The Crystal Structure of Stromeyerite, *AgCuS*: A Possible Defect Structure.

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With 4 figures.

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Abstract.

Stromeyerite, below 93° C., forms orthorhombic crystals having space group symmetry *Cmcm*, with $a = 4.06$ Å; $b = 6.66$ Å; $c = 7{,}99$ Å. The unit cell contains $Ag_4Cu_4S_4$, with each element occupying 4-fold special positions. The *Ag* is at 000, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The *Cu* and *S* atoms are at $0\,y\,\frac{1}{4}$, $0\,\overline{y}\,\frac{3}{4}$, $\frac{1}{2}\frac{1}{2}+y\,\frac{1}{4}$, and $\frac{1}{2}\frac{1}{2}-y\,\frac{3}{4}$, where the y parameter for *Cu* is 0.46 and for *S* is 0.80.

The volumes of the principal Brillouin zones of stromeyerite have been computed. The assumed electron-to-atom ratio will not exactly fill any of the principal zones. Consequently, a small portion of the electrons must be at a higher energy level separated by an energy gap from the others. A defect structure with up to 0.1 of the *Ag* atoms missing at random is proposed as a possible lower energy structure. This suggestion is in agreement with the experimental data found in the literature on the preparation of synthetic stromeyerite.

Introduction.

Stromeyerite, *AgCuS*, occurs in nature both as a supergene and as a hypogene mineral (Lindgren, 1933). According to the *Dana System of Mineralogy* (Palache, Berman and Frondel, 1944), stromeyerite crystallizes in the orthorhombic dipyramidal class ($2/m\ 2/m\ 2/m$) with a prismatic pseudo-hexagonal [001] habit, the more common forms being {001}, {010}, {110} and {114}. As these data appear to be based solely upon the work of Gustave Rose in 1833 on only one crystal, the reliability is open to question.

Recently Suhr (1955) determined the cell constants as follows:

$$a = 4.06 \text{ Å}$$
$$b = 6.66 \text{ Å}$$
$$c = 7.99 \text{ Å}$$
$$a:b:c = 0.6096:1:1.1997.$$

The space group symmetry was determined as either $Cmc2_1$ (C_{2v}^{12}) or $Cmcm$ (D_{2h}^{17}). With the density of 6.2—6.3 the cell contains 4 $AgCuS$.

According to SCHWARTZ (1935), stromeyerite inverts to another structural form at 93° C. SCHWARTZ (1935) prepared stromeyerite synthetically by compressing the proper proportions of powdered Ag_2S and Cu_2S and subjecting the compressed pellets to subsequent heat treatment. Table 1 has been abstracted from the tabulation of experimental data reported by SCHWARTZ. It should be noted that in many instances silver existed as an additional phase.

Table 1.

Composition by wt. %		Temperature	Time	Rate of Cooling	Product
Cu_2S	Ag_2S	° C	hours		
39.11	60.89	285	72	cooled in furnace	Stromeyerite
,,	,,	390	120	,, ,, ,,	Stromeyerite + Silver
,,	,,	300	96	quenched in water	Stromeyerite + Chalcocite + Silver
above sample returned		300	48	slow cool 5 hours	Stromeyerite + Silver
39.11	60.89	200	72	,, ,, 5 ,,	Stromeyerite
,,	,,	75	72	,, ,, 5 ,,	Stromeyerite
,,	,,	500	3	cooled in furnace	Stromeyerite + Silver
,,	,,	800	4	,, ,, ,,	Stromeyerite
,,	,,	700	2	slow cool 7 hours	Stromeyerite
,,	,,	650	3	,, ,, 20 ,,	Stromeyerite
,,	,,	675	2	cooled in furnace	Stromeyerite

More recently SUHR (1955) prepared stromeyerite by compressing the proper proportions of the powdered elements. SUHR reported that in samples prepared from the atomic proportions $Ag : Cu : S$ of 1 : 1 : 1, a trace of jalpaite, Ag_3CuS_2, detectable by x-ray diffraction, appeared with the stromeyerite. When atomic proportions $Ag : Cu : S$ of 0.9 : 1.1 : 1 were used, a diffraction pattern of stromeyerite alone was produced. It was suggested that stromeyerite was either a defect structure with a deficiency of silver atoms (holes substituted for silver), or a structure in which some copper atoms occupy silver positions.

Structure Determination.

The unit cell and space group as reported above was confirmed, using a single crystal of stromeyerite from Altai, Siberia, obtained from the U. S. National Museum (U. S. N. M. No. 78426), and using a single crystal from Gowganda, Ontario, obtained through the courtesy of Professor Clifford Frondel from the Harvard University Museum (No. 97 962). The Buerger Precession technique using $MoK\alpha = 0.710$ Å was used in confirming the dimensions. The powder diffraction records of samples from both localities were checked against that of the synthetic material prepared from the elements, and were found to conform.

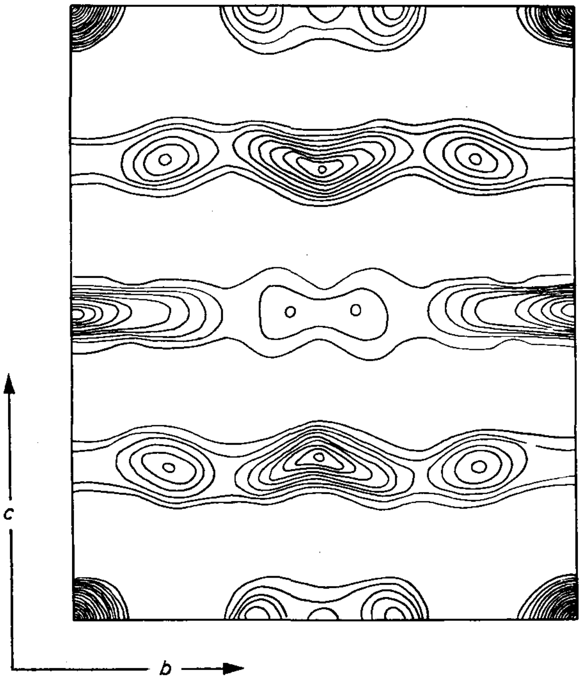

Figure 1. Harker-Patterson section, $P(0yz)$.

a axis, zero, first, and second level intensity data were gathered from a small fragment of a crystal from Gowganda using the equi-inclination Weissenberg technique with $CuK\alpha$ radiation. The intensities were estimated visually by comparison with a scale of graded exposures. Intensities were corrected for the Lorentz and polarization factors by the accepted method (Buerger and Klein, 1945).

As there are 4 *AgCuS* per cell, all the atoms must fall on special positions with their *x* coordinates equal to zero in either of the possible space groups $Cmc2_1$, or *Cmcm*. A distinction between the space groups will arise when the *y* and *z* coordinates are considered. It was assumed that a HARKER-PATTERSON section on $(0yz)$ would give the most information. From this section (Fig. 1), which represents the projection of all interatomic vectors that have an x component of zero, the interatomic distances were determined. These distances led to a trial arrangement of the atoms in accordance with the centro-symmetric space group *Cmcm*, with the silver atoms occupying the special positions 000, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; the copper and sulfur atoms at $0y\frac{1}{4}$, $0\bar{y}\frac{3}{4}$, $\frac{1}{2}\frac{1}{2}+y\frac{1}{4}$, and $\frac{1}{2}\frac{1}{2}-y\frac{3}{4}$ where the y parameter for copper was taken as 0.46 and for sulfur as 0.80.

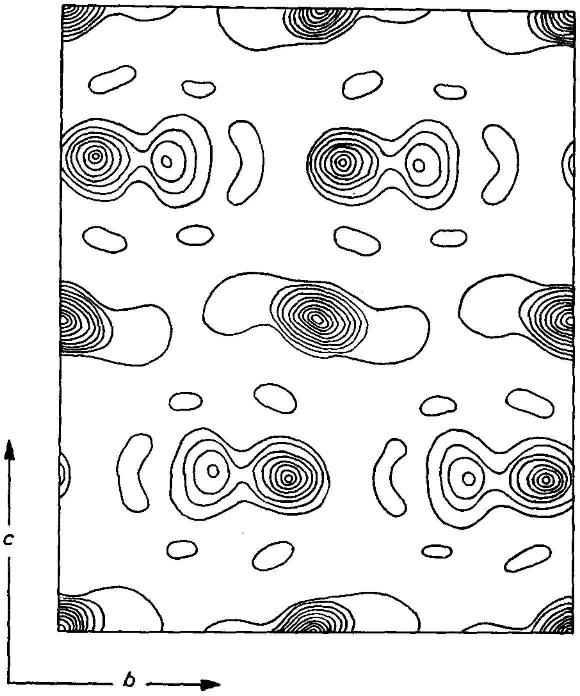

Figure 2. Electron density projection on (100).

From the above values the signs were calculated and an electron density projection on (100) was computed. This projection (Fig. 2) confirmed the proposed arrangement and parameters. Structure factors were calculated from

$$F_{hkl} = 4\sum_n f_n \cos^2 2\pi\left(\frac{h+k}{4}\right)\cos 2\pi\left(ky+\frac{l}{4}\right)\cos 2\pi\left(lz-\frac{l}{4}\right),$$

and are compared with those transformed from the observed intensities, in Table 2.

Table 2. Observed data from equi-inclination WEISSENBERG camera using *CuKα* radiation and corrected for LORENTZ and polarization factors.

hkl	sin Θ	*F* cal.	*F* obs.	*hkl*	sin Θ	*F* cal.	*F* obs.
002	0.193	4	10	080	0.928	11	10
004	0.386	63	84	081	0.933	7	10
006	0.579	4	13	082	0.947	30	7
008	0.772	44	42	083	0.972	6	1
0,0,10	0.965	4	10				
020	0.232	51	34	110	0.223	21	18
021	0.251	18	27	111	0.243	6	—
022	0.302	27	34	112	0.294	55	42
024	0.450	40	38	113	0.365	4	9
025	0.535	13	7	114	0.445	17	24
026	0.623	20	22	115	0.531	4	—
027	0.714	11	24	116	0.620	39	39
028	0.806	29	24	117	0.711	3	—
040	0.464	44	34	118	0.803	13	18
041	0.474	7	13	119	0.896	3	—
042	0.502	18	13	130	0.396	12	15
043	0.546	6	13	131	0.408	19	30
044	0.603	38	34	132	0.414	53	45
045	0.669	5	—	133	0.491	17	21
046	0.742	15	17	134	0.553	10	12
047	0.819	5	10	135	0.624	15	27
048	0.900	30	17	136	0.702	41	27
049	0.984	4	10	137	0.783	13	6
060	0.695	28	17	138	0.868	8	—
061	0.702	21	20	139	0.955	11	18
062	0.722	22	20	150	0.610	30	30
063	0.753	20	24	151	0.618	14	18
064	0.795	26	24	152	0.640	23	18
065	0.847	18	13	153	0.675	13	—
066	0.905	19	13	154	0.722	27	27
067	0.970	11	10	155	0.778	12	18

A reliability factor $R = \frac{\Sigma \left| |F| \text{ obs.} - |F| \text{ cal.} \right|}{\Sigma |F| \text{ obs.}}$ for all non zero reflections, after $\Sigma |F|$ obs. had been set equal to $\Sigma |F|$ cal., was computed as $R = 0.30$. The data, visually estimated and uncorrected for absorption, do not warrant further refinement of parameters.

The Structure.

The structure (Fig. 3) is essentially made up of zig-zag chains of silver and sulfur atoms paralleling the *c* axis. The planes parallel to

(001) are composed of layers of loosely packed face-centered silver atoms alternating with layers of triangularly coordinated sulfur and copper atoms. The silver-sulfur distance in the chain is 2.40 Å which is identical to that found (HARKER, 1936) in similar silver-sulfur chains in proustite, Ag_3AsS_3, and pyrargyrite, Ag_3SbS_3. The silver-sulfur-silver bond angle is about 113° and the sulfur-silver-sulfur bond angle is 180°. In the copper sulfur layers each copper atom has two sulfur atoms at 2.29 Å and one sulfur atom at 2.26 Å. This planar copper-sulfur layer is much like that in covellite (OFTEDAL, 1932, and BERRY, 1954) where the sulfur-copper distance is 2.20.

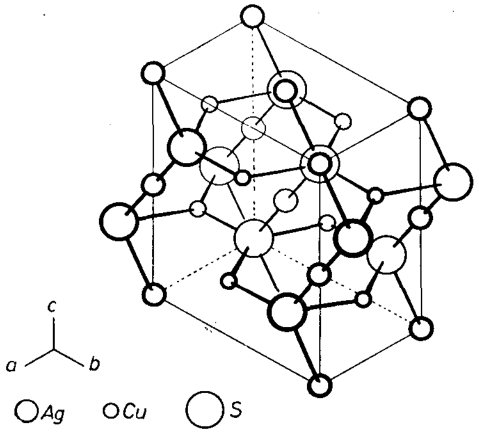

Figure 3. The structure of stromeyerite.

Euhedral crystals of stromeyerite are rare and the only measurements of interfacial angles found in the literature are those of ROSE (1833). The pseudo-hexagonal nature caused by the highly developed {110} and {010} forms reported both by ROSE and by MÜGGE (1920) might be expected from the evident pseudo-hexagonal nature of the structure.

Stromeyerite has a metallic luster characteristic of many sulfide minerals and should be classed as a semi-metal. The bonding is undoubtedly somewhat metallic in nature, and a limited application of the electronic theories of the metallic state as suggested for other sulfide minerals (FRUEH, 1954) is justified. The low symmetry and the similarity in intensity of many of the x-ray reflections make quite numerous the possible important BRILLOUIN zones enclosed by various combinations of different forms. Some of these zones as well as their volumes and their electron-to-atom capacities are listed in Table 3.

Table 3.

Indices of forms determining zone	Volume of zone $\times b^3$	Electron-to-atom ratio of filled zone
110 020 021 112	8.40	1.02
110 021 112	8.53	1.04
110 020 021	11.58	1.41
110 021	11.71	1.43
020 112	16.05	1.96
112 022 004	18.12	2.21
112 022	18.38	2.24
112 023 004 130	20.54	2.50
112 023 130	20.84	2.54
112 004 130	21.60	2.63
112 130	22.12	2.69
112 023 004	22.86	2.79
112 023	23.16	2.82
112 004 040	23.39	2.85
112 004	26.24	3.20
112	26.76	3.26

If we assume that all the outer shell electrons contribute to the Fermi body that occupies the important Brillouin zone, then copper and silver would each contribute one electron while sulfur would contribute six. Stromeyerite would have an electron-to-atom ratio of 8: 3 or 2.67.

It would then appear that stromeyerite of the stoichiometric composition *AgCuS* would fill to capacity the zone composed of {112} {004} {130} (Fig. 4) and have a few electrons left over to be accommodated at a higher energy level beyond the boundary of the zone. As the forms {112} and {004} represent the two most intense reflections of the diffraction pattern, and the form {130} one of rather strong intensity, they must represent an effective electron barrier. If the energy gap at this barrier is appreciable, then those few electrons not accommodated in this zone must be at a considerably higher energy level. It may involve less of a total energy gain to omit electron-contributing atoms from the structure than to accommodate the extra electrons.

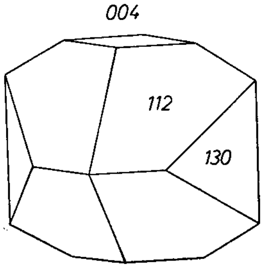

Figure 4. Brillouin zone of stromeyerite.

From the structure of stromeyerite it can be seen that the substitution of a hole, which might be considered as an atom contributing zero electrons, for a silver atom would involve the breaking of two bonds, whereas if a hole were substituted for a copper atom or a sulfur atom it would involve the breaking of three or five bonds respectively. Consequently, the system would incur less of an energy gain by the omission of some silver atoms than by the omission of any of the other atoms. If 0.1 of the silver atoms were removed from the structure, the electron-to-atom ratio would be changed to 2.63 and all the electrons could be accommodated within the zone described above. Considering the experimental evidence of SCHWARTZ and SUHR mentioned earlier in this paper, this would suggest that a more accurate formula for stromeyerite would be $Ag_{1-x}CuS$, where x has some value between 0 and 0.1.

Although the thermodynamic data are not yet known that will permit the calculation of the energy involved in the removal of a silver atom from stromeyerite, perhaps an idea as to the order of magnitude to be expected can be obtained from the available data on silver sulfide Ag_2S. As the heat of formation of Ag_2S is reported as 7.5 kil. cal. per mole (KUBASCHEWSKI and EVANS, 1951) it would take about 0.33 e. v. to break apart one Ag_2S molecule or about the order of 0.2 e. v. to remove a silver atom from a crystal of Ag_2S. This appears to be a lower value than the gap energies, ranging from 0.5 to 2.0, that have been computed for various semi-metals. Thus the order of magnitude of these values would seem to support the idea expressed above and its further validity rests upon the securing of thermodynamic data on stromeyerite and the calculation of the gap energy at the boundry of the full BRILLOUIN zone.

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