

Strontium Disulphide Prepared at High Pressure

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Abstract. SrS₂, tetragonal, *I4/mcm*, *a* = 6.095, *c* = 7.616 Å, *Z* = 4, *D_x* = 3.56 g cm⁻³. Crystals were prepared at high pressure (20 kbar) by heating an S-excess mixture of SrS and S up to 900°C in a boron nitride capsule. S₂²⁻ ions (S-S bond length 2.103 Å) lie in sheets parallel to (001). Sr ions are located between these sheets and coordinated to eight S atoms. This structure belongs to the CuAl₂ structure type.

Introduction. Polycrystalline SrS₂ was synthesized under normal pressure by Lutz (1965, 1966). He gave the *d* values of powder data but no crystal or structural data. In our present investigation single crystals have been obtained at high pressure and high temperature. They are pale, greenish yellow. The size of the specimen examined by X-rays was 0.13 × 0.13 × 0.23 mm. The intensity data were collected on a Rigaku four-circle diffractometer with Mo Kα₁ (λ = 0.70926 Å) radiation monochromatized by graphite. In the range of 2θ < 90°, 2616 reflexions were measured, of which 1056 were below the limit of observation. The observed intensities were corrected for absorption effects (average μ_r = 3.35).

The systematic absences were *hkl*: *h* + *k* + *l* = 2*n* + 1 and *0kl*: *l* = 2*n* + 1, giving possible space groups *I4cm* (No. 108), *I4c2* (No. 120) and *I4/mcm* (No. 140). The structure determination has verified *I4/mcm*.

The positions of the Sr atoms were obtained from a Patterson map. A difference Fourier synthesis revealed the positions of the S atoms. The structure was refined by the full-matrix least-squares method with the program *ORFLS* (Busing, Martin & Levy, 1962) and anisotropic temperature factors. The final *R* was 0.062 and the weighted *R* 0.022 for 294 observed reflexions.* The atomic scattering factors for Sr and S were taken from Hanson, Herman, Lea & Skillman (1964).

Discussion. The atomic parameters of SrS₂ are given in Table 1. In the structure of SrS₂ the S₂²⁻ ions, with an S-S bond length of 2.103 Å, lie parallel to (001) at *z* = 0 and $\frac{1}{2}$. Sr²⁺ is located between the sheets of S₂²⁻ ions and surrounded by eight S atoms; the Sr-S distance is 3.080 Å (Figs. 1 and 2).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31878 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic parameters (× 10⁴)

The anisotropic temperature factors are expressed as $\exp \{ -[(h^2 + k^2)\beta_{11} + l^2\beta_{33} + 2hk\beta_{12}] \}$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{33}	β_{12}
Sr	0	0	$\frac{1}{2}$	89 (1)	37 (1)	0
S	1220 (2)	$\frac{1}{2} + x$	0	67 (2)	41 (2)	-3 (2)

The structure of SrS₂ is isotypic with that of the CuAl₂ group intermetallic compounds (Friauf, 1927; *Strukturbericht*, 1931). Wyckoff (1963) chose Fe₂B rather than CuAl₂ as the representative of this type. On account of the short S-S distance within each S₂²⁻ ion lying parallel to (001), the *c/a* ratio of 1.25 in SrS₂ is distinctly greater than those (0.75–0.88) in the intermetallic compounds (Schubert, 1964). Similar short S-S distances in S₂²⁻ ions are also observed, for instance, in pyrite (FeS₂, 2.10 Å) and BaS₂ (2.118 Å).

The structure of BaS₂ (Kawada, Kato & Yamaoka, 1975) is closely related to that of SrS₂. If we rearrange the S atoms in SrS₂ so as to form a *C* lattice instead of the *I* lattice of *I4/mcm* and then distort the tetrag-

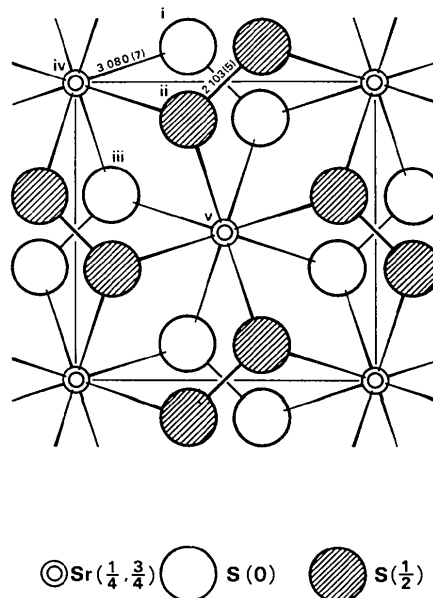


Fig. 1. The structure of SrS₂ projected on (001). The fractional *z* coordinates of the atoms are given in parentheses after the chemical symbols. The Sr-S and S-S bond lengths are indicated in Å. For the symmetry-operation superscripts see Table 2.

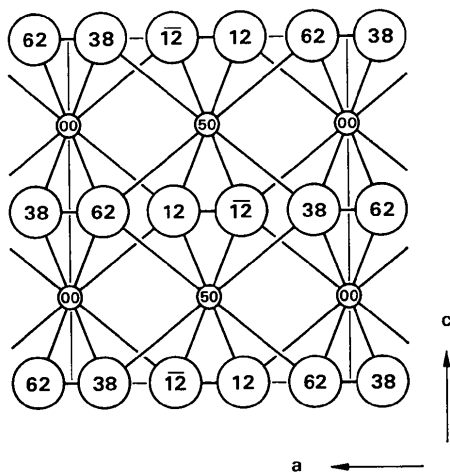


Fig. 2. Projection of the structure on (010). Small circles are Sr atoms and large circles S atoms. Fractional y coordinates ($\times 10^2$) are shown in the circles.

onal symmetry of SrS_2 in such a way that, referring to Fig. 1, we separate the two overlapping metal atoms at $z = \frac{1}{4}$ and $\frac{3}{4}$ along the a_1 axis, then stretch the a_2 axis and shift the S atoms slightly from the levels of $z = 0$ and $\frac{1}{2}$, we obtain Fig. 1 of our previous paper on BaS_2 (Kawada *et al.*, 1975).

Among the structures of the other metal chalcogenides, those of the isostructural compounds TlSe (Ketelaar, t'Hart, Moerel & Polder, 1939) and TlS (Hahn & Klinger, 1949; Scatturin & Frasson, 1956) are very closely related to the structure of SrS_2 . In these compounds, Tl atoms occupy two sites, 4(a) and 4(b), in the same space group $I4/mcm$. If we omit the Tl atom in the latter site, we obtain the SrS_2 structure type.

Further, it should be mentioned that the structure of KHF_2 (Peterson & Levy, 1952) is also closely related to that of SrS_2 . In the former structure, an H atom forms the linear bonding F-H-F at the same z level. If we regard only the K and F atoms in KHF_2 , both compounds belong to the same structure type.

Interatomic distances and angles were calculated with the program *ORFFE* (Busing, Martin & Levy, 1964) and are listed in Table 2. The calculations were carried out on the FACOM 270-20 of this Institute.

Table 2. Interatomic distances and bond angles

Sr-S^{I}	3.080 (7) Å	$\text{S}^{\text{I}}-\text{Sr}-\text{S}^{\text{II}}$	83.2 (2)°
S-S^{I}	2.103 (5)	$\text{S}^{\text{I}}-\text{Sr}-\text{S}^{\text{III}}$	67.5 (1)
S-S^{II}	4.088 (10)	$\text{S}^{\text{II}}-\text{Sr}-\text{S}^{\text{III}}$	91.2 (2)
S-S^{III}	3.424 (9)	$\text{Sr-S}^{\text{I}}-\text{S}$	111.0 (2)
$\text{S}^{\text{I}}-\text{S}^{\text{III}}$	4.424 (9)	$\text{Sr-S}^{\text{II}}-\text{Sr}^{\text{v}}$	88.8 (1)
$\text{S}^{\text{II}}-\text{S}^{\text{III}}$	4.401 (9)		
Sr-Sr^{IV}	3.808 (10)		
Sr-Sr^{v}	4.310 (10)		

Symmetry code

(i)	$-x, 1-y, z$	(iv)	$x, y, \frac{1}{2}+z$
(ii)	$x, 1-y, \frac{1}{2}+z$	(v)	$\frac{1}{2}+x, \frac{1}{2}+y, z$
(iii)	$1-y, x, z$		

The standard deviations of lattice constants a and c were roughly estimated to be 0.02 Å. Because of rather poor diffraction-peak profiles, a more accurate measurement was not attempted.

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