

REFINEMENT OF THE STRUCTURE OF Co_9S_8

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ABSTRACT

Because of uncertainty in Geller's refinement (Geller 1962), the structure of a single crystal of synthetic Co_9S_8 (of composition $\text{Co}_{8.88}\text{S}_8$ and $a = 9.923(1)$ Å, Sp. Gr. $Fm\bar{3}m$), grown by the vapor transport technique using iodine as the transporting agent, was refined using three-dimensional x -ray intensity data to an R factor of 0.029. The observed octahedral cobalt-sulphur distance, 2.359 (2) Å, is slightly larger than the corresponding distances in cobalt monosulphide (2.34 Å) and in cobalt disulphide (2.32 Å) and is significantly larger than the octahedral cobalt-sulphur distance, 2.22 Å, in Co_9S_4 . Previously reported physical properties, aspects of bonding and the observed bond distances suggest that the octahedral cobalt in Co_9S_8 could be in the low-spin state although the apparent valency of cobalt in the structure is less than two ($\mu' = 1.78$).

INTRODUCTION

Recent crystal chemical studies on pentlandites using single-crystal x -ray diffraction techniques showed that the structures of natural pentlandites including Fe-Ni pentlandite, cobalt pentlandite and argentian pentlandite are essentially similar to that of synthetic Co_9S_8 (Rajamani & Prewitt 1973; Hall & Stewart 1973). The structure of Co_9S_8 was refined previously by Geller (1962) using visually estimated two-dimensional x -ray intensity data. In this study, the positional parameter of the sulphur atom in equipoint (24e) (which is coordinated to octahedral metal atom in addition to tetrahedral metal atoms) could not be refined satisfactorily. The observed octahedral Co-S distance, 2.39 Å, using the unrefined positional parameter of the sulphur atom is significantly larger than the corresponding distances in other cobalt sulphides (2.34 Å in Co_{1-x}S , Kuznetsov 1965; 2.32 Å in CoS_2 , Elliot 1960; 2.22 Å in Co_9S_4 , Knop *et al.* 1968) where octahedral cobalt is believed to be in the low-spin state. A knowledge of the nature of cobalt (*i.e.*, its valency and spin state) is very desirable

in understanding the solid solution behavior of iron, cobalt and nickel in the pentlandite structure. Vaughan & Burns (1971) predicted that octahedral cobalt in Co_9S_8 could probably be in the trivalent low spin state. Nevertheless, the reported ^{57}Co -S distance in Co_9S_8 is too large even for a divalent low spin cobalt. Because of this discrepancy which may well be due to uncertainty in Geller's refinement and to provide more information on the structure and bonding of pentlandite, the structure of Co_9S_8 was refined using a single-crystal grown by vapor transport techniques and is reported here.

EXPERIMENTAL

Single crystals of Co_9S_8 were synthesized by a chemical transport technique using iodine vapor as the transporting agent. The details of the technique including synthesis of other sulphides will be described elsewhere. To check the stoichiometry of the crystals, two large crystals were analyzed using an ARL-electron probe micro-analyzer. Homogeneous, stoichiometric FeS_2 and CoS_2 crystals, grown by similar techniques (Bouchard 1968) were used as standards for sulphur and cobalt, respectively. The crystals of Co_9S_8 analyzed are also very homogeneous. One crystal of dimensions $0.19 \times 0.15 \times 0.13$ mm with well-defined crystal faces was mounted on the [110] axis and precession photographs were taken to check the space group. The cell parameter was determined from 2θ values measured on the Picker four-circle diffractometer. Integrated intensities of 420 reflections were collected on the diffractometer. The details of data collection and reduction including absorption correction and refinement were similar to those described earlier (Rajamani & Prewitt 1973). Crystal data including cell parameter, composition and starting positional parameters (after Geller 1962) are listed in Table 1.

During the refinement it was observed that the intensities of strong reflections such as 440, 800, and 12.4.0 are greatly affected by secondary extinction. Therefore, an attempt was made to collect another set of intensity data after subjecting the crystal to thermal shock by dipping

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Table 1. Crystal data for synthetic Co₉S₈.

Microprobe anal., At. %:	Co = 52.5(2), S = 47.5(2)
Chemical composition:	Co _{8.85} S ₈
Space group:	Fm3m
Cell parameter <i>a</i> :	9.923(1)Å
Starting positional 4b(M0):	1/2, 1/2, 1/2
Parameters as given 32f(M(T)):	0.126, 0.126, 0.126
by Geller (1962) 8c(S1):	1/4, 1/4, 1/4
24e(S2):	0.259, 0, 0

it repeatedly in liquid nitrogen. However, the results were not significantly changed by the above procedure.

Since the composition of the crystals is Co_{8.85}S₈ instead of Co₉S₈, the occupancy of Co in the tetrahedral sites was refined assuming cation vacancies. This did not improve the results of the refinement. The observed (after absorption correction and averaging) and calculated structure factors are listed in Table 2. The refined positional parameters and temperature factors including *R* factor, and interatomic distances and angles are listed in Tables 3 and 4, respectively.

RESULTS AND DISCUSSION

The cell parameter of synthetic Co₉S₈ was shown to be sensitive to the stoichiometry of the phase, being smaller when the phase is saturated with sulphur and larger when it is saturated

with cobalt (Knop & Ibrahim 1961). The observed cell parameter, 9.923(1)Å, is smaller than the previously reported value, 9.929Å, for the stoichiometric Co₉S₈. This suggests that the crystals of Co₉S₈ grown by vapor transport technique are slightly cation deficient. This is not entirely unexpected because the crystals were grown from a vapor phase which was always saturated with sulphur, as indicated by the presence of sulphur at the end of each run. Microprobe analysis of the crystals also revealed that the crystals are cobalt deficient Co_{8.85}S₈ in agreement with the prediction based on the lattice parameter. The above observation tends to support the idea that the nonstoichiometry in pentlandite is due to netal addition and omission solid solution (Donnay & Shewman 1971; Rajamani & Prewitt 1973).

Table 3. Final atomic parameters in Co₉S₈.*

4b	B	0.45(4)	8c	B	0.51(4)
	x	0.12623(3)		x	0.2623(1)
32f	**	β ₁₁ 0.00117(7)	24e	**	β ₁₁ 0.00074(2)
		β ₁₂ 0.00006(2)		***	β ₂₂ 0.00117(9)
	B	0.46(3)		B	0.42(4)

$$R = [Ew\{|F_o| - |F_c|\}^2 / Ew\{F_o\}^2]^{1/2} = 0.029.$$

$$\text{Secondary extinction correction factor } c = 1.79 \times 10^{-5}.$$

*The numbers in parentheses represent calculated standard errors (1σ) and refer to the last decimal place.

$$**\beta_{11} = \beta_{22} = \beta_{33} \quad \beta_{12} = \beta_{13} = \beta_{23}.$$

$$***\beta_{22} = \beta_{33} \quad \beta_{12} = \beta_{13} = \beta_{23} = 0.$$

TABLE 2. OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Co₉S₈

<i>h k l</i>	<i>F_o</i>	<i>F_c</i>	<i>h k l</i>	<i>F_o</i>	<i>F_c</i>	<i>h k l</i>	<i>F_o</i>	<i>F_c</i>	<i>h k l</i>	<i>F_o</i>	<i>F_c</i>
2 0 0	87	89	5 1 1	293	317	12 2 2	19	20	11 7 3	131	131
4 0 0	224	241	7 1 1	136	141	4 4 2	57	56	9 9 3	154	156
6 0 0	96	102	9 1 1	33	34	6 4 2	64	63	4 4 4	204	189
8 0 0	670	727	11 1 1	129	130	8 4 2	44	45	6 4 4	78	75
10 0 0	30	31	13 1 1	151	155	10 4 2	48	49	8 4 4	603	602
12 0 0	95	97	3 3 1	203	190	12 4 2	16	15	10 4 4	23	23
2 2 0	107	96	5 3 1	108	106	6 6 2	164	161	12 4 4	88	87
4 2 0	90	88	7 3 1	193	191	8 6 2	40	39	6 6 4	54	53
6 2 0	70	72	9 3 1	200	199	10 6 2	120	121	8 6 4	22	22
8 2 0	38	39	11 3 1	122	123	12 6 2	21	21	10 6 4	50	50
10 2 0	56	58	13 3 1	21	20	8 8 2	21	20	8 8 4	98	97
12 2 0	25	26	5 5 1	45	45	10 8 2	37	37	10 8 4	53	53
4 4 0	882	928	7 5 1	198	194	3 3 3	267	251	5 5 5	256	247
6 4 0	42	42	9 5 1	206	207	5 3 3	252	245	7 5 5	65	66
8 4 0	143	142	11 5 1	79	81	7 3 3	177	174	9 5 5	12	10
10 4 0	76	77	7 7 1	147	144	9 3 3	67	67	11 5 5	123	122
12 4 0	474	447	9 7 1	56	56	11 3 3	101	101	7 7 5	133	128
6 6 0	66	66	11 7 1	88	88	13 3 3	127	127	9 7 5	149	147
8 6 0	58	58	9 9 1	10	9	5 5 3	251	244	6 6 6	141	139
10 6 0	49	49	2 2 2	307	286	7 5 3	117	114	8 6 6	41	40
12 6 0	11	11	4 2 2	77	75	9 5 3	25	26	10 6 6	104	105
8 8 0	498	514	6 2 2	192	192	11 5 3	110	111	8 8 6	37	37
10 8 0	20	18	8 2 2	43	45	7 7 3	122	119	7 7 7	154	150
1 1 1	178	153	10 2 2	141	140	9 7 3	138	136	9 7 7	73	73
3 1 1	333	337									

Our refinement results confirm that the structure of Co₉S₈ as proposed by Lindqvist, Lundqvist & Westgren (1936) is essentially correct. The details of the structure had been adequately described in earlier studies, referred to earlier. Only the positional parameter of the S2 sulphur atom in (24e) has changed significantly from 0.259 to 0.2623. The change is particularly important because of its influence on the interatomic distances. The octahedral Co-S distance, 2.359Å, though smaller than the value 2.392Å reported by Geller, is still slightly larger than the corresponding distances, 2.32Å and 2.34Å in CoS₂ and Co_{1-x}S, respectively. Similarly, the mean ^{IV}Co-S distance, 2.202Å, is also larger than the ^{IV}Co-S distance, 2.184Å, in the thiospinel Co₉S₄ which is a normal spinel (Knop *et al.* 1968). It should be noted here that the observed ^{VI}Co-S distance in Co₉S₈ is even larger for a divalent low spin cobalt; therefore, the octahedral cobalt could not be in the trivalent low-spin state. The isotropic temperature factors are slightly

smaller than those that were observed in natural pentlandites. This could be due to the presence of only one kind of atom in the present case and also because of the greater covalency of the Co-S bond as compared to Fe-S and Ni-S bonds in sulphides (Rajamani & Prewitt 1972).

Aspects of bonding in Co_9S_8 appear to be similar to that in the thiospinel Co_9S_4 because both these phases were observed to be metallic and Pauli paramagnetic (Vaughan 1971; Vaughan *et al.* 1971). Also, both these structures are based on the cubic close packing (f.c.c.) of sulphur atoms and the metal atoms are located in the octahedral and tetrahedral interstices. However, in the case of Co_9S_4 , $\frac{1}{8}$ of the available tetrahedral sites and $\frac{1}{2}$ of the octahedral sites are occupied by metal atoms; whereas in Co_9S_8 metal atoms occupy $\frac{1}{8}$ of the available octahedral and $\frac{1}{2}$ of the tetrahedral sites. This structural similarity suggests that in Co_9S_8 three metal-metal interactions are possible which include: (1) $M(T)-M(T)$ direct interaction as indicated by the $M(T)-M(T)$ distance, 2.50 Å. This distance is well below the critical separation R_c which is 3.27 Å for cobalt in sulphides (Goodenough 1967). This direct interaction (or bonding) leads to the formation of the metallic cube cluster of tetrahedral metal atoms. (2) $M(T)-S1-M(T)$ interaction which involves 109.47° cation-anion-cation coupling and links the metallic cube cluster in the [110] direction. This interaction could also be strong because the $M(T)-S1$ distance, 2.127 Å, indicates that the bonding between $^{IV}\text{Co}-^{IV}\text{S}$ is highly covalent and the strength of cation-cation interactions are directly related to the degree of covalent bonding (Goodenough 1969). (3) $M(T)-S2-M(O)$ interaction which is between the tetrahedral and octahedral cobalt through the S2 sulphur atom. These three metal-metal interactions would lead to the formation of d bands of the antibonding d orbitals and the antibonding d electrons would be completely

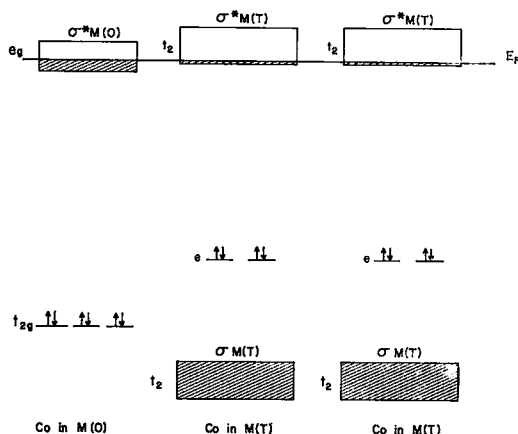


FIG. 1. Schematic energy level diagram for the 3d orbitals in Co_9S_8 .

delocalized in these bands. This is illustrated in the schematic energy level diagram shown in Fig. 1. All these three d bands, $\sigma^*_{M(O)}$ and $2\sigma^*_{M(T)}$ (with respect to direct metal-metal bonding in the cube cluster) may coalesce to form a single, broad, partially filled band giving rise to the metallic conductivity and Pauli paramagnetism. The absence of Jahn-Teller distortion for the octahedral low spin Co(II) ($t_{2g}^6 e_g^1$) could be due to the delocalization of the unpaired e_g electron in the broad d band.

Although the observed $^{IV}\text{Co}-\text{S}$ is slightly larger than the corresponding distances in CoS_2 and Co_{1-x}S where $^{VI}\text{Co(II)}$ is believed to be in the low spin state, it is not surprising when we consider the stoichiometry of Co_9S_8 . Assuming S is divalent (S^{2-}), it can be argued that Co in Co_9S_8 could not be entirely divalent. It must be emphasized here that in compounds such as Co_9S_8 possessing metallic properties, assignment of formal valencies is not a valid procedure (Goodenough 1969, p. 272). The apparent valency of cobalt, μ' , can be calculated using the expression $m\mu' = xX'$ for a compound of the type $\text{M}_m^m \text{X}_x^{X'}$ (Hulliger 1968) and is found to be 1.78. The observed larger $^{VI}\text{Co}-\text{S}$ distance (2.359 Å as against 2.34 Å in Co_{1-x}S) and $^{IV}\text{Co}-\text{S}$ distance (2.202 Å as against 2.184 Å in Co_9S_4) in Co_9S_8 could be due to the reduced valency of cobalt in the pentlandite structure. The presence of metallic properties in Co_9S_8 indicates that "cation" s and p electrons are also involved in the metal-metal interaction, in addition to d electrons. This is because "a cation concentration yielding more s and p electrons than are needed to saturate the anion valencies must produce

Table 4. Interatomic distances and angles in Co_9S_8 .

ATOM	DISTANCE (Å)	ATOM	ANGLE (DEG.)
M(O) - S2[6]**	2.359(2)	S2 - M(O) - S2	90
M(T) - S1	2.127(1)	S1 - M(T) - S2	107.42(6)
M(T) - S2[3]	2.227(1)	S2 - M(T) - S2	111.44(5)
Mean M(T) - S	2.202		
		M(T) - M(T) - M(T)	90
M(T) - M(T)[3]	2.505(1)		
- M(T)[3]	3.543(1)	M(T) - S1 - M(T)	109.47
- M(T)[3]	3.474(1)		
		M(T) - S2 - M(T)	68.44(6)
S2 - S2[4]	3.336(3)	M(T) - S2 - M(O)	127.32(6)

* The numbers in parentheses represent calculated standard errors (1σ) and refer to the last decimal place.

** The numbers in brackets refer to the multiplicity of the bond.

metallic properties" (Hulliger 1968, p. 68), thereby supporting the reduced valency of cobalt in the pentlandite structure.

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