CRUICKSHANK, D. W. J. & ROBERTSON, A. P. (1953). *Acta Cryst.* **6**, 698.
IBERS, J. A. (1957). *Acta Cryst.* **10**, 86.
International Tables for X-ray Crystallography (1952). Vol. 1. Birmingham: Kynoch Press.
KJEKSHUS, A. & PEDERSEN, G. (1961). *Acta Cryst.* **14**, 1065.
OFTEDAL, I. (1928). *Z. Kristallogr.* **66**, 517.
PAULING, L. (1960). *The Nature of the Chemical Bond.* 3rd Edition. Ithaca: Cornell University Press.
ROSENQVIST, T. (1953). *Acta Met.* **1**, 761.
SANDS, D. E., JOHNSON, Q. C., ZALKIN, A., KRIKORIAN, O. H. & KROMHOLTZ, K. L. (1962). *Acta Cryst.* **15**, 832.
SANDS, D. E., ZALKIN, A. & KRIKORIAN, O. H. (1959). *Acta Cryst.* **12**, 461.
THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.
ZALKIN, A., SANDS, D. E. & KRIKORIAN, O. H. (1959). *Acta Cryst.* **12**, 713.
ZHURAVLEV, N. N. & ZHDANOV, G. S. (1956). *Kristallografiya*, **1**, 509.

Acta Cryst. (1962). **15**, 1195

Refinement of the Crystal Structure of Co_9S_8

BY S. GELLER

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.

(*Received* 1 *March* 1962)

The structure of Co_9S_8 has been refined in space group O_h^5–$Fm3m$ by the least-squares technique applied to selected single-crystal data. The lattice constant of Co_9S_8 is $9{\cdot}928 \pm 0{\cdot}001$ Å and there are four Co_9S_8 in the unit cell. There are two kinds of cobalt atoms in the structure: one is surrounded by a regular octahedron of sulfur atoms with Co–S distance, $2{\cdot}39 \pm 0{\cdot}03$ Å; the other is surrounded by a tetrahedron of S atoms, one Co–S distance being $2{\cdot}13 \pm 0{\cdot}02$ Å, and the other three being $2{\cdot}21 \pm 0{\cdot}02$ Å. Each of the cobalt atoms with tetrahedral sulfur coordination is also linked to three similarly coordinated cobalt atoms at a distance of $2{\cdot}50 \pm 0{\cdot}02$ Å which is essentially the Co–Co distance in the elementary cobalts. Some comparison is made with the Rh–S coordination in $Rh_{17}S_{15}$ and it is tentatively concluded that an anomaly exists in the apparent sizes of the *octahedrally* coordinated metal atoms.

Introduction

The crystal structure of Co_9S_8 was solved by Lindqvist, Lundqvist & Westgren (1936) from powder data. In their paper, Lindqvist *et al.* point out that several authors had proposed erroneous formulas for this compound or its isomorph pentlandite, ($(Ni,Fe)_9S_8$). Also Alsén (1925), assuming a formula of (Ni, Fe)S for pentlandite, had proposed an apparently erroneous structure.

As was pointed out in a recent paper on the structure of $Pd_{17}Se_{15}$ (Geller, 1962*a*), the interest in Co_9S_8 resulted from the possibility of a close relationship of its structure to that of the isostructural $Pd_{17}Se_{15}$ and $Rh_{17}S_{15}$ crystals. This was particularly so because of the reported (Juza *et al.*, 1935) formula, Rh_9S_8, for the latter compound. Because of some difficulty with the solution of the structures of $Pd_{17}Se_{15}$ and $Rh_{17}S_{15}$, it was decided to check the Co_9S_8 structure with single-crystal data. The single-crystal material used in this analysis was very kindly given to us by Dr J. R. Stubbles*; it had resulted from his investigations on self-diffusion in Co_9S_8.

In our study of the single-crystal data from Co_9S_8, concluded that the structure proposed by Lindqvist *et al.* was essentially correct. The refinement, however, gives a substantially different viewpoint on the Co–S interatomic distances.

Experimental

A slightly imperfect sphere of average diameter 0·28 mm. was made from the single-crystal material with the Bond (1951) sphere grinder. The crystal was aligned along [100] as rotation axis and a set of Weissenberg photographs* taken with Mo $K\alpha$ radiation, for which the absorption coefficient, $\mu = 164{\cdot}0$ cm.$^{-1}$, $\mu R = 2{\cdot}3$. A set of precession-camera photographs was also taken with Mo $K\alpha$ radiation and [100] as precession axis. However only $hk0$ and $hk1$ intensities from the Weissenberg photographs (50 and 24 hr. exposures respectively) were estimated visually, by comparison with a calibrated intensity strip.

The diffraction symmetry of the crystal is $m3m$ with reflections hkl present only when $h+k$ and $k+l$ are even. There are no further systematic absences. Thus the probable space groups are: O_h^5–$Fm3m$, T_d^2–$F\bar{4}3m$ or O^3–$F432$.

---

* Now at the University of Manchester, England.

* Customarily, when using Mo $K\alpha$ radiation, the author uses a three film pack with sheets of Cu foil interleaved resulting in a film:film intensity ratio of approximately 4:1.

Table 1. *Final values of parameters*

Atom	Position	x	y	z	B	$\sigma(x)$	$\sigma(B)$
Co	4*b*	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0·55 Å^2		0·21 Å^2
Co	32*f*	0·1260	0·1260	0·1260	0·39	0·0003	0·03
S	8*c*	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·07		0·25
S	24*e*	0	0	0·2591	0·17	0·0011	0·11

The lattice constant, 9·928 ± 0·001 Å, in good agreement with the value 9·927 Å (converted from 9·907 kX. units) reported by Lindqvist *et al.* (1936), was obtained from a powder photograph taken with a Norelco Straumanis-type camera of 114·59 mm. diameter; Co $K\alpha$ radiation was used. The cell volume is 978·56 Å^3 and with four Co_9S_8 per unit cell, the X-ray density is 5·34 g.cm.$^{-3}$.

Lorentz-polarization and absorption corrections were applied to the visually estimated single-crystal intensities, the latter by means of the table for spherical crystals given by Bond (1959). The appropriate data were used to calculate* (001) Patterson and electron-density projections and the analogous $l = 1$ generalized projections. These had a twofold purpose: (1) they were compared with analogous projections of $Pd_{17}Se_{15}$ and $Rh_{17}S_{15}$ to determine what, if any, similarities there were between the two structures (this was done mainly to aid in the structure solution of the latter two compounds, Geller, 1962*a*); (2) to corroborate the structure of Lindqvist *et al.*

Refinement of the structure

Although the most probable space group of Co_9S_8 is not necessarity the centrosymmetric one, $Fm3m$, (Geller, 1962*a*) the structure was refined in this space group, in which the atoms of Co_9S_8 are situated as follows: 4 Co in *b*, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; 32 Co in *f*, $\pm(xxx, x\bar{x}\bar{x}, \circlearrowleft)$; 8 S in *c*, $\pm\frac{1}{4}\frac{1}{4}\frac{1}{4}$; and 24 S in *e*, $\pm(x00, \circlearrowleft)$; all plus face centering. Thus there are two positional parameters to be refined. No attempt was made to refine anisotropic thermal parameters; it was found that the isotropic temperature factors were *very* sensitive to observational errors. This was also noticed in the refinement of the $Pd_{17}Se_{15}$ (Geller, 1962*a*) and the $Rh_{17}S_{15}$ (Geller, 1962*b*) structures.

Refinement was carried out using the IBM 704 Busing–Levy (1959) least-squares program adapted to the IBM 7090 with a compatibility program. In the first least-squares cycle all amplitudes for reflections actually observed were given unit weight while those of reflections too weak to be observed were given zero weight. The Co x-parameter was taken initially as 0·126 and that of S as 0·252. The thermal parameters for the Co atoms in both *a* and *f* were taken initially as 0·10 Å^2 and those of all S atoms, 0·20 Å^2. In the calculation of structure amplitudes the atomic scattering factors used for Co were those of Thomas & Umeda (1957) and, for sulfur, those of Dawson (1960). The real part of the dispersion correction (Dauben & Templeton, 1955) was applied to the Co scattering factors. At the end of the first least squares cycle the calculated correction to x_{Co} was $+0{\cdot}00003$ and that to x_S was $+0{\cdot}0078$ leading to $x_S = 0{\cdot}2593$. The thermal parameter of S in *e* became $-0{\cdot}05$ Å^2.

In all, six iterations were carried out. In the final four iterations all reflections for which $|\Delta F| \geq 50$ were given zero weight. The total number of amplitudes used to refine the parameters was then 56. Including two scale factors, one for each of the Weissenberg levels, there were eight parameters. The final values of the scale factors were 1·038 and 0·960 for the zeroth and first layers respectively with σ's 0·017 and 0·023 respectively. The remaining values of parameters and their standard deviations are given in Table 1.

Table 2. *Observed and calculated structure factors*

hk0				hk0				hk1			
h	k	F_o	F_c	h	k	F_o	F_c	h	k	F_o	F_c
2	0	87	90	12	6	< 50	15	3	1	311	-333
4	0	211	-224	14	6	< 50	41	5	1	319	-302
6	0	90	91	16	6	< 52	20	7	1	129	136
8	0	725	744	18	6	< 52	32	9	1	< 70	51
10	0	< 43	30	20	6	< 52	- 2	11	1	125	-144
12	0	104	-100	22	6	< 46	27	13	1	181	-160
14	0	87	66	24	6	< 39	2	15	1	92	89
16	0	420	372	26	6	< 27	20	17	1	< 89	11
18	0	< 52	13	8	8	595	564	3	3	240	178
20	0	67	- 60	10	8	< 48	18	5	3	103	111
22	0	< 48	46	12	8	51	- 82	7	3	236	-199
24	0	176	175	14	8	51	51	9	3	207	-201
26	0	< 31	6	16	8	386	312	11	3	125	122
2	2	87	93	18	8	< 52	8	13	3	< 83	36
4	2	85	84	20	8	48	- 55	15	3	71	- 88
6	2	70	69	22	8	< 43	38	17	3	89	-108
8	2	39	42	24	8	146	154	5	5	62	61
10	2	56	54	10	10	< 50	44	7	5	280	-200
12	2	< 48	30	12	10	< 52	38	9	5	271	-205
14	2	< 50	42	14	10	< 52	35	11	5	102	89
16	2	< 52	9	16	10	< 52	2	13	5	< 83	11
18	2	< 52	34	18	10	< 52	31	15	5	87	- 95
20	2	< 52	5	20	10	< 46	13	17	5	90	-114
22	2	< 48	27	22	10	< 42	24	7	7	204	139
24	2	< 40	- 4	24	10	< 31	- 6	9	7	76	68
26	2	< 31	22	12	12	394	340	11	7	115	-106
4	4	773	921	14	12	< 52	6	13	7	139	-125
6	4	37	43	16	12	74	- 61	15	7	89	97
8	4	157	-142	18	12	< 48	35	17	7	< 89	26
10	4	58	71	20	12	164	186	9	9	< 81	12
12	4	502	501	22	12	< 31	3	11	9	108	-120
14	4	< 51	17	24	12	32	- 39	13	9	142	-137
16	4	66	- 72	14	14	< 52	33	15	9	< 90	56
18	4	< 53	53	16	14	< 51	25	11	11	86	107
20	4	266	246	18	14	< 46	26				
22	4	< 48	8	20	14	< 39	- 4				
24	4	48	- 46	22	14	< 31	24				
26	4	< 29	35	16	16	213	199				
6	6	66	60	18	16	< 40	0				
8	6	48	57	20	16	47	- 43				
10	6	53	48								

It is seen that there was no significant difference in the values of the two positional parameters obtained in the first and last cycles. There were changes in the

---

* In all of these calculations, IBM 704 programs by R. G. Treuting were used.

temperature factors and these, as indicated earlier, were very sensitive to the removal from the calculation of the several amplitudes for which $|\Delta F| \geq 50$. Also the standard deviations indicate that perhaps only the thermal parameter of Co in *f* is meaningful. It is particularly unlikely that the S temperature factors would actually be smaller than those of Co.

Observed and calculated amplitudes are listed in Table 2. The positional parameters used in the calculations were those listed in Table 1, but the temperature factors, in Table 1 order were: 0·562, 0·387, 0·164 and 0·164 Å^2 respectively. The discrepancy factor, including consideration of multiplicity, is 0·13.

Discussion of the structure

The interatomic distances in Co_9S_8 are given in Table 3. Fig. 1, like that of Lindqvist *et al.* gives the arrangement of atoms in two octants of the unit cell.* The one difference between the two figures, which may perhaps be noticed, is the arrangement of the S atoms in *e*. Lindqvist *et al.* had arrived at a value of $\frac{1}{4}$ for the parameter of these atoms as opposed to the more accurate value of 0·259 given here. The *x*-parameter, 0·126, of the Co atom obtained in the present work, however, is not very different from the $\frac{1}{8}$ reported by the previous authors.

Table 3. *Interatomic distances and standard errors*

Atom	Neighbors	Distance	σ
Co(*b*)	6 S(*e*)	2·392 Å	0·011 Å
Co(*f*)	1 S(*c*)	2·132	0·005
	3 S(*e*)	2·208	0·008
	3 Co(*f*)	2·501	0·006
	3 Co(*f*)	3·481	0·008
S(*c*)	4 Co(*f*)	2·132	0·005
	12 S(*e*)	3·511	0·000
S(*e*)	1 Co(*b*)	2·392	0·011
	4 Co(*f*)	2·208	0·008
	4 S(*e*)	3·382	0·015
	4 S(*e*)	3·512	0·015
	4 S(*c*)	3·511	0·000

In Co_9S_8 each Co atom in *b* is surrounded by a regular octahedron of S(*e*) atoms at 2·39 Å (as against 2·48 Å reported by Lindqvist *et al.*). Each Co atom in *f* is surrounded by a tetrahedron of S atoms: 1 S(*c*) at 2·13 Å and 3 S(*e*) at 2·21 Å (as against 2·14 Å for all, found by Lindqvist *et al.*). The Co(*f*) atoms lie at corners of cubes centered at positions 4*a* and with cube edge, 2·50 Å. Thus, in addition to the tetrahedral coordination to S atoms, each Co(*f*) atom is coordinated to three Co(*f*) atoms at 2·50 Å. This distance is slightly less than the Co–Co distance, 2·506 Å, in elementary cubic cobalt, (Taylor & Floyd, 1950); in hexagonal cobalt, there are two Co–Co distances, 2·507 and 2·495 Å (Taylor & Floyd, 1950).

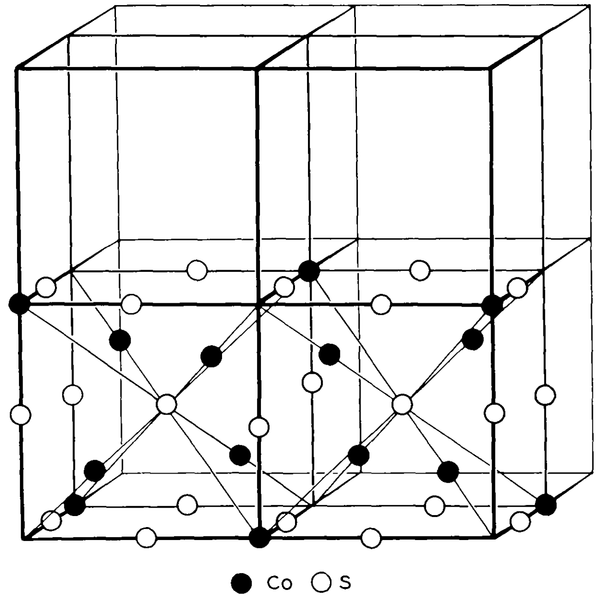

Fig. 1. The arrangement of atoms in Co_9S_8. Atoms in only two octants are shown (after Lindqvist *et al.*).

The three Co(*f*)–Co(*f*) bonds about a Co(*f*) atom are relatively stronger than the analogous Rh(*m*)–Rh(*m*) and Pd(*m*)–Pd(*m*) bonds in $Rh_{17}S_{15}$ and $Pd_{17}Se_{15}$ respectively (Geller, 1962*b*, *a*). The relations are shown in Table 4.

Table 4. *Values of analogous metal–metal distances in* Co_9S_8, $Rh_{17}S_{15}$ *and* $Pd_{17}Se_{15}$ *compared with elementary distances*

Compound	Average metal–metal distance	Distance, in elementary metal
Co_9S_8	2·50 Å	2·51 Å
$Rh_{17}S_{15}$	2·85	2·69
$Pd_{17}Se_{15}$	3·15	2·75

An S atom in *c* is at the center of a regular tetrahedron of Co(*f*) atoms. An S atom in *e* is coordinated to 1 Co(*b*) atom at 2·39 Å and 4 Co(*f*) atoms at 2·21 Å, the Co atoms being at the corners of a pyramid with square base. Thus an S(*c*) atom is at the corner of four tetrahedra and an S(*e*) atom is at the corner of one octahedron and four tetrahedra. In a sulfur tetrahedron each of the three edges involving only S(*e*) atoms is shared by another tetrahedron. The sulfur octahedra share only corners with tetrahedra.

A comparison of the octahedral Rh–S distance, 2·34 Å in $Rh_{17}S_{15}$ with the octahedral Co–S distance, 2·39 Å, in Co_9S_8, indicates an anomaly: the Rh–S distance would be expected to be the larger one. (See, e.g., last column of Table 4. Also the lattice constant of pyrite-type RhS_2 is 5·585 Å (Thomassen, 1929) whereas that of pyrite-type CoS_2 is 5·523 Å (Kerr, 1945).) The coordination of S to Rh atoms in $Rh_{17}S_{15}$ which is most closely related to the tetrahedral

---

* There is another figure of this structure showing a complete unit cell in *Strukturbericht* for 1936, Vol. IV, p. 26.

S to Co coordination in Co_9S_8 is that of the Rh(m) with the S(f), S(i) and S(j) atoms. The average distance for these is 2·33 Å (Geller, 1962b) compared with the average tetrahedral Co–S distance, 2·19 Å. Moreover, the relatively longer Rh(m)–Rh(m) than Co(f)–Co(f) distances (Table 4) would imply a relative shortening of Rh(m)–S distances. Thus we are able to conclude that the 4-coordination distances are relatively as one would have predicted.

It is possible that the more complex bonding and packing in the $Rh_{17}S_{15}$ results in the shortening of the bonds of the single Rh atom in the unit cell having octahedral coordination. By studying the systems in which Co replaces Rh in $Rh_{17}S_{15}$ and that in which Rh replaces Co in Co_9S_8, we hope to gain some further insight into the bonding and atom sizes as well as effects on the superconductive properties of $Rh_{17}S_{15}$.

References

ALSÉN, N. (1925). *Geol. Fören. Förhandl.* **47**, 54.

BOND, W. L. (1951). *Rev. Sci. Instrum.* **22**, 344.

BOND, W. L. (1959). *Acta Cryst.* **12**, 375.

BUSING, W. R. & LEVY, H. (1959). ORNL Central Files Memorandum 59-4-37, April.

DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.

DAWSON, B. (1960). *Acta Cryst.* **13**, 403.

GELLER, S. (1962a). *Acta Cryst.* **15**, 713.

GELLER, S. (1962b). *Acta Cryst.* **15**, 1198.

JUZA, R., HÜLSMAN, O., MEISEL, K. & BILTZ, W. (1935). *Z. anorg. Chem.* **225**, 369.

KERR, P. F. (1945). *Amer. Min.* **30**, 483.

LINDQVIST, M., LUNDQVIST, D. & WESTGREN, A. (1936). *Svensk Kem. Tidsk.* **48**, 156.

TAYLOR, A. & FLOYD, R. W. (1950). *Acta Cryst.* **3**, 285.

THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.

THOMASSEN, L. (1929). *Z. Phys. Chem.* (B), **4**, 277.

Acta Cryst. (1962). **15**, 1198

The Crystal Structure of the Superconductor $Rh_{17}S_{15}$

BY S. GELLER

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.

(*Received* 1 *March* 1962)

Crystals of $Rh_{17}S_{15}$, isostructural with those of $Pd_{17}Se_{15}$, belong to one of three space groups O_h^1–$Pm3m$, T_d^1–$P\bar{4}3m$ or O^1–$P432$, have a lattice constant of 9·911 ± 0·001 Å, and two formula units per unit cell. The structure of $Rh_{17}S_{15}$ has been refined in $Pm3m$ from selected single-crystal X-ray data. It is shown that there are relatively short Rh–Rh contacts in $Rh_{17}S_{15}$.

Introduction

To date, only $Rh_{17}S_{15}$ and $Pd_{17}Se_{15}$ are known to crystallize with the structure to be described in this paper. A detailed account of the structural study of $Pd_{17}Se_{15}$ has already been given (Geller, 1962); it was mentioned that X-ray data from both $Rh_{17}S_{15}$ and $Pd_{17}Se_{15}$ were useful in the solution of the structural problem. The main purpose of the present paper is to report on the structural details of $Rh_{17}S_{15}$ and to point out how they differ from those of $Pd_{17}Se_{15}$.

The rhodium–sulfur system was first investigated by Juza, Hulsmann, Meisel & Biltz (1935). They found a compound that they designated Rh_9S_8, which appeared from X-ray powder diffraction data to have primitive cubic symmetry. The compound was found to be superconducting by Matthias, Corenzwit & Miller (1954). Recently, Kjekshus (1960) carried out X-ray studies over a temperature range on compounds alleged to be Rh_9S_8 and Pd_9Se_8. The structural study has conclusively shown, however, that the correct formulae of the compounds are $Rh_{17}S_{15}$ and $Pd_{17}Se_{15}$, as shown in the paper on the latter compound.

Experimental

The lattice constant obtained from a powder photograph (taken with a 114·6 mm. diameter Norelco Straumanis camera and using Cu K radiation) of a specimen with an originally intended composition Rh_9S_8 is 9·911 ± 0·001 Å. This value probably represents the lattice constant of $Rh_{17}S_{15}$ well within experimental error. A compound Rh_9S_8 would contain 78·31% Rh by weight while $Rh_{17}S_{15}$ contains 78·44% Rh by weight; the difference is small. Furthermore a specimen made up with intended composition Rh_8S_7 (78·58% Rh) contained elementary rhodium as shown by an X-ray photograph. Excess sulfur would be difficult to see in the 'Rh_9S_8.' The phase appears to be fairly sharply defined in the Rh–S system, but even *if* there were some solution of sulfur in the $Rh_{17}S_{15}$, there would probably not be a significant difference in lattice constant between 'Rh_9S_8' and $Rh_{17}S_{15}$.

With two $Rh_{17}S_{15}$ in the unit cell, the X-ray density 7·60 g.cm.$^{-3}$ is in good agreement with the value 7·68 g.cm.$^{-3}$ obtained pycnometrically on an 'Rh_9S_8' specimen.