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The Structure of $SrSi_2$: a Crystal of Class *O* (432)

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$SrSi_2$ is already known to be cubic with $a = 6{\cdot}515$ Å. The structure has now been established by single-crystal Weissenberg photography. The space group is $P4_332$ (No. 212) or $P4_132$ (No. 213), $Z = 4$. The silicon atoms behave as three-covalent anions bonded to neighbours at a distance of 2·39 Å; the three-dimensional network could be regarded as formed by breaking one quarter of the bonds in pure silicon. The cation Sr^{2+} exhibits the point symmetry D_3 (32) with eight contacts to Si^-; two, which are axial, correspond to a cation radius of 1·1 Å, and six, which are pseudo-equatorial, show a shortening of 0·1 Å possibly due to partial covalent character. The crystal class *O* (432) is of rare occurrence.

Introduction

Compounds of the type MSi_2 present a diversity of structure described by Wells (1962) and also differ markedly from the analogous acetylides because Si^- shows less tendency to dimerize than does C^- in C_2^{2-}. Disilicides of Group 2 cations Ca^{2+} and Sr^{2+} are not isostructural. The former were examined by Böhm & Hassel (1927) and, at that time, were described as the only known example of the space group $R\bar{3}m$. Strontium disilicide belongs to a still less common space group, and its class [point group *O* (432)], comprising eight space groups (two of which are enantiomorphous) is occupied by only one or two known examples.

The material

Strontium disilicide has been prepared either by direct synthesis from the elements with SrF_2 as a flux at 1180°C (Rocktäschel & Weiss, 1962), or by carbon reduction of oxide mixtures (Bradley, 1900; Wöhler & Schuff, 1932; Faulring & Malizie, 1967). The last-named authors examined the product in its silicon matrix metallographically and by electron microprobe, and identified it as the paler grey material against a darker background of silicon, whilst some FeS_2 present showed as needles of intermediate shade. After grinding, the material could be separated by flotation of silicon since the density (calculated value 3·45 g.cm^{-3}) of the compound exceeds that of methylene iodide, 3·3 g.cm^{-3}. They thus obtained and indexed an X-ray diffraction pattern of separated powder by Straumanis photography in Cu $K\alpha$ radiation and so determined the lattice as cubic with cell edge 6·515 Å. They proposed a space group of low cubic symmetry, which, however, was not established definitely. From the microprobe work it appeared that the compound contained a small proportion of calcium which was assumed to have replaced an equivalent amount of strontium.

Further X-ray examination of the symmetry

A sample of the material was ground and separated by flotation of silicon, and a small single crystal was selected for Weissenberg photography. Layers 0–5 were recorded up the principal axis with Cu $K\alpha$ radiation, the camera having been set for integration by the Wiebenga device. Film packs of four films were used and the intensities were measured by means of a microdensitometer.

The permitted reflexions were

hkl; no conditions
*h*00; $h = 4n$, denoting fourfold screw axes.

The space group was determined as either $P4_132$ or the enantiomorphous group $P4_332$.

The size of the crystal used (mean radius $r \sim 0{\cdot}02$ mm) and the calculated absorption coefficient of the pure substance ($\mu = 34{\cdot}5$ mm^{-1}) give an approximate value of $\mu r = 0{\cdot}7$. There was some evidence of systematic variability across the films, but as there were separate measurements of equivalent reflexions which could be averaged, these average values were corrected only for mean spherical absorption. The correction factors from *International Tables for X-ray Crystallography* (1959) were included in the normal structure-factor program for this purpose. Reflexions related only by Friedel's Law were not merged.

The crystal structure and its refinement

The simplest qualitative solution of the structure was immediately determined as:

$P4_332$: 4Sr at Wyckoff position (*a*) $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ + equivalents
$P4_132$: 4Sr at Wyckoff position (*b*) $\frac{7}{8}, \frac{7}{8}, \frac{7}{8}$ + equivalents
Either space group: 8Si at Wykoff position (*c*) x, x, x + equivalents

All these atoms lie on threefold axes, and, in addition to the systematic absences given in *International Tables for X-ray Crystallography* (1965) we should expect the reflexion $h0l$ to be absent if $h+l=4n+2$. The absence of 402 and 802 gave support to the proposed structure.

The particular values $x=0$ or $-\frac{1}{4}$ would correspond to the arrangement of atoms in pure silicon. The value $x=-\frac{1}{6}$ is that for which the two distances from Sr along the cube diagonal to Si become exactly equal to the six pseudo-equatorial Sr–Si distances; the coordination is then 8/4.

After refinement of the structure to convergence by least-squares computation, the x coordinate was fairly close to $-\frac{1}{6}$. The final parameters in Table 1 include anisotropic thermal parameters U_{ij} of which only two elements are independent for each atom type.

The weighting function for least-squares refinement was

$$w=(p_o+F_o+p_1F_o^2)^{-1} \text{ with } p_0 \approx 20, \quad p_1 \approx 0{\cdot}0125$$

and the final R value was 0·0765 on 235 planes.

Absolute configuration

In the later cycles of refinement, the anomalous dispersion term f'' was included in the atomic scattering, (*International Tables for X-ray Crystallography*, 1962), and parameter corrections were computed in the enantiomorphous space groups in parallel. To increase the contrast, we may compare the two R values, denoted by R_1' and R_3', based only on those reflexions for which the calculated structure factors F_{C1} in $P4_132$ differ from the corresponding set F_{C3} in $P4_332$ when the same parameters are assumed.

It was found that

$$\left.\begin{array}{l} R_1'=0{\cdot}0744 \\ R_3'=0{\cdot}0721 \end{array}\right\} \text{ on 108 reflexions.}$$

The calculated differences for these reflexions gave

$$\sum||F_{C1}|-|F_{C3}||/\sum|F_C|=0{\cdot}0174.$$

Since $\sqrt{(0{\cdot}0721^2+0{\cdot}0174^2)}=0{\cdot}0742$ it seems that the contrast was approximately what would be expected, if the deviations from Friedel's Law were independent of the errors of measurement. The space group $P4_332$ is significantly favoured in the case of the particular crystal selected.

Observed and calculated structure factors are listed in Table 2.

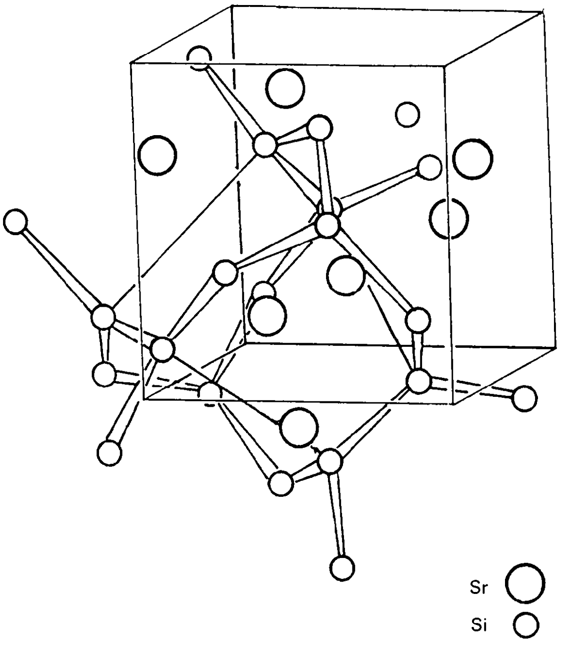


Fig. 1. SrSi$_2$, clinographic projection of the structure.

Table 1. SrSi$_2$ *parameters*

Standard deviations are given in parentheses.

	Fractional coordinates	Thermal parameters (Å^2) (crystal axes)		Thermal parameters (Å^2) (site symmetry axes)	
	$x=y=z$	U_{ii}	$2U_{ij}(i \neq j)$	U_{zz}	$U_{xx}=U_{yy}$
Sr	0·1250	0·013 (1)	0·004 (1)	0·017	0·011
Si	−0·1731 (5)	0·009 (1)	0·002 (2)	0·011	0·008

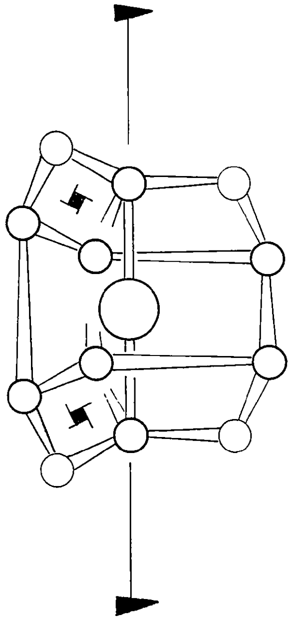
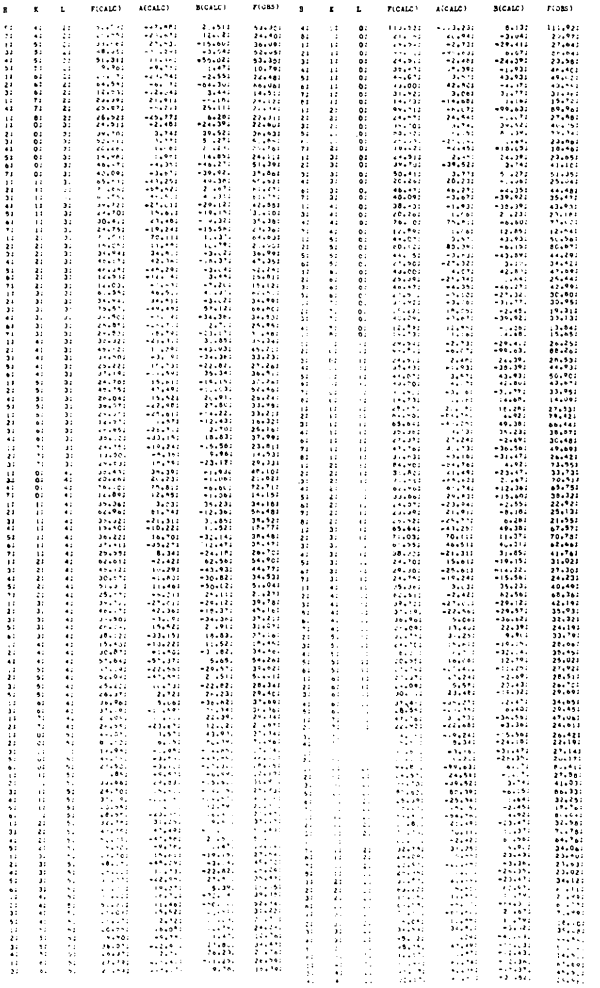


Fig. 2. The arrangement around Sr; point symmetry D_3 (32) shown with the unique axis vertical, viewed down a cubic axis of the structure.

Table 2. $SrSi_2$ *observed and calculated structure factors* $P4_332$



H	K	L	F(CALC)	A(CALC)	B(CALC)	F(OBS)	H	K	L	F(CALC)	A(CALC)	B(CALC)	F(OBS)

Discussion of the bonding

Each silicon atom is bonded to three others at crystallographically equal distances related by the threefold axis. The bond length 2·387 (1) Å is that of a typical single Si–Si bond as in $ThSi_2$. The silicon framework is effectively a macroscopic anion carrying probably an average of one electron charge per atom, and constitutes a σ skeleton which could be regarded as being formed by breaking one quarter of the bonds in pure silicon in a systematic way. With the resulting expansion of the cubic lattice from $a = 5{\cdot}431$ to $a = 6{\cdot}515$ Å there arise holes large enough to accommodate the Sr^{2+} ions; the Si–Si–Si interbond angle thereby increases from 109·5° to 117·7°. The non-bonding contacts between Si atoms are at a distance of 4·556 (10) Å, giving a maximum ionic radius of 2·28 Å. The strontium cation has point symmetry D_3 (32) which is rather unusual for an eight-coordinated group. This is made of six almost equatorial Si atoms at a distance of 3·240 (4) Å, and two axial Si atoms at 3·364 (5) Å. The equatorial bond is about 0·1 Å shorter than the sum of the ionic radii, whereas the axial contact is close to that expected if Sr^{2+} has a radius of 1·09 Å. In the calcium compound the cation is at the centre of a trigonal antiprism, with a further axial anion at a distance (3·06 Å) slightly greater than that of the other six at 3·02 Å.

The structure of the enantiomorph $P4_332$ is depicted clinographically in Fig. 1, and the arrangement round Sr in Fig. 2.

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