets are formed by four atoms in the repeat unit and eight atoms in the unit cell. The crystal classes of these two nets are cubic and tetragonal. Equidistant coplanar bonds in the repeat unit and bond angles of 120° were derived for the most symmetrical configurations. In Fig. 1a the ideal cubic 3D 3C net is shown; in Fig. 1b the ideal tetragonal one.

However, the cubic 3D 3C net is found in a less symmetrical arrangement in $SrSi_2$ (*7–9*) and the tetragonal one in its most symmetrical configuration in α-$ThSi_2$ (*10*). The cubic net in $SrSi_2$ is slightly distorted from the configuration in space group $I4_132$ to that one in $P4_332$ (or $P4_132$). Instead of coplanar bonds with bond angles of 120° the four Si atoms of the repeat unit are found in very flat trigonal pyramids with bond angles of 117.8°. The top atom of this pyramid is 0.36 Å out of plane of the base atoms. On the other hand, the tetragonal framework in α-$ThSi_2$ shows highest symmetry in space group $I4_1/amd$ with nearly equidistant coplanar bonds in the repeat unit, bond angles of nearly 120° and a c/a axial ratio of nearly $2(3)^{1/2}$. Distortion in the tetragonal net occurs in many binary phases if the c/a ratio is different from $2(3)^{1/2}$ and /or the positional parameter z deviates from the ideal value of 5/12. An orthorhombic distortion of the tetragonal net is found in the $GdSi_2$ type of structure in space group *Imma* (*11*).

Recently it has been shown that in $SrSi_2$ the

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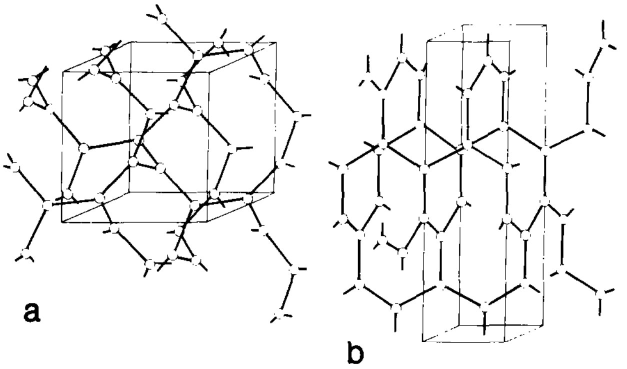

FIG. 1. Three-dimensional three-connected nets in their most symmetrical configurations. (a) cubic net; (b) tetragonal net.

cubic 3D 3C net can be transformed into the tetragonal one by high-pressure–high-temperature treatment in a belt-type apparatus (*12–14*). The purpose of this paper is to study the transformation of the 3D 3C nets in $SrSi_2$ in order to get some thermochemical information which can be correlated with structural data. Differential thermal analysis (DTA) has been used for the measurement of the speed and energy of transformation under nonequilibrium conditions at ambient pressure. Equilibrium energy transformation has been derived from the change in molar volume and the slope in the p–T diagram applying the Clausius–Clapeyron equation.

Experimental Procedure

1. Preparation of samples. High purity $SrSi_2$ was prepared by inductively heating electronic grade silicon with ultrahigh vacuum "reactively" distilled strontium (*15*) in a high-vacuum-tight cold copper boat under argon atmosphere. In order to control the evaporation losses of strontium during melting of the disilicide buttons (250–300 mg), in a first stage, samples were prepared with about 5 wt% higher Sr content than needed for stoichiometric composition. In those buttons vapor pressure of strontium is about two orders of magnitude lower than in Sr metal. After weighing of the buttons the small silicon amount which must be added to achieve 1:2 composition can be easily calculated. Remelting leads to nearly stoichiometric samples.

Due to the reactivity of $SrSi_2$ against humidity and air all samples were handled in a glove box with purified argon. Details of the equipment used for preparation of divalent metal disilicides have been given elsewhere (*14, 16–18*).

2. High-pressure treatment. Equipment of belt type was used for the high-pressure experiments. Typical conditions for the high-pressure–high-temperature treatment were 40 kbar, 1000–1500°C, 20–30 min. After quenching to room temperature, pressure was released. Details are quoted elsewhere (*19*).

3. X-ray characterization. Due to the fact that isolation of single crystals of tetragonal $SrSi_2$ failed up to now structural determinations were done on powders by Debye–Scherrer technique in Straumanis arrangement (camera diameter 114.6 mm, 0.3-mm glass capillaries). Radiation was nickel-filtered copper $K\alpha$. After correction for film shrinkage unit-cell parameters were calculated from back-reflection regions where both cubic and tetragonal modification of $SrSi_2$ showed clearly resolved $\alpha_1\alpha_2$ splitting.

4. Differential thermal analysis. The apparatus used for DTA experiments consisted of a high-temperature furnace (Linseis L62/091) and a proportional-type temperature programmer (L70/1768). Due to the reactivity of $SrSi_2$ against air and moisture defined atmosphere is required to get reproducible results. With a self-constructed vacuum system (mechanical pump 3.2 m^3/hr, diffusion pump 30 liter/sec, Leybold–Heraeus) high vacuum could be achieved and measured with a Penning gauge. After flooding with argon a dynamic-argon-flow atmosphere of 20 cm^3/min was chosen. Pt 10% Rh–Pt thermocouples, a sample holder with low thermal capacity (L62/40) and tantalum crucibles were used. In order to get sufficient peak heights all DTA-experiments were performed with a heating rate of 20°/min. The output voltage from the differential thermocouple was recorded on a two-channel recorder (L61/120) with 50 μV full scale and a recorder speed of 10 mm/min. At standard conditions the equipment was calibrated by melting weighed amounts of gallium, indium, tin, lead, zinc, magnesium, and germanium. The calibration curve is shown in Fig. 2.

For transformation experiments the high-pressure samples were scraped off from boron nitride with a razor blade and used without powdering. Typical weights for DTA runs were in the range between 60–80 mg. After transformation the furnace was cooled to room temperature and then heated again. By this procedure a very good agreement of the base lines was achieved. For determination of transformation energies DTA peaks were integrated with intervals of 25°C.

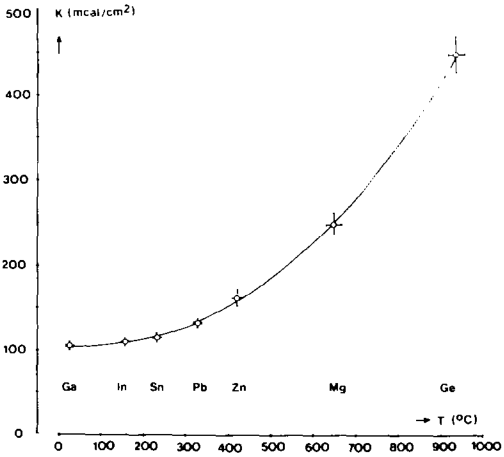

FIG. 2. Calibration curve of the DTA apparatus at standard conditions.

For transformations which proceed sluggishly erroneus energies of transformation can be obtained by the DTA method. Therefore, speed of the transformation was checked. When the DTA peak was recorded and a temperature of 700°C was achieved the furnace was opened and the sample quenched to room temperature. This procedure was performed within 30–45 sec. After this an X-ray powder photograph was taken and quantitative transformation verified. By the same procedure the start of the transformation was checked.

Results

Table I presents the structural data for cubic and tetragonal $SrSi_2$ and Table II the thermochemical data derived from two different DTA runs. A typical transformation run is shown in Fig. 3a and a second heating cycle after transformation in Fig. 3b. As it is very strikingly demonstrated by these two figures, the tetragonal phase of $SrSi_2$ is metastable at ambient conditions since the transformation by heating is exothermic and irreversible. At a heating rate of 20°C/min the transformation starts at 590°C and ends at 690°C (Fig. 3a, Table II). This results in a total time of 5 min for complete transformation. As average value for the energy of transformation at ambient pressure (tetragonal into cubic phase) a value of -1.6 ± 0.3 kcal/mole has been determined. This value can be compared to the equilibrium energy of transformation (tetragonal into cubic phase) of -1.9 ± 0.4 kcal/mole which is obtained from the change in molar volume and the slope of the equilibrium line in the p–T diagram applying the Clausius–Clapeyron equation (*20*).

Due to the metastable character of tetragonal $SrSi_2$ at ambient conditions the transformation temperatures are a function of the

TABLE I

STRUCTURAL DATA FOR CUBIC AND FOR TETRAGONAL $SrSi_2$

Phase	Normal pressure	High pressure
Crystal class	Cubic	Tetragonal
Type of structure	$SrSi_2$	α-$ThSi_2$
Space group	O^6-$P4_332$ or O^7-$P4_132$	$D^{19}_{4h} - I4_1/amd$
Lattice parameters (Å)	$a = 6.535 \pm 0.005$	$a = 4{,}438 \pm 0.003$ $c = 13.83 \pm 0.02$
Cell volume ($Å^3$)	279.1	272.4
Density (g/cm^3)		
Observed	3.40	3.4_7
X-ray	3.423	3.507
Molar volume (cm^3/mole)	42.01	41.01
Formula units	4	4
Positions	4 Sr in 4*a*	4 Sr in 4*a*
	$(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})(\frac{5}{8}, \frac{3}{8}, \frac{7}{8})$	$(0, 0, 0)(0, \frac{1}{2}, \frac{1}{4})$
	$(\frac{7}{8}, \frac{5}{8}, \frac{3}{8})(\frac{3}{8}, \frac{7}{8}, \frac{5}{8})$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})(\frac{1}{2}, 0, \frac{3}{4})$
	8 Si in 8*c*, $x = 0.423$	8 Si in 8*e*, $z = 0.414$
	$(x, x, x)(\frac{1}{2} + x, \frac{1}{2} - x, \bar{x})$	$(0, 0, z)(0, 0, \bar{z})$
	$(\bar{x}, \frac{1}{2} + x, \frac{1}{2} - x)(\frac{1}{2} - x, \bar{x}, \frac{1}{2} + x)$	$(0, \frac{1}{2}, \frac{1}{4} + z)(0, \frac{1}{2}, \frac{1}{4} - z)$
	$(\frac{1}{4} - x, \frac{1}{4} - x, \frac{1}{4} - x)(\frac{3}{4} - x, \frac{1}{4} + x, \frac{3}{4} + x)$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z)(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z)$
	$(\frac{3}{4} + x, \frac{3}{4} - x, \frac{1}{4} + x)(\frac{1}{4} + x, \frac{3}{4} + x, \frac{3}{4} - x)$	$(\frac{1}{2}, 0, \frac{3}{4} + z)(\frac{1}{2}, 0, \frac{3}{4} - z)$

TABLE II

THERMOCHEMICAL DATA OF THE PHASE TRANSFORMATION TETRAGONAL INTO CUBIC $SrSi_2$

Transformation character at ambient pressure		Exothermic, irreversible	
Heating rate		20°C/min	
Sample weight (mg)	66.06		75.39
Transformation peak (°C)			
Start	588		593
Medium	633		633
End	685		691
Energy of transformation at ambient pressure (cal/mole)	-1530 ± 310		-1660 ± 330
Average value of the energy of transformation at ambient pressure (kcal/mole)		-1.6 ± 0.3	

heating rate. For this case it is only possible to define a temperature below which the transformation does not take place. In a high-temperature X-ray camera with heating intervals of 50°C/8 hr the transformation can be performed between 400 and 450°C. At lower temperatures the barrier of activation energy stops the transformation although cubic $SrSi_2$ is at ambient pressure about 1.6 kcal/mole lower in energy than the tetragonal phase. From these facts it can be understood that tetragonal $SrSi_2$ can be stored at room temperature over a period of more than 1 yr without showing any signs of transformation.

Discussion

Although the silicon atoms in $SrSi_2$ remain three-connected in both three-dimensional nets there is an increase in coordination numbers.

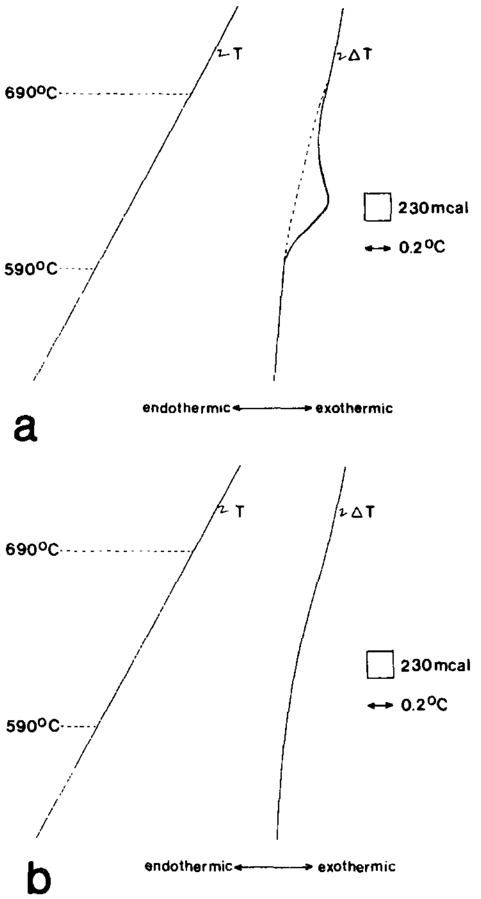

FIG. 3. (a) Thermogram of first heating cycle of 66 mg tetragonal SrSi$_2$ at ambient pressure. (b) Thermogram of second heating cycle.

TABLE III

NUMBER OF NEIGHBORS AND BOND DISTANCES FOR CUBIC AND TETRAGONAL SrSi$_2$

Phase	Cubic (Å)	Tetragonal (Å)
Strontium neighbors	6 Sr 4.00	4 Sr 4.11 4 Sr 4.44
	6 Si 3.25 2 Si 3.37	4 Si 3.17 8 Si 3.36
Silicon neighbors	3 Si 2.39	1 Si 2.3$_8$ 2 Si 2.4$_7$
	3 Sr 3.25 1 Sr 3.37	2 Sr 3.17 4 Sr 3.36

Table III shows the number of neighbors and bond distances of the Sr and the Si atoms for the cubic and the tetragonal net (*14*). Indeed, it is clearly demonstrated that the coordination increases from 8 : 4 for the cubic net (Sr has 8 Si, Si has 4 Sr neighbors) to 12 : 6 for the tetragonal one (Sr has 12 Si, Si has 6 Sr neighbors).

From a structural point of view solid-state transformations can be classified into displacive and reconstructive ones (*21*, *22*). As is very well known, displacive transformations are connected with a distortion of the old lattice in order to form the new one. No bonds are broken. In agreement, displacive transformations proceed rapidly and show smaller entropy changes. On the other hand, in reconstructive transformations bonds are broken and then reorganized. Therefore, reconstructive transformations proceed sluggishly and require higher entropy changes.

Unfortunately, no caloric experience of transformations in compounds related to SrSi$_2$ exists. In order to derive some characteristic details, the thermogram of the transformation in SrSi$_2$ may be compared to that in CsCl, bearing in mind that they are at different equilibrium conditions. The transformation in CsCl can be considered as classic example (*23*) where by a rather simple deformation of the old lattice the new one is formed. Expansion along a trigonal axis and contraction at right angles to the axis transforms the simple cubic cell in CsCl into the face-centered cubic one (*21*, *22*). Using standard DTA conditions (20°C/min heating rate, comparable molar amounts) the transformation in CsCl can be achieved within 3 min (at about 130°C lower in temperature than in SrSi$_2$). Although transformation kinetics are, both experimentally and theoretically, a very complex subject, direct comparison to the 3D 3C net transformation in SrSi$_2$ at ambient pressure may be allowed neglecting influences of different equilibrium conditions, crystal order and impurities. The transformation time of 5 min in

$SrSi_2$ is higher but remains still comparable to the high speed of transformation in CsCl. However, the DTA peak of the transformation in CsCl shows a very sharp start with a nearly straight line slope contrary to the slow starting in $SrSi_2$ (Fig. 3a). In addition, at heating the energy of the exothermic transformation in $SrSi_2$ at ambient pressure (-1.6 ± 0.3 kcal/mole) is higher than that of the endothermic one in CsCl (0.7 kcal/mole) (*24*, *25*).

At equilibrium transformation the phases have equal free energies, and changes in internal energy ΔU_{coex} are related to changes in molar volumes ΔV and in molar entropies ΔS ($\Delta U_{\text{coex}} = -p\Delta V + T\Delta S$; p: pressure, T: temperature), and, in what follows, the sense of change is taken to be

$$(SrSi_2)_{\text{cub}} \rightarrow (SrSi_2)_{\text{tetr}}.$$

Neglecting differences of thermal expansion and compressibility of the phases gives as a first approximation

$$\Delta V = -1.0\ \text{cm}^3/\text{mole} \qquad \text{(Table I)}$$

so that the term $-p\Delta V$ for equilibrium conditions (say 33 kbar, 1000°K), contributes 0.8 kcal/mole. From the slope of the equilibrium line in the p–T diagram (*20*) $\Delta p/\Delta T = -47$ bars/deg an entropy change $\Delta S = 1.1$ cal/deg · mole is obtained, the positive sign being consistent with the rule that the higher-temperature form has higher entropy. $T\Delta S$ therefore contributes at 1000°K 1.1 kcal/mole, leading to a total equilibrium transformation energy ΔU of $0.8 + 1.1 = 1.9 \pm 0.4$ kcal/mole compared with the nonequilibrium value 1.6 ± 0.3 kcal/mole at ambient pressure and 600–700°C. At 1450 ± 400°C ($(1723 \pm 400) \cdot 1.1 = 1.9 \pm 0.4$ kcal/mole) the two phases could be in equilibrium at ambient pressure, but the melting point of the cubic phase intervenes at 1150°C.

From the caloric experiments two conclusions can be derived: The transformation tetragonal into cubic $SrSi_2$ (at ambient pressure) is relatively rapid and the entropy change is relatively small. Therefore, one could speculate that a complete breakdown of the old lattice in order to form the new one should not be necessary.

A projection of four unit cells of the ideal cubic 3D 3C net is shown in Fig. 4a. Each unit cell contains 8 three-connected atoms which are located in 4_1 helices. The configuration with highest symmetry is achieved for the positional parameter $x = 0.375$. Shortest direct connections between the helices correspond also to bonds. However, for reasons of clearness these connections are not shown. In the tetragonal 3D 3C net the three-connected atoms are also located in 4_1 helices. The highest symmetry is achieved for a $c_{\text{tetr}}/a_{\text{tetr}}$ axial ratio of $2(3)^{1/2}$ and a positional parameter of $z = 5/12$. For the transformation of the 3D 3C nets into each other the helices have to rotate by 45° and also to change their "diameter" (Figs. 4a and 4b). This can be performed between two conditions. Either bond distances in the 3D 3C nets remain unchanged or the volumes of the cubic and the tetragonal unit cells, V_{cub} and V_{tetr}, respectively.

In the ideal 3D 3C nets the following relations hold for bond distances between the three-connected atoms

ideal cubic net:
bond distance $= \frac{1}{4}(2)^{1/2} a_{\text{cub}} = 0.3536 a_{\text{cub}}$
ideal tetragonal net:
bond distance $= \frac{1}{3}(3)^{1/2} a_{\text{tetr}} = 0.5774 a_{\text{tetr}}$.

For equal bond distances in both nets a 20.5% decrease in V_{tetr} is calculated (from $V_{\text{cub}} = a^3_{\text{cub}}$ to $V_{\text{tetr}} = \frac{9}{16}(2)^{1/2} a^3_{\text{cub}}$). On the other hand, for constancy of V_{cub} and V_{tetr} an 8% decrease in bond distances is derived (from $\frac{1}{3}(3)^{1/2} a_{\text{tetr}}$ to $\frac{1}{4}(2)^{1/2}(2(3)^{1/2})^{1/3} a_{\text{tetr}} = 0.5350\, a_{\text{tetr}}$). In Table IV for given tetragonal conditions ($a = 4.140$ Å, $c = 14.340$ Å, $c/a = 2(3)^{1/2} = 3.464$, $z = 5/12$) changes in cubic bond distances and cubic unit-cell volumes have been calculated between these extrema. With minor changes this tetragonal net can be compared to that one which is found in thoriumdisilicide ($a = 4.126$ Å, $c = 14.346$ Å,

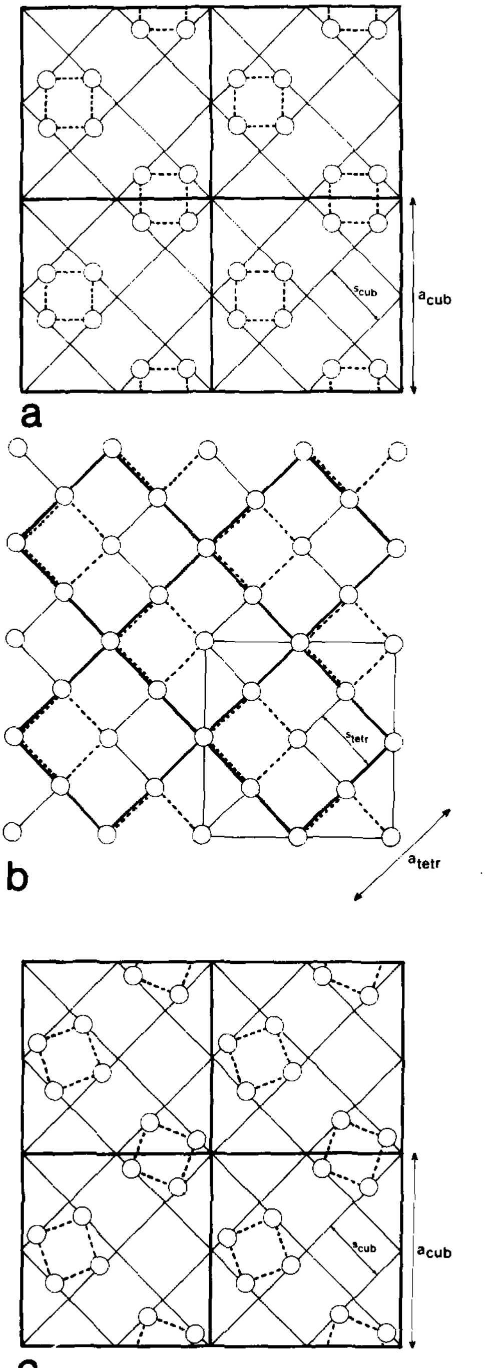

FIG. 4. (a) Projection of four unit cells of the cubic 3D 3C net with positional parameter $x = 0.375$. (b) Projection of the tetragonal 3D 3C net down (001)-direction. (One cubic cell is also shown.) (c) Projection of four unit cells of the cubic 3D 3C net with observed positional parameter $x = 0.423$.

TABLE IV

VARIATION OF BOND DISTANCES AND UNIT-CELL VOLUMES IN THE IDEAL CUBIC NET FOR A GIVEN IDEAL TETRAGONAL ONE[a]

$Si–Si_{cub}$ (Å)	V_{cub} (Å^3)
2.39	308.9
2.35	293.7
2.34	289.9
2.30	275.3
2.25	257.9
2.23	250.7
2.21	244.2

[a] $a_{tetr} = 4.140$ Å; $c_{tetr} = 14.34$ Å; $Si–Si_{tetr} = 2.39$ Å; $V_{tetr} = 245.8$ Å^3.

$c/a = 3.477$) (*10*). By inspection of Table IV it is clearly demonstrated that for constant bond distances (2.39 Å) the unit-cell volume increases from 245.8 to 308.9 Å^3 and that for constant unit-cell volumes (245.8 Å^3) bond distances decrease from 2.39 to 2.21 Å. The value of 2.21 Å is unusually short for Si–Si bonds. Even for decrease of 2% in bond distance (2.34 Å) an increase of 18% in unit-cell volume (289.9 Å^3) is derived. From the data in Table IV it can be concluded that the ideal cubic 3D 3C net in $ThSi_2$ is not easy to create.

However, in $SrSi_2$ the three-connected nets are both distorted from their configurations with highest symmetry. In the cubic net the repeat unit consists of very flat trigonal pyramids instead of equilateral triangles and in the tetragonal net only of isosceles triangles. In Fig. 4c a projection of four unit cells of the cubic 3D 3C net in $SrSi_2$ is shown. The experimentally determined parameter deviates from the ideal value of $x = 0.375$. Best agreement of observed and calculated X-ray intensities was achieved with $x_{Si} = 0.428$ (*7*, *8*) and, later on, with $x_{Si} = 0.423$ (*9*). This deviation from the ideal value results in a rotation of the helices against each other and in an increase of the "diameter" of the helices (Figs. 4a, c). Instead of a rotation of 45° for the transformation of the ideal helices into each other, for positional parameter $x = 0.423$ they have to rotate only by 24°. In addition, conditions for changes of unit-cell volumes and bond distances for transformation of the distorted 3D 3C nets in $SrSi_2$ are less stringent than for the ideal nets. By inspection of Tables I and III it is shown that in $SrSi_2$ a change in unit-cell volume of 2.5% (279.1 Å^3/272.4 Å^3) is connected to a 2% change in bond distances (2.39 Å/medium value 2.44 Å). The corresponding values for the ideal nets are 2.5% volume/7% bond distance change (250.7 Å^3/2.23 Å) and 2% bond distance/18% volume change (2.34 Å/289.9 Å^3) (Table IV).

For the experimentally determined tetragonal lattice parameters of $SrSi_2$ (Table I) a c_{tetr}/a_{tetr} ratio of 3.12 is calculated. Surprisingly, this value is very near to the medium of $c/a = 2(2)^{1/2} = 2.83$ and $c/a = 2(3)^{1/2} = 3.46$ for which one derives $c/a = 3.15$. The value of $c/a = 2(2)^{1/2}$ corresponds to the situation when s_{cub} and s_{tetr} (Figs. 4b and 4c) remain unchanged. As discussed above $c/a = 2(3)^{1/2}$ is needed for equidistant bonds in the tetragonal net. From this agreement one can conclude that, obviously, bond conditions allow a good compromise for these geometrical relations.

By inspection of Figs. 4b and c one would at first sight also expect that by a small distortion the 4_3 helices of the cubic net can be transformed to the 4_1 ones of the tetragonal net. Nevertheless, this is not possible. In Fig. 5a two 4_3 helices of the cubic and in Fig. 5b one 4_1 helix of tetragonal net are shown. It can be seen that a "cubic" helix is only half the length of a "tetragonal" one. Therefore, for the same length the "cubic" helix rotates twice the "tetragonal" one. In order to transform the 3D 3C nets into each other, the linkage between the helices (one-third of the bonds between the three-connected atoms) has to be broken. After rearrangement in the helices (two-thirds of the bonds) (Fig. 5a and b) the linkage must be reorganized. Due to these facts the 3D 3C transformation can be classified as reconstructive one.

It would be very interesting to study this transformation also in other compounds. For binary phases the cubic net is only known in $SrSi_2$, but a number of those with tetragonal net do exist. As discussed above, a c_{tetr}/a_{tetr}

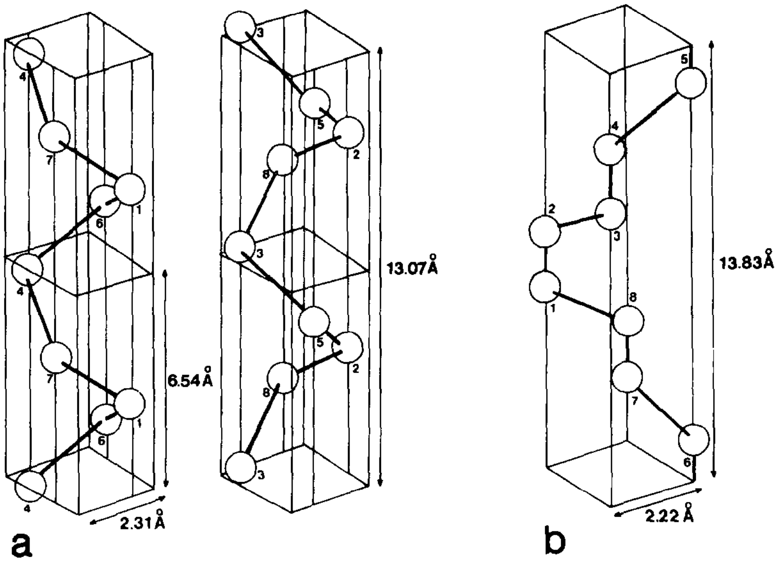

FIG. 5. (a) Two 4_3 helices of the cubic 3D 3C net in $SrSi_2$, $x = 0.423$. (b) One 4_1 helix of the tetragonal 3D 3C net in $SrSi_2$, $z = 0.414$. (Numbers of atoms refer to silicon positions of Table I.)

ratio of 3.15 seems to be favored. Such values are observed in the high-pressure phases of $CaSi_2$ ($c/a = 3.16$ (*26*, *14*) and of $BaGe_2$ ($c/a = 3.10$ (*27*) and also in $EuSi_2$ ($c/a = 3.17$ (*11*, *14*). It may be that for one of those phases also a cubic net could be created.

Acknowledgments

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