be Sc, Y, or one of the lanthanides, together with Zr, Hf, or Sn. For a compound with M from group VI and $n = 8$, there is, in addition to the possibility $Q_o = Q_t = 3$, one with (Q_t, Q_o) of (2, 4) or (4, 2). For these, A and B might be Mg or Ca, together with Zr, Hf, or Sn.

CONTRIBUTION FROM RCA LABORATORIES,
PRINCETON, NEW JERSEY

The Preparation, Properties, and Crystal Structures of Some Scandium Sulfides in the Range Sc_2S_3–ScS

BY J. P. DISMUKES AND J. G. WHITE

Received March 6, 1964

Scandium sesquisulfide, Sc_2S_3, was prepared by the high-temperature reaction of hydrogen sulfide with scandium sesquioxide. Due to the problem of stoichiometry associated with the high melting point, 1775°, stoichiometric crystals of Sc_2S_3 were prepared by chemical transport with I_2 at 950°. A nonstoichiometric material containing an excess of scandium compared with Sc_2S_3 was prepared by heating Sc_2S_3 under vacuum at 1650°. Crystals of ScS were prepared by the reaction of scandium metal with sulfur. The crystal structure of Sc_2S_3 is closely related to that of NaCl, but the unit cell is twelve times as large due to a complex ordering arrangement of the cation voids. Each "octahedron" surrounding sulfur has two vertices empty, and the bond angles are all very close to 90°. The nonstoichiometric material has a much simpler structure which is also closely related to that of NaCl, with $Sc_{1.37}S_2$ per rhombohedral unit cell. This structure, in which one cation site is filled and the other is only partially occupied, could exist over the whole range between Sc_2S_3 and ScS, which was found to have the NaCl structure. Stoichiometric Sc_2S_3 is a semiconductor with a band gap of about 2 e.v., but the materials between Sc_2S_3 and ScS are good electrical conductors. Electrical conduction in the latter materials appears to involve a 3d band.

Introduction

Trivalent scandium differs from other trivalent ions of the first transition series in that it has a closed outer electron shell with the argon configuration. For this reason the chemistry of trivalent scandium compounds is of particular interest with regard to crystal structure and semiconducting properties.[1] This paper discusses the preparation of scandium sesquisulfide, Sc_2S_3, a nonstoichiometric sulfide, $Sc_{1.37}S_2$, and scandium monosulfide, ScS, some of their chemical and physical properties, and the determination of their crystal structures.

Klemm[2] first prepared Sc_2S_3 by the reaction of H_2S with $ScCl_3$ at elevated temperature, but was unable to determine its crystal structure from X-ray diffraction powder photographs. Men'kov, *et al.*,[3] also prepared Sc_2S_3 in polycrystalline form and concluded that the material had a β-In_2S_3 structure. In a recent review, however, Hahn[4] stated, with reference to a private communication from Klemm, that Sc_2S_3 crystallizes in a defect NaCl-type structure with random voids in the metal sublattice and that ScS crystallizes in the NaCl structure. Hahn, therefore, postulated that a range of homogeneity or disordered solid solution exists between them. No details of the preparation of ScS, nor a value for its lattice parameter, have been published.

Cation-deficient structures, with the voids either ordered or disordered, derived from the zinc blende structure have been known for many years. Indium telluride[5] is a striking example. However, we have been unable to find in the literature reference to any cation-deficient sodium chloride type structure other than scandium sesquisulfide, and this in itself makes the study of the crystal structure and properties of this compound of fundamental importance.

Experimental

Preparation of Sc_2S_3.—Scandium sesquisulfide, Sc_2S_3, was prepared by induction heating at 470 kc. of scandium sesquioxide, Sc_2O_3, with H_2S in a high-purity graphite crucible at elevated temperature, using a modification (Fig. 1) of the apparatus developed by Eastman[6] and co-workers for preparing Ce_2S_3. Pure Sc_2S_3 was obtained when the hydrogen sulfide was passed through a 10-g. charge of finely divided Sc_2O_3 (Michigan Chemical Co.) for 2–3 hr. at 1550° or higher, with the H_2S flow rate adjusted to 15 l. hr.$^{-1}$. The X-ray diffraction powder photographs of material prepared at 1450° or lower can be explained as a combination of the patterns of Sc_2S_3 and Sc_2O_2S. Complete reaction was not obtained at this temperature even when the product was ground to a powder and allowed to react again (Table I).

Emission spectrographic analysis showed that Sc_2O_3 used as a starting material contained the following impurities (p.p.m.): Mn, 100; Fe, 300; Cu, 300; Pb, 300; Al, 100; Si, 100; P, 30; Cr, 30; and Ca, 20. During the synthesis of Sc_2S_3, Pb, Si, P, Cr, and Ca were reduced to below 1 p.p.m. However, the product was contaminated with about 0.2 wt. % of carbon and about 0.2 wt. % of oxygen. Scandium was determined by complexometric titration with EDTA,[7,8] and sulfur was determined using

---

[1] E. Mooser, *Science*, **132**, 1285 (1960).

[2] W. Klemm, K. Meisel, and H. U. von Vogel, *Z. anorg. allgem. Chem.*, **190**, 123 (1930).

[3] A. A. Men'kov, L. N. Komisarova, Yu. P. Simanov, and V. I. Spitsyn, *Chem. Abstr.*, **56**, 9543*a* (1962).

[4] H. Hahn, Special Publication No. 12, The Chemical Society, London, 1958, pp. 263–283.

[5] J. C. Woolley, B. R. Pamplin, and P. J. Holmes, *J. Less-Common Metals*, **1**, 362 (1959).

[6] E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, *J. Am. Chem. Soc.*, **72**, 2248 (1950).

[7] K. L. Cheng and T. R. Williams, *Chemist Analyst*, **44**, 96 (1955).

[8] K. L. Cheng, *Anal. Chem.*, **33**, 761 (1961).

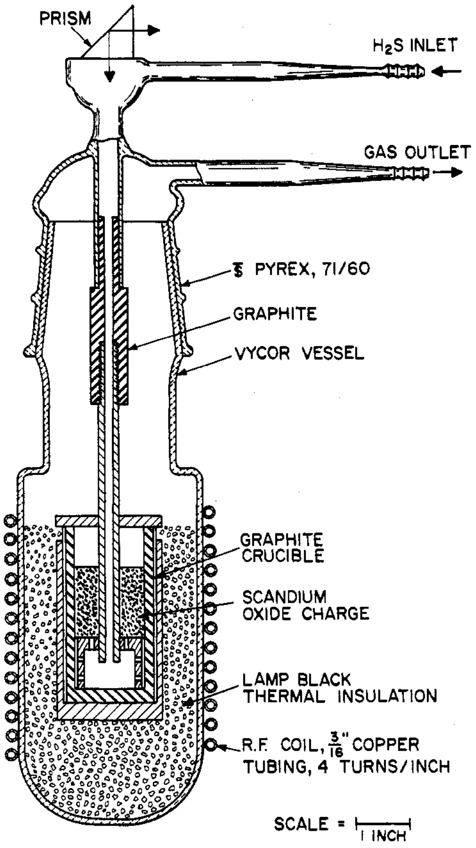

Fig. 1.—Apparatus used for the preparation of Sc_2S_3.

the iodometric method for hydrogen sulfide.[9] Oxygen and carbon were determined by an inert gas fusion technique,[10] using a Leco oxygen analyzer, which consists of an induction furnace and a conductometric analyzer. *Anal.* Calcd. for Sc_2S_3: Sc, 48.3; S, 51.7. Found: Sc, 47.8; S, 50.0.

TABLE I

REACTION CONDITIONS USED FOR THE PREPARATION OF Sc_2S_3

Scandium sulfide sample no.	Starting matl.	H_2S flow rate, l./hr.	Temp., °C.	Time, hr.	X-Ray diffraction powder photograph
SY-25	Sc_2O_3 (4 g.)	15	1400	2.5	$Sc_2S_3 + Sc_2O_2S$
SY-28	SY-25 (4 g.)	15	1450	2	$Sc_2S_3 + Sc_2O_2S$
SY-29	SY-28 (3.5 g.)	15	1550	2	Sc_2S_3
SY-30	SY-29 (3 g.)	15	1650	3	Sc_2S_3
SY-38	Sc_2O_3 (10 g.)	15	900	2	Sc_2S_3
			1550	2	
			1650	0.5	

Chemical Transport of Sc_2S_3.—The melting point of scandium sesquisulfide determined under black body conditions at a pressure of 10^{-2} mm. in an induction-heated tantalum crucible was 1775 ± 25°. Since Sc_2S_3 evolves sulfur above 1100° and becomes nonstoichiometric, the chemical transport technique[11-13] was used to prepare stoichiometric crystals of this compound. It was determined that transport of Sc_2S_3 with I_2 occurs from the hot zone to the cold zone by positioning an ampoule with the Sc_2S_3 charge in the center of the temperature gradient provided by a two-zone furnace (Fig. 2). The direction of transport of Sc_2S_3 indicates that the equilibrium constant of the reaction

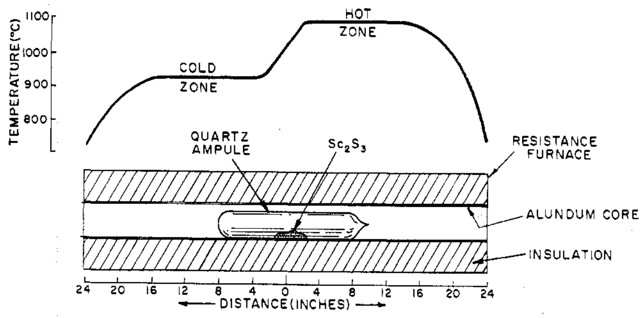

Fig. 2.—Chemical transport of Sc_2S_3 using a two-zone furnace.

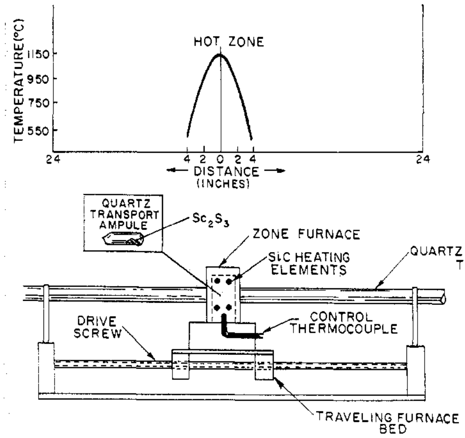

Fig. 3.—Chemical transport of Sc_2S_3 using a horizontal Bridgman arrangement.

$$Sc_2S_3(s) + 3I_2(g) \rightleftarrows 2ScI_3(g) + {}^3/_2S_2(g) \qquad (1)$$

increases with increasing temperature over the range 900–1150° and that, therefore, the reaction is endothermic.[11-13] In subsequent experiments crystal growth was controlled by moving a steep temperature gradient provided by a narrow zone furnace with respect to the transport ampoule at a constant rate[14] (Fig. 3). Transported crystals of Sc_2S_3 are yellow to transmitted light, which indicates that the optical band gap is about 2 e.v. Further experimental details are given in Table II. The normalized rates of transport, $\dot{m}l/A$, are relatively insensitive to variation of I_2 concentration in the range 1.6–8 mg./cm.^{3}. The sublimation temperature, 908°, of ScI_3[15] is an approximate lower limit on the cold zone temperature for reasonable transport rates. The density of a compact, polycrystalline mass obtained in experiment T-5 was determined to be 2.897 ± 0.014 g. cm.$^{-3}$ by the method of hydrostatic weighing,[16] employing Archimedes' principle and using water as an immersion fluid.

The X-ray diffraction powder photographs of the vapor-transported Sc_2S_3 samples were identical with those of Sc_2S_3 prepared by the high temperature synthesis at 1550° or higher. No change in the impurity content occurred during the transport experiments. *Anal.* Calcd. for Sc_2S_3: Sc, 48.3; S, 51.7. Found: Sc, 48.6; S, 51.0.

Chemical Properties of Sc_2S_3.—Reactions of Sc_2S_3 with various reagents were compared with those of Ce_2S_3.[17] Neither compound reacts with water or dilute NaOH. Both react with bromine water or $KMnO_4$ solution, Sc_2S_3 being much less reactive

---

(9) I. M. Kolthoff and P. J. Elving, "Treatise on Analytical Chemistry," John Wiley and Sons, New York, N. Y., 1961, Part II, Vol. 7, p. 75.

(10) C. V. Banks, J. W. O'Laughlin, and G. J. Kamin, *Anal. Chem.*, **32**, 1613 (1960).

(11) H. Schafer, H. Jacob, and K. Etzel, *Z. anorg. allgem. Chem.*, **286**, 27 (1956); H. Schafer, "Chemische Transportreaktionen," Verlag Chemie, G.m.b.H., 1962.

(12) R. Nitsche, *J. Phys. Chem. Solids*, **17**, 163 (1960).

(13) R. Nitsche. H. U. Bolsterli, and M. Lichtensteiger, *ibid.*, **21**, 199 (1961).

(14) R. L. Bube, E. L. Lind, and A. B. Dreeben, *Phys. Rev.*, **128**, 532 (1962).

(15) W. Fischer, R. Gewehr, and H. Wingschen, *Z. anorg. allgem. Chem.*, **242**, 161 (1939).

(16) A. Smakula and V. Sils, *Phys. Rev.*, **99**, 1744 (1955).

(17) Prepared using the technique described for Sc_2S_3.

Table II

Reaction Conditions Used for the Chemical Transport of Sc_2S_3

Transport Expt. no.	Time, hr.	Rate of transport, $\dot{m}$, mg./hr.	Normalized rate of transport $\dot{m}l/A$, mg./hr. cm.	Rate of furnace travel, in./hr.	Length of ampoule, cm.	Diameter of ampoule, cm.	Concn. of I_2, mg./cm.^{3}	Hot zone temp., °C.	Cold zone temp., °C.
T-1	40	6.3	74	0^a	38	2.0	1.6	1090	920
T-2	<18	>27.6	$>56^c$	0.125^b	7	2.5	5.4	1150	950
T-5	<50	>27	$>34^c$	0.01^b	4	2.0	8.0	1150	950

[a] Figure 2. [b] Figure 3. [c] This is a lower limit, since all the charge was transported during the time of the experiment.

than Ce_2S_3. Scandium sesquisulfide reacts moderately with strong acids and apparently not at all with dilute acetic acid, whereas Ce_2S_3 reacts violently with strong acids and moderately with dilute acetic acid. In this respect, the chemical behavior of Sc_2S_3 is similar to that of Cr_2S_3 and V_2S_3.[18] Scandium sesquisulfide reacted with scandium sesquioxide in 1:2 mole ratio at 1150° in an evacuated quartz ampoule to form a gray powder which dissolved slowly in boiling aqua regia. This material, Sc_2O_2S, gives an X-ray diffraction powder photograph which can be indexed on the basis of a hexagonal unit cell with $a = 3.52_7$, $c = 6.26_7$ Å.[19] Spectrographic analysis of this substance shows that no reaction occurred with the quartz ampoule. X-Ray examination showed that Sc_2S_3 is not oxidized by air in 16 hr. at 300°, but that in the same time at 700° it is oxidized to Sc_2O_3.

Nonstoichiometric Scandium Sesquisulfide, $Sc_{1.37}S_2$.—A black, electrically conducting specimen of scandium sulfide was prepared by heating a pressed compact of nonconducting Sc_2S_3 powder at less than 10^{-3} mm. pressure for 2 hr. at 1650° in a carbon crucible. The concentration of all metallic impurities except Si (100 p.p.m.) was reduced below 1 p.p.m. during the sintering. *Anal.* Calcd. for $Sc_{1.37}S_2$: Sc, 49.0. Found: Sc, 49.0.

The temperature dependence of the thermoelectric power Q and of the electrical resistivity ρ was measured on a rectangular parallelepiped ($0.75 \times 0.1 \times 0.1$ in.) cut from this specimen, to which two 0.003-in. Pt—Pt,–13% Rh thermocouples were attached with electrically conducting Sauereisen cement in 0.010-in. holes spaced 0.3 in. apart. The thermocouples served both as potential probes for an a.c measurement of resistivity by the four-probe technique and as probes for measuring Q by establishing a temperature difference of about 10° between them.[21] The temperature dependence of Q and ρ measured between 300 and 850°K. is shown in Fig. 4.

Scandium Monosulfide, ScS.—Scandium monosulfide, ScS, was prepared by the reaction in an evacuated quartz ampoule of about 0.25 g. of scandium metal contained in an alumina boat with a stoichiometric amount of sulfur. Heating at 1150° for about 70 hr. was required for completion of the reaction. The scandium metal (Fairmount Chemical Co.) contained the following metallic impurities (p.p.m.); Al, 1000; Cu, 1000; Fe, 300; Mn, 100; Ag, 100; Ni, 30; Mg, 10; Ca, 10; and Si, 10. During the synthesis of ScS, Mn, Mg, and Ca were reduced to below 1 p.p.m. Scandium monosulfide has a gold color similar to that of cerium monosulfide. The density of ScS, determined on a 36-mg. sample by hydrostatic weighing, was 3.59 ± 0.14 g. cm.$^{-3}$. The absolute Q of ScS at 300°K. was $+0.5$ μv./deg., and its approximate ρ was less than 10^{-3} ohm cm.

X-Ray Measurements.—All the X-ray intensity data for Sc_2S_3 were recorded on Weissenberg photographs from one crystal approximately cubic in shape, with edge 0.10 mm., using Ni-filtered Cu Kα radiation. Intensities were estimated visually by comparison with a standard intensity scale, and the intensities were modified by absorption corrections appropriate to a spherical crystal of equal volume to that actually used. The three-dimensional $[F_o]$ list is given in Table III where the scale has been adjusted to that of the final calculated values.

The crystal data for Sc_2S_3 are: Sc_2S_3, mol. wt. 186.12; orthorhombic bipyramidal; systematically absent spectra: hkl with $h + k$, $k + l$, $l + h$ odd; $hk0$ with $h + k \neq 4n$, $h0l$ with $h + l \neq 4n$, $0kl$ with $k + l \neq 4n$; space group Fddd; $a = 10.41 \pm 0.01$, $b = 7.38 \pm 0.01$, $c = 22.05 \pm 0.02$ Å.; volume of unit cell 1695 Å.^{3}; 16 formula units per unit cell; d_{calcd} 2.917 g. cm.$^{-1}$, d_{obsd} 2.897 ± 0.014 g. cm.$^{-3}$; 25°.

Results

Structure Determination and Refinement for Sc_2S_3.—The unit cell dimensions are quite simply related to those of a NaCl-type structure with $a = 5.21$ Å. Thus a, b, and c of the orthorhombic unit cell are 2, $\sqrt{2}$, and $3\sqrt{2}$, respectively, times 5.21 Å.; the pseudosymmetry of the X-ray diffraction patterns indicated that such a cubic subcell exists. Further, the intensities of the strongest group of reflections, those for which h, k, and l are even when indexed with respect to the subcell, agree very closely with those expected for the sum of maximum contributions from both the cations and anions. It appeared, therefore, that the structure is basically a NaCl type, the large orthorhombic unit cell being required by an ordering of the positions where one-third of the cations are missing.

The orthorhombic unit cell contains 48 sulfur atoms and 32 scandium atoms. In the space group, Fddd, there are general 32-fold positions and four different types of 16-fold positions.[22] The atoms could, therefore, be arranged in this cell at NaCl sites in various ways. At least two groups of atoms, however, must be in positions having a free z parameter, since some of the NaCl sites are at odd twenty-fourths of the c axis. After several trials it was concluded that only one arrangement could give agreement with the three-dimensional intensity data. The atomic positions chosen as the starting point for refinement are as follows: 16 Sc-I in (g) $^1/_8$, $^1/_8$, $^1/_{24}$; 16 Sc-II in (g) $^1/_8$, $^1/_8$, $^3/_8$; 16 S-I in (f) $^1/_8$, $^3/_8$, $^1/_8$; 32 S-II in (h) $^1/_8$, $^3/_8$, $^{11}/_{24}$.

This postulated structure gave a reliability coefficient $R = 0.122$ (where R is $\Sigma\{|F_o| - |F_c|\}/\Sigma F_o$) for the $h0l$ reflections, and refinement was carried out first by ρ_{obsd} and $\rho_{\text{obsd}} - \rho_{\text{calcd}}$ synthesis of the $h0l$ zone. Here the free z parameters of Sc-I and S-II could be determined directly, since the deviation of overlapping atoms from the ideal positions was in the same direction. Three-dimensional refinement was then carried out by computation of direct and differ-

---

[18] H. Remy, "Treatise on Inorganic Chemistry," Elsevier Publishing Co. New York, N. Y., Vol. II, 1956, pp. 96 and 137.

[19] The intensity distribution in the X-ray pattern of Sc_2O_2S is quite similar to that found in the rare earth oxysulfides.[20]

[20] H. Eick, *J. Am. Chem. Soc.*, **80**, 43 (1958).

[21] R. R. Heikes and R. W. Ure, Jr., "Thermoelectricity; Science and Engineering," Interscience, New York, N. Y., 1961, Chapter 10.

[22] International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, Vol. I, 1952, p. 161.

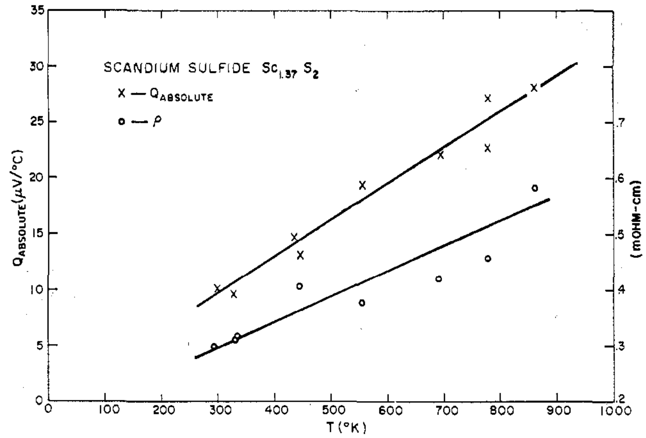

Fig. 4.—Temperature dependence of Q and ρ of $Sc_{1.37}S_2$.

ence synthesis through the center of each atom perpendicular to both *b* and *c*, and all the free parameters were determined. The cation voids are the (g) positions $^1/_8$, $^1/_8$, $^{13}/_{24}$, etc. The difference electron density maps showed a slightly negative region at these sites and consequently there is no evidence for any disorder in the structure.

The refined coordinates are listed in Table IV and the observed and final values of the structure factors calculated on the basis of these coordinates are given in Table III. The scattering factors used are those given in the International Tables[23] corrected for anomalous dispersion.[24] An over-all isotropic temperature factor, $\exp[-B(\sin \theta/\lambda)^2]$, with $B = 1.05$ Å.^{2}, has been included. The latest difference electron density maps indicated a very slightly greater temperature factor for sulfur than for scandium, but the agreement between the observed and calculated data was not improved by the use of separate temperature factors. For the 244 observed reflections the final value of R is 0.078. The standard deviations calculated by Cruickshank's method[25] are 0.003–0.004 Å. for each positional parameter and 0.2–0.3° for the bond angles. However, these values may be rather low in view of the number of reflections insensitive to small positional changes.

Description of the Structure of Sc_2S_3.—The structure may be visualized from Fig. 5, which shows the projection down the crystal *b* axis. Viewed in this direction the atoms overlap in pairs: two sulfurs, two scandiums, or one scandium and a cation void as compared with the NaCl structure. For simplicity the *y* coordinates given beside each atom are the "ideal" ones without the small distortions obtained by refinement. The exact positions may be obtained from the coordinates of Table IV and the space group positions.[22] The numbers give the height of the atoms in eighths of *b*, the numbers in parentheses referring to voids. The origin of the NaCl pseudo-subcell is displaced by $^1/_8$, $^1/_8$, $^1/_{24}$ from that of the orthorhombic unit cell and is indicated by an arrow. The axes of this subcell are parallel to *a*, and at right angles to this direction and ±45° from the projection plane.

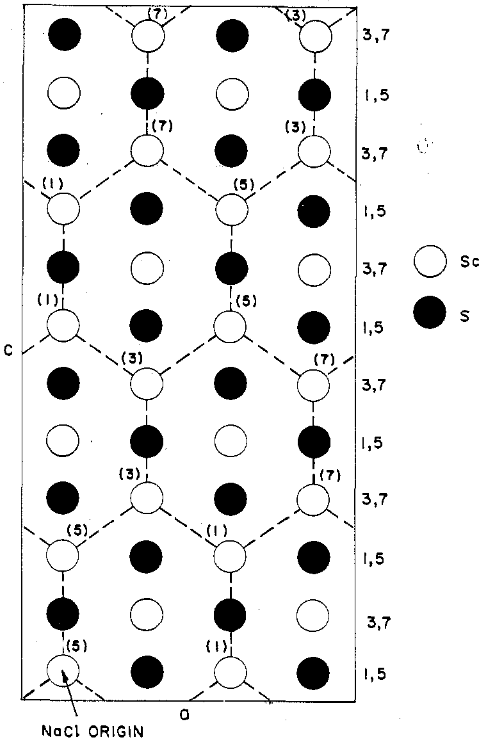

Fig. 5.—The structure of Sc_2S_3 projected down the crystal *b* axis. The numbers alongside each row of atoms are the heights × *b*/8. The numbers in parentheses refer to the cation voids which are joined by dotted lines.

The cation voids are connected by dotted lines. In projection this gives the appearance of a hexagonal network. However, in three dimensions each projection hexagon is an infinite spiral running through the crystal in the *y* direction. The row of spirals centered at a given level of *z* are all of the same hand, while those in the next row are of opposite hand. An alternative way to describe the arrangement of the cation voids is in terms of coplanar, infinite chains lying alternately, proceeding along *c*, in the (110) and $(1\bar{1}0)$ planes. These features can be seen in Fig. 6 which shows a model of one unit cell of the structure with the *a* axis vertical, so that the comparison with one unit cell of the NaCl structure may easily be made.

Since there are two crystallographically independent scandium atoms and two crystallographically independent sulfur atoms in the structure, all the independent bond distances and angles may be calculated by considering the partial or complete octahedron surrounding each of the independent atoms in turn. These data are collected in Table V where the particular atoms considered are designated in parentheses. The numbering system follows the listing of space group positions.[22] For example, for S-II, (1)–(8) are the coordinates listed for the *h* positions, (9)–(16) these coordinates + 0, $^1/_2$, $^1/_2$; (17)–(24) and (25)–(32) the same + $^1/_2$, 0, $^1/_2$ and + $^1/_2$, $^1/_2$, 0, respectively. In each case (1) is the atom with coordinates listed in Table IV.

---

(23) International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, Vol. III, 1962, pp. 202–204.

(24) C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 842 (1955).

(25) D. W. J. Cruickshank, *ibid.*, **2**, 65 (1949).

Table III

Calculated and Observed Values of the Structure Factors for Sc_2S_3 × 0.125

hkℓ	F_c	F_o	hkℓ	F_c	F_o	hkℓ	F_c	F_o	hkℓ	F_c	F_o
400	$\overline{128}$	114	6,0,22	$\overline{1}$	< 4	315	$\overline{18}$	15	7,1,11	$\overline{11}$	10
800	80	82	804	$\overline{10}$	12	317	14	11	7,1,13	$\overline{7}$	6
12,00	$\overline{53}$	54	808	7	7	319	0	< 3	7,1,15	0	< 4
040	$\overline{105}$	108	8,0,12	$\overline{65}$	71	3,1,11	16	18	7,1,17	$\overline{8}$	7
080	57	62	8,0,16	10	10	3,1,13	10	9	7,1,19	4	< 3
004	$\overline{22}$	25	8,0,20	$\overline{3}$	< 4	3,1,15	0	< 4	7,1,21	0	< 3
008	12	12	10,02	8	8	3,1,17	13	11	7,1,23	8	7
00,12	$\overline{104}$	111	10,06	6	7	3,1,19	$\overline{6}$	< 4	911	$\overline{12}$	15
00,16	14	15	10,0,10	3	6	3,1,21	0	< 4	913	0	< 4
00,20	$\overline{3}$	< 6	10,0,14	$\overline{10}$	9	3,1,23	$\overline{10}$	9	915	$\overline{11}$	13
00,24	57	61	10,0,18	$\overline{4}$	4	3,1,25	$\overline{5}$	< 3	917	$\overline{10}$	11
00,28	$\overline{10}$	7	12,04	7	8	3,1,27	0	< 2	919	0	< 4
202	21	17	12,08	$\overline{4}$	5	511	18	20	9,1,11	$\overline{11}$	12
206	8	13	12,0,12	46	47	513	0	< 3	9,1,13	8	9
2,0,10	7	7	111	$\overline{25}$	22	515	17	18	9,1,15	0	< 3
2,0,14	$\overline{17}$	16	113	0	< 2	517	14	14	9,1,17	9	10
2,0,18	$\overline{6}$	6	115	$\overline{22}$	24	519	$\overline{1}$	< 3	9,1,19	6	6
2,0,22	1	< 6	117	$\overline{17}$	18	5,1,11	16	17	11,1,1	$\overline{6}$	5
2,0,26	12	8	119	0	< 3	5,1,13	$\overline{11}$	10	11,1,3	0	< 4
404	16	15	1,1,11	$\overline{18}$	24	5,1,15	0	< 4	11,1,5	$\overline{6}$	5
408	$\overline{10}$	9	1,1,13	12	12	5,1,17	$\overline{11}$	11	11,1,7	5	< 3
4,0,12	89	92	1,1,15	0	< 4	5,1,19	$\overline{7}$	6	11,1,9	0	< 3
4,0,16	$\overline{13}$	12	1,1,17	13	14	5,1,21	1	< 3	11,1,11	7	7
4,0,20	3	< 5	1,1,19	7	7	5,1,23	$\overline{10}$	10	11,1,13	4	< 3
4,0,24	$\overline{51}$	49	1,1,21	$\overline{1}$	< 4	5,1,25	5	4	11,1,15	0	< 2
602	$\overline{13}$	14	1,1,23	11	11	711	11	11	13,1,1	8	10
606	$\overline{4}$	5	1,1,25	$\overline{5}$	4	713	0	< 4	13,1,3	0	< 2
6,0,10	$\overline{5}$	< 5	1,1,27	0	< 2	715	11	10	13,1,5	8	10
6,0,14	13	12	311	$\overline{20}$	15	717	$\overline{9}$	6	022	16	15
6,0,18	5	6	313	0	< 3	719	0	< 4	026	$\overline{128}$	116
02,10	17	18	4,2,24	0	< 4	10,2,10	0	< 5	3,3,17	12	13
02,14	$\overline{6}$	7	4,2,26	$\overline{2}$	< 3	10,2,12	$\overline{5}$	7	3,3,19	$\overline{7}$	< 5
02,18	72	72	620	$\overline{4}$	5	10,2,14	0	< 4	3,3,21	0	< 5
02,22	$\overline{12}$	11	622	0	< 3	10,2,16	1	< 3	3,3,23	$\overline{7}$	6
02,26	1	< 4	624	$\overline{9}$	8	12,2,2	$\overline{5}$	6	3,3,25	3	< 3
220	8	7	626	0	< 4	12,2,4	0	< 4	531	13	12
222	0	< 3	628	13	12	12,2,6	48	47	533	$\overline{1}$	< 6
224	13	12	6,2,10	0	< 6	12,2,8	0	< 3	535	17	18
226	0	< 4	6,2,12	5	6	12,2,10	$\overline{8}$	7	537	$\overline{14}$	14
228	$\overline{18}$	18	6,2,14	0	< 6	131	$\overline{16}$	9	539	0	< 5
2,2,10	0	< 5	6,2,16	1	< 6	133	1	< 5	5,3,11	$\overline{11}$	10
2,2,12	$\overline{4}$	6	6,2,18	0	< 5	135	$\overline{20}$	20	5,3,13	$\overline{8}$	7
2,2,14	0	< 6	6,2,20	$\overline{12}$	10	137	17	16	5,3,15	1	< 6
2,2,16	$\overline{2}$	< 6	6,2,22	0	< 4	139	0	< 6	5,3,17	$\overline{12}$	13
2,2,18	0	< 6	6,2,24	$\overline{4}$	4	1,3,11	13	13	5,3,19	8	7
2,2,20	14	11	822	8	8	1,3,13	9	9	5,3,21	1	< 5
2,2,22	0	< 5	824	0	< 5	1,3,15	0	< 6	5,3,23	8	8
2,2,24	5	5	826	$\overline{72}$	70	1,3,17	14	15	731	$\overline{8}$	< 7
2,2,26	0	< 3	828	0	< 5	1,3,19	$\overline{8}$	8	733	3	< 7
422	$\overline{12}$	11	8,2,10	10	10	1,3,21	0	< 6	735	$\overline{12}$	12
424	0	< 4	8,2,12	0	< 5	1,3,23	$\overline{8}$	8	737	$\overline{9}$	9
426	104	96	8,2,14	0	< 5	1,3,25	$\overline{4}$	< 4	739	0	< 7
428	0	< 4	8,2,16	0	< 5	331	13	10	7,3,11	$\overline{6}$	< 7
4,2,10	$\overline{14}$	14	8,2,18	51	50	333	0	< 3	7,3,13	4	< 6
4,2,12	0	< 5	8,2,20	0	< 3	335	17	16	7,3,15	0	< 6
4,2,14	5	5	10,2,0	6	7	337	15	13	7,3,17	10	10
4,2,16	0	< 6	10,2,2	0	< 6	339	0	< 4	7,3,19	5	< 5
4,2,18	$\overline{65}$	66	10,2,4	5	6	3,3,11	11	10	7,3,21	0	< 4
4,2,20	0	< 5	10,2,6	0	< 5	3,3,13	7	< 6	931	$\overline{9}$	11
4,2,22	11	9	10,2,8	$\overline{9}$	9	3,3,15	0	< 5	933	0	< 4

TABLE III (*Continued*)

hkℓ	F_c	F_o	hkℓ	F_c	F_o	hkℓ	F_c	F_o	hkℓ	F_c	F_o
935	$\overline{13}$	16	2,4,20	0	< 5	844	8	8	351	14	15
937	11	13	2,4,22	$\overline{1}$	< 4	846	0	< 6	353	0	< 5
939	0	< 5	2,4,24	0	< 3	848	$\overline{5}$	6	355	8	< 6
9,3,11	9	11	440	90	92	8,4,10	0	< 6	357	$\overline{7}$	< 6
9,3,13	7	7	442	0	< 4	8,4,12	55	63	359	0	< 6
9,3,15	$\overline{1}$	< 4	444	$\overline{11}$	11	8,4,14	0	< 5	3,5,11	$\overline{13}$	15
9,3,17	10	13	446	0	< 5	8,4,16	$\overline{8}$	9	3,5,13	$\overline{9}$	10
11,3,1	5	< 5	448	7	7	8,4,18	0	< 3	3,5,15	0	< 6
11,3,3	0	< 5	4,4,10	0	< 6	10,4,2	$\overline{7}$	5	3,5,17	$\overline{7}$	< 6
11,3,5	7	7	4,4,12	$\overline{71}$	66	10,4,4	0	< 4	3,5,19	4	< 5
11,3,7	6	6	4,4,14	0	< 6	10,4,6	$\overline{5}$	< 4	3,5,21	0	< 4
11,3,9	0	< 4	4,4,16	11	10	10,4,8	0	< 3	3,5,23	10	10
11,3,11	4	< 4	4,4,18	0	< 5	10,4,10	$\overline{3}$	< 3	551	$\overline{14}$	15
11,3,13	$\overline{3}$	< 3	4,4,20	$\overline{3}$	< 5	10,4,12	0	< 3	553	0	< 6
044	13	13	4,4,22	0	< 4	10,4,14	8	7	555	$\overline{9}$	10
048	$\overline{8}$	8	4,4,24	45	44	12,4,0	45	44	557	$\overline{8}$	7
04,12	79	78	642	10	10	12,4,2	0	< 3	559	0	< 6
04,16	$\overline{12}$	11	644	0	< 7	151	16	17	5,5,11	$\overline{13}$	16
04,20	3	< 6	646	6	< 7	153	0	< 5	5,5,13	9	9
04,24	$\overline{48}$	46	648	0	< 7	155	10	10	5,5,15	0	< 5
242	$\overline{13}$	13	6,4,10	4	< 7	157	8	6	5,5,17	7	8
244	0	< 4	6,4,12	0	< 7	159	0	< 5	5,5,19	5	4
246	$\overline{4}$	< 5	6,4,14	$\overline{11}$	9	1,5,11	15	18	5,5,21	$\overline{1}$	< 3
248	0	< 5	6,4,16	0	< 6	1,5,13	$\overline{10}$	10	751	$\overline{10}$	10
2,4,10	$\overline{5}$	< 5	6,4,18	$\overline{5}$	< 5	1,5,15	0	< 5	753	0	< 7
2,4,12	0	< 5	6,4,20	0	< 4	1,5,17	$\overline{7}$	6	755	$\overline{6}$	< 7
2,4,14	13	11	6,4,22	1	< 3	1,5,19	$\overline{4}$	< 5	757	4	< 6
2,4,16	0	< 5	840	$\overline{66}$	64	1,5,21	1	< 4	759	0	< 6
2,4,18	5	< 5	842	0	< 7	1,5,23	$\overline{10}$	11	7,5,11	10	10
7,5,13	$\overline{7}$	5	462	7	9	173	$\overline{1}$	< 5	779	0	< 3
7,5,15	$\overline{1}$	< 5	464	0	< 7	175	13	16	7,7,11	4	< 3
7,5,17	4	< 4	466	$\overline{66}$	70	177	$\overline{11}$	11	084	$\overline{7}$	< 8
951	11	13	468	0	< 7	179	0	< 5	088	4	< 6
953	0	< 5	4,6,10	9	10	1,7,11	$\overline{6}$	< 5	08,12	49	46
955	7	8	4,6,12	0	< 6	1,7,13	$\overline{4}$	< 4	282	7	8
957	5	7	4,6,14	3	< 6	1,7,15	1	< 3	284	0	< 4
959	$\overline{1}$	< 4	4,6,16	0	< 5	1,7,17	$\overline{11}$	13	286	$\overline{5}$	< 4
9,5,11	10	12	4,6,18	48	50	371	$\overline{5}$	< 6	288	0	< 4
9,5,13	$\overline{8}$	9	4,6,20	0	< 3	373	$\overline{1}$	< 6	2,8,10	3	< 3
11,5,1	7	6	660	6	6	375	$\overline{11}$	12	2,8,12	0	< 3
11,5,3	0	< 2	662	0	< 6	377	$\overline{10}$	10	2,8,14	$\overline{8}$	7
11,5,5	4	< 2	664	7	7	379	0	< 6	480	$\overline{52}$	50
062	$\overline{8}$	8	666	0	< 5	3,7,11	$\overline{5}$	< 6	482	0	< 5
066	72	70	668	$\overline{9}$	9	3,7,13	4	< 5	484	6	7
06,10	$\overline{11}$	11	6,6,10	0	< 5	3,7,15	0	< 4	486	0	< 4
06,14	4	< 5	6,6,12	$\overline{5}$	5	3,7,17	10	12	488	$\overline{4}$	5
06,18	$\overline{52}$	52	6,6,14	0	< 4	571	$\overline{6}$	6	4,8,10	0	< 3
260	$\overline{5}$	< 6	6,6,16	$\overline{1}$	< 4	573	1	< 5	4,8,12	45	45
262	0	< 6	862	$\overline{6}$	5	575	$\overline{12}$	17	682	$\overline{6}$	6
264	$\overline{7}$	8	864	0	< 5	577	10	13	684	0	< 3
266	0	< 6	866	52	52	579	0	< 5	686	$\overline{4}$	4
268	11	10	868	0	< 4	5,7,11	6	6	688	0	< 2
2,6,10	0	< 6	8,6,10	$\overline{7}$	7	5,7,13	4	< 4	191	$\overline{11}$	11
2,6,12	4	< 6	8,6,12	0	< 3	5,7,15	$\overline{1}$	< 3	193	$\overline{2}$	< 4
2,6,14	0	< 6	10,6,0	$\overline{5}$	4	771	4	< 5	195	$\overline{4}$	< 4
2,6,16	1	< 5	10,6,2	0	< 3	773	1	< 5	197	$\overline{6}$	< 4
2,6,18	0	< 4	10,6,4	$\overline{4}$	4	775	9	11	391	$\overline{9}$	9
2,6,20	$\overline{13}$	8	171	6	< 6	777	7	8	393	0	< 2

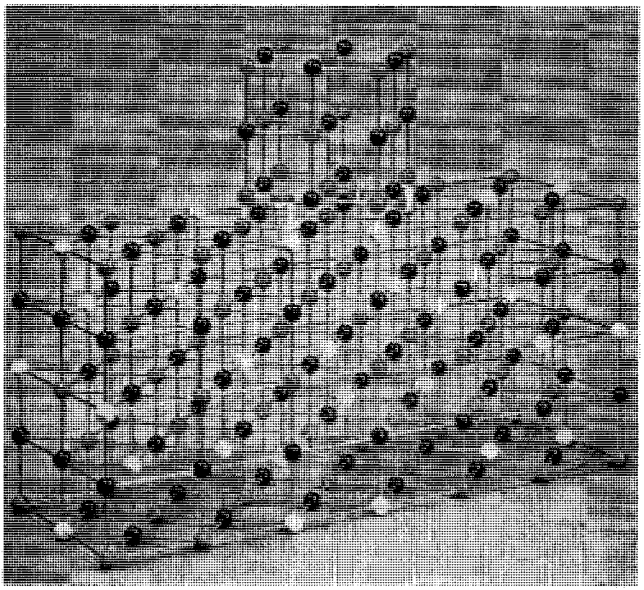

Fig. 6.—Crystal model of one unit cell of Sc_2S_3 with *a* vertical. The gray balls represent scandium atoms, the black balls sulfur atoms, and the white balls cation voids. For direct comparison a unit cell of sodium chloride has been placed on top in the corresponding orientation.

Table IV

Coordinates of the Atoms in Sc_2S_3

Atom	x	y	z	σ, Å.
Sc-I	0.1250	0.1250	0.0408	0.003_3
Sc-II	0.1250	0.1250	0.3761	0.003_5
S-I	0.1250	0.3697	0.1250	0.004_1
S-II	0.1231	0.3783	0.4561	0.007_0

Nonstoichiometric Scandium Sesquisulfide, $Sc_{1.37}S_2$.—The X-ray powder pattern of the black, electrically conducting scandium sulfide is much simpler than that of Sc_2S_3. The strongest lines again fit a NaCl-type structure, but there are weak additional lines. This pattern can be indexed on the basis of a rhombohedral unit cell with $a_r = 6.33_1$ Å., $\alpha = 33° 34'$, or $a_h = 3.65_7$ Å., $c_h = 17.91$ Å., referred to the triply primitive hexagonal unit cell. Since $a_h = 1/\sqrt{2} \times 5.17$ and $c_h = 2/\sqrt{3} \times 5.17$, the volume of the rhombohedral cell is one twenty-fourth of the unit cell of Sc_2S_3. As it is very probable that the close-packed structure of the sulfur atoms remains intact and that the sulfur deficiency is therefore actually a scandium excess, the contents of the unit cell can be formulated from the chemical analysis as $Sc_{1.37\pm0.02}S_2$. Since no sulfur analysis was carried out, there is some uncertainty in the exact deviation from the sesquisulfide stoichiometry.

The closest relation to the NaCl structure is obtained by placing the atoms in the following positions of the space group $R\bar{3}m$: 1 Sc in (a) 0, 0, 0; 0.37 Sc in (b) $^1/_2$, $^1/_2$, $^1/_2$; 2 S in (c) $\pm x, x, x$ with $x = 0.25$. This type of structure is well known for the case where different cations occupy the (a) and (b) positions; *e.g.*, one phase of $AgBiSe_2$[26] and the only known phase of $TlSbTe_2$.[27] Intensities calculated for this postulated structure show very good qualitative agreement with those actually observed (Table VI). Clearly this must be at least a close approximation to the structure, but the powder data are quite limited. Without single crystal measurements it is not certain that small distortions to lower symmetry may not be present.

Table V

Bond Distances and Angles for Sc_2S_3

Atoms	Bond distance, Å.	Atoms	Bond angle, deg.
Octahedron Surrounding Sc-I(11)			
Sc-I(11)–S-II(25)	2.58_4	S-II(29)–Sc-I(11)–S-II(8)	88.6
Sc-I(11)–S-II(4)		S-I(16)–Sc-I(11)–S-I(15)	88.5
Sc-I(11)–S-II(29)	2.61_0	S-I(15)–Sc-I(11)–S-II(8)	91.6
Sc-I(11)–S-II(8)		S-I(16)–Sc-I(11)–S-II(29)	
Sc-I(11)–S-I(16)	2.59_1	S-II(25)–Sc-I(11)–S-II(8)	91.9
Sc-I(11)–S-I(15)		S-II(4)–Sc-I(11)–S-II(29)	
		S-II(25)–Sc-I(11)–S-II(29)	90.3
		S-II(4)–Sc-I(11)–S-II(8)	
		S-II(25)–Sc-I(11)–S-I(16)	88.5
		S-II(4)–Sc-I(11)–S-I(15)	
		S-II(25)–Sc-I(11)–S-I(15)	89.3
		S-II(4)–Sc-I(11)–S-I(16)	
Octahedron Surrounding Sc-II(16)			
Sc-II(16)–S-I(1)	2.60_2	S-II(22)–Sc-II(16)–S-II(15)	93.4
Sc-II(16)–S-I(10)		S-II(16)–Sc-II(16)–S-II(21)	90.3
Sc-II(16)–S-II(16)	2.57_0	S-II(15)–Sc-II(16)–S-II(16)	88.2
Sc-II(16)–S-II(21)		S-II(21)–Sc-II(16)–S-II(22)	
Sc-II(16)–S-II(22)	2.57_2	S-I(1)–Sc-II(16)–S-II(15)	89.3
Sc-II(16)–S-II(15)		S-I(10)–Sc-II(16)–S-II(22)	
		S-I(1)–Sc-II(16)–S-II(16)	88.6
		S-I(10)–Sc-II(16)–S-II(21)	
		S-I(1)–Sc-II(16)–S-II(21)	90.7
		S-I(10)–Sc-II(16)–S-II(16)	
		S-I(1)–Sc-II(16)–S-II(22)	91.4
		S-I(10)–Sc-II(16)–S-II(15)	
Incomplete Octahedron Surrounding S-I(15)			
S-I(15)–Sc-II(13)	2.60_2	Sc-I(11)–S-I(15)–Sc-I(12)	91.5
S-I(15)–Sc-II(6)		Sc-I(11)–S-I(15)–Sc-II(6)	91.0
S-I(15)–Sc-I(11)	2.59_1	Sc-II(13)–S-I(15)–Sc-I(12)	
S-I(15)–Sc-I(12)		Sc-I(12)–S-I(15)–Sc-II(6)	90.2
		Sc-II(13)–S-I(15)–Sc-I(11)	
Incomplete Octahedron Surrounding S-II(8)			
S-II(8)–Sc-I(5)	2.58_4	Sc-II(12)–S-II(8)–Sc-II(15)	91.8
S-II(8)–Sc-II(12)	2.57_0	Sc-I(5)–S-II(8)–Sc-II(15)	91.1
S-II(8)–Sc-II(15)	2.57_2	Sc-I(11)–S-II(8)–Sc-I(5)	89.7
S-II(8)–Sc-I(11)	2.61_0	Sc-I(5)–S-II(8)–Sc-II(12)	91.9
		Sc-II(12)–S-II(8)–Sc-I(11)	90.6

The rhombohedral cell dimensions are extremely close to the "ideal" values derived from a face-centered cubic unit cell without distortion on lowering of the symmetry to rhombohedral. Only one observed diffraction line, that at the highest Bragg angle, shows a broadening, probably due to a very slight rhombohedral splitting of separate reflections. The discrepancy in the calculated intensity of the unobserved line calculated at 0.789 Å. is probably due to a lowering of the peak maximum to background level by a small spreading out of the three component reflections.

Scandium Monosulfide, ScS.—Weissenberg photographs were taken of a small single crystal of ScS. The pattern was that of a NaCl-type structure with lattice constant 5.19 Å. The powder pattern of bulk material showed a slight broadening in the back reflection region probably due to a slight inhomogeneity in composition. The measured density, 3.59 ± 0.14 g. cm.$^{-3}$, agrees with the X-ray density, 3.66 g. cm.$^{-3}$, to within the accuracy of the determination.

---

(26) S. Geller and J. H. Wernick, *Acta Cryst.*, **12**, 46 (1959).
(27) E. F. Hockings and J. G. White, *ibid.*, **14**, 328 (1961).

TABLE VI

CALCULATED AND OBSERVED LATTICE SPACINGS AND INTENSITIES FOR $Sc_{1.37}S_2$

Hexagonal indices (Cu Kα radiation)

hkl	d_{calcd}	d_{obsd}	I_{calcd} ($\times 10^{-3}$)	I_{obsd}[a]
003	5.97	5.96	36	w+
101	3.12	3.11	21	w
006; 012	2.98	...	1	...
104	2.59	2.58	248	vs
015	2.37	2.37	7	vw
107; 009	1.989	1.985	6	vw
018; 110	1.828	1.826	151	s
113	1.749	1.747	7	vw
021	1.577	1.575	2	vvw
1,0,10; 116; 202	1.552	...	0	...
024; 00,12	1.492	1.491	48	m
205; 01,11	1.448	1.445	3	vvw
027; 119	1.346	1.344	4	vvw
208	1.293	1.290	22	w+
1,0,13	1.261	...	1	...
211; 00,15	1.192	...	2	...
01,14; 122; 02,10	1.184	...	0	...
214; 1,1,12	1.155	1.154	64	m
125; 2,0,11	1.135	1.132	2	vvw
217	1.082	...	1	...
1,0,16; 128; 300	1.056	1.055	52	m
02,13; 303	1.037	...	2	...
1,1,15; 01,17	0.999	0.999	2	vvw
00,18; 2,0,14; 306; 2,1,10	0.993	...	0	...
1,2,11	0.963	...	1	...
309	0.931	...	1	...
220; 02,16	0.914	0.914	25	w
1,0,19; 2,1,13; 223	0.902	...	2	...
2,0,17; 321	0.875	...	2	...
1,1,18; 1,2,14; 232; 226	0.872	...	1	...
324; 01,20; 3,0,12	0.862	0.862	71	m
00,21; 235	0.851	...	2	...
229; 327	0.829	...	3	...
2,1,16; 238	0.817	0.817	73	m
02,19	0.808	...	1	...
1,2,17; 3,0,15; 401	0.789	...	6	...
1,0,22; 3,2,10; 042	0.787	...	1	...
2,0,20; 404; 2,2,12	0.780	0.780	153	m+ (br)

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; vvw, very very weak.

Discussion

Crystal Structures.—The measured density, 2.897 g. cm.$^{-3}$, of Sc_2S_3 is in good agreement not only with the X-ray density, 2.917 g. cm.$^{-3}$, but also with Klemm's[2] measured density, 2.890 g. cm.$^{-3}$. Contrary to Hahn's description[4] and the conclusions of Men'kov, *et al.*,[3] we have found that the cation voids in Sc_2S_3 are ordered, not disordered.

The arrangement of the cation voids in Sc_2S_3 described above is a very complex one. In every sulfur-centered "octahedron" two and only two of the vertices are empty. This would seem to be the result of the principle of local neutralization of charge, for if any octahedra were complete or missing only one cation, others would necessarily be more than one-third deficient. The most remarkable feature of such a cation-deficient structure is the constancy of the bond angles. The average deviation of all the bond angles from 90° is only 1.2°. For the bond angles of the sulfur atoms, which are surrounded by incomplete octahedra, the deviations are systematically toward angles greater than 90°, thus, the bond angles of the groups surrounding S-I and S-II average 90.8 and 91.0°, respectively.

The constancy of the bond angles, even though one-third of the cations are missing as compared with the NaCl structure, is indicative of a high degree of ionic character. The average scandium–sulfur bond distance is 2.59 Å., and the sulfur–sulfur nearest neighbor distances are all close to $2.59\sqrt{2} = 3.66$ Å., in good agreement with twice Pauling's ionic radius for S^{2-}, 3.68 Å.[28] The sulfur atoms are close packed, and thus the effective radius for Sc^{3+} in this structure is $2.59 - 1.83 = 0.76$ Å. This value may be compared with the calculated Pauling radius[28] of 0.81 Å. and an empirical value of 0.73 Å. obtained by multiplying the lattice parameter of Sc_2O_3 by 0.21441 and subtracting the oxide ion radius, 1.38 Å.[29] The cation to anion radius ratio, 0.416, is almost identical with the instability ratio,[28] 0.414, for transition between sixfold and fourfold coordination. This fact suggests that Sc_2S_3 may form extensive solid solutions with sulfides having the zinc blende structure, such as ZnS and CdS. Furthermore, it is possible that a tetrahedral modification of Sc_2S_3 may exist.

The three-dimensional network of the cation voids has no very pronounced directional concentration. Therefore, we might expect that bulk physical properties, which would be influenced by the existence of these voids, will not be markedly anisotropic in these crystals. Sufficiently large crystals have not yet been prepared to check this experimentally.

It would seem possible that a continuous range of composition might exist between the Sc_2S_3 and the ScS structures. This would be similar to the situation in the system $CoTe_2$–CoTe[30] where a continuous range exists between the CdI_2-type and the NiAs-type structures. However, the structure actually found for $Sc_{1.37}S_2$ requires a discontinuity between Sc_2S_3 and this composition. The structure of $Sc_{1.37}S_2$ is a partially disordered cation-deficient NaCl structure and this structure could exist continuously over the range to ScS by filling the partially occupied cation sites.

If we consider that the region between Sc_2S_3 and ScS consists of Sc^{3+} and Sc^{2+} ions coexisting in the same crystal, then the general formula, $Sc_{2+x}S_3$, can be written $Sc^{III}{}_{2-2x}Sc^{II}{}_{3x}S^{II-}{}_3$. No experimental value is available for the ionic radius of Sc^{2+}. However, by comparing the empirical divalent and trivalent radii of Ti, V, and Cr,[28] we might expect the Sc^{II}–S bond distance to be about 0.13 Å. longer than the Sc^{III}–S bond distance, 2.6 Å. Thus, if all the scandium atoms in ScS are divalent, the lattice constant would be about 5.47 Å. In fact the equivalent lattice constants, calculated by taking the cube root of volumes

---

(28) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, Chapter 13.

(29) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5237 (1954).

(30) S. Tengner, *Z. anorg. allgem. Chem.*, **239**, 126 (1938).

containing equal numbers of sulfur atoms, are about 0.5% smaller in $Sc_{1.37}S_2$ and ScS than in Sc_2S_3. The structural data suggest that the electronic distribution on all the scandium ions is equivalent. The simplest formula for the scandium-rich phases thus becomes $Sc^{III}{}_{2+x}(e^-)_{3x}S^{II-}{}_3$, in which (e^-) represents a delocalized electron participating in metal–metal bonding.

Electrical Properties of Nonstoichiometric Scandium Sesquisulfide.—The sulfur-deficient compound $Sc_{1.37}S_2$ discussed above shows a metallic-type temperature dependence of Q and ρ (Fig. 4) between 300 and 850°K., and the conductivity is n-type as determined from the sign of the thermoelectric power. An estimate of the charge carrier mobility at 300°K., taking for the charge carrier concentration the value 1.5×10^{21} cm.$^{-3}$ calculated from the stoichiometry, is $\mu = 14$ cm.^{2} v.$^{-1}$ sec.$^{-1}$. A more detailed investigation of the electrical transport properties would be required to decide unambiguously between conduction by divalent scandium ions involving an activated hopping model and conduction by electrons involving a band model. The order of magnitude of the mobility, the temperature dependence of the thermoelectric power and resistivity, and the structural data discussed above suggest that conduction is by electrons in a 3d band. Such an interpretation is reasonable, since the overlap of 3d wave functions in the first transition series is largest for scandium.[31] Determination of magnetic susceptibility as a function of temperature would be extremely valuable in determining the valence of scandium and thus the conduction mechanism.

Acknowledgments.—We thank K. L. Cheng and B. Goydish for chemical analyses, H. H. Whitaker for spectrographic analyses, R. J. Paff for X-ray powder diffraction data, J. L. Cooper and M. Allen for preparative work and experimental measurements, P. Sahm for the melting point determination, H. Hyman of the RCA Semiconductor and Materials Division, Somerville, N. J., for oxygen and carbon analyses, and Mrs. D. Garrison for processing the crystallographic computations. The research reported in this paper was sponsored by the U. S. Department of the Navy, Bureau of Ships, under Contract Number Nobs 84660, and RCA Laboratories, Princeton, N. J.

[31] N. B. Hannay, "Semiconductors," Reinhold Publishing Corp., New York, N. Y., 1959, Chapter 14.

Contribution from the Department of Chemistry,
University of Aberdeen, Old Aberdeen, Scotland

The Preparation and Crystal Data of the Cadmium Silicates $CdSiO_3$, Cd_2SiO_4, and Cd_3SiO_5

By L. S. DENT GLASSER and F. P. GLASSER

Received March 5, 1964

Three compounds of CdO and SiO_2 exist stably over the temperature range 800–1200° (approximately): $CdSiO_3$, Cd_2SiO_4, and Cd_3SiO_5. These compounds are structurally related to $CaSiO_3$, Na_2SO_4(V), and Ca_3SiO_5, respectively.

Introduction

Although cadmium silicates are of technical interest because of their properties as phosphors, no systematic study of the CdO–SiO_2 system has been reported. $CdSiO_3$ and Cd_2SiO_4 have been prepared by melting CdO and SiO_2,[1] but because of the volatility of CdO it is difficult to prepare pure compounds. The melting points of $CdSiO_3$ and Cd_2SiO_4 were reported as 1241 ± 5° and 1243 ± 1°, respectively, and it was suggested that the latter might be isomorphous with willemite (α-Zn_2SiO_4). Cd_2SiO_4 has also been prepared in autoclaves.[2] There are numerous other scattered references to compounds of CdO and SiO_2, mostly with few preparative details; no structural work appears to have been done.

Experimental

A series of "gels" was prepared containing 20.0, 25.0, 30.0, 33.3, 40.0, 50.0, 60.0, and 80.0 mole % SiO_2. Starting materials were Analar $Cd(NO_3)_2\cdot 4H_2O$ and colloidal silica (Syton). To each weighed portion of cadmium nitrate the calculated volume of Syton was added, and the mixture was heated gently to drive off water. Ignition at 500° decomposed the nitrate, and the product was shown by X-ray powder photographs to be essentially amorphous.

Several series of heating experiments were made to overcome the problem of CdO loss. Runs were made in gold or platinum envelopes, weighing the envelope and contents before and after each heating in order to determine the CdO loss, and hence the final composition. It was found that loss of CdO from higher temperature runs (>1000°) could be minimized by first allowing the sample to react at 700–800°. Loss of excess CdO from the surface of sintered samples could be controlled by packing the envelopes at the bottom of a larger envelope or crucible filled with CdO.

Results

Phase Relations.—Three binary compounds were detected: $CdSiO_3$, Cd_2SiO_4, and Cd_3SiO_5. The congruent melting points of the first two are 1285 ± 10° and 1270 ± 10°, respectively. The $CdSiO_3$–Cd_2SiO_4 eutectic temperature is 1180 ± 10°. These data and the relatively high volatility of CdO from "open"

---

[1] F. M. Jaeger and van Klooster, *Verslag. Akad. Amsterdam*, **24**, 921 (1915).

[2] C. J. van Nieuwenburg and H. B. Blumendal, *Rec. trav. chim.*, **50**, 989 (1931).