THE CRYSTAL STRUCTURE OF COVELLITE, CuSe AND KLOCKMANNITE, CuSe

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Abstract

The crystal structure proposed by Oftedal (1932) for covellite, CuS, is confirmed and found to hold also for klockmannite, CuSe. They are hexagonal with space group D_{6h}^4-$P6_3/mmc$; covellite with $a=3.796$, $c=16.36$ Å and cell content 6[CuS]; klockmannite, with $a=3.938$, $c=17.25$ Å, and cell content 6[CuSe]. The atoms are in the following positions: 2Cu in (*d*) $\frac{1}{3}, \frac{2}{3}, \frac{3}{4}$; 2S or 2Se in (*c*) $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$; 4Cu in (*f*) $\frac{1}{3}, \frac{2}{3}, z$, with $z=0.107$ in CuS and $z=0.10_7$ in CuSe; 4S or 4Se in (*e*) $00z$, with $z_S=0.064$ and $z_{Se}=0.06_6$.

Covellite

Oftedal (1932) has described the crystal structure of covellite as

Hexagonal, D_{6h}^4—$P6_3/mmc$; $a = 3.80$, $c = 16.4$ kX
2Cu in (*d*) $\frac{1}{3}, \frac{2}{3}, \frac{3}{4}$; 4Cu in (*f*) $\frac{1}{3}, \frac{2}{3}, z$, with $z = 0.107$
2S in (c) $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$; 4S in (*e*) $0, 0, z$, with $z = \frac{1}{16}$

The lattice dimensions were taken from the earlier work of Roberts & Ksanda (1929) and Gossner & Mussgnug (1927).

In order to check this structure in connection with the study of klockmannite, a small cleavage flake (0.05×0.5×2 mm.) from the Leonard mine, Butte, Montana was mounted for single crystal study. Unfortunately it was not possible to obtain an equidimensional fragment because of the perfect basal cleavage of covellite. Rotation and Weissenberg films with Cu*K* ($K\alpha=1.5418$ Å) and Mo$K\alpha$ (0.7107 Å) radiation yielded the cell dimensions

$$a = 3.796, \qquad c = 16.36 \text{ Å}$$

Three sets of zero layer Weissenberg films, using three films in each set separated by brass foil, yielded intensity data for about ninety $h0\bar{h}l$ reflections with Mo$K\alpha$ radiation. The intensities, estimated by visual comparison with a standard series of graded exposures, were converted to $|F_o|$ values using the Lp factor and a scale factor (Table 1). The signs of the structure factors were calculated assuming Oftedal's structure for covellite, and a two dimensional Fourier series was summed in a plane perpendicular to an *a* axis, using Patterson-Tunell strips. The resulting Fourier map showed high peaks at $(\frac{2}{3}, -, \frac{1}{4})$ and $(\frac{1}{3}, -, \frac{6.5}{60})$ and moderate peaks at $(\frac{1}{3}, -, \frac{1}{4})$ and $(0, -, \frac{3.8}{60})$ The positions of these peaks correspond closely to the atomic positions given by Oftedal, the high peaks representing copper atoms and the moderate peaks sulphur atoms.

TABLE 1. COVELLITE: STRUCTURE FACTOR DATA FOR THE $h0\bar{h}l$ ZONE

$h0\cdot l$	$\|F_o\|$	F_c	$h0\cdot l$	$\|F_o\|$	F_c	$h0\cdot l$	$\|F_o\|$	F_c
00.0	270	270	10.26	0	0	30.26	0	−5
00.2	12	−19	10.27	7	4	30.28	11	11
00.4	15	−16	10.28	8	−7			
00.6	115	−148	10.29	8	−3	40.0	0	−9
00.8	49	63				40.1	12	−8
00.10	0	−10	20.0	33	−23	40.2	14	14
00.12	24	30	20.1	24	19	40.3	22	−23
00.14	55	−56	20.2	35	36	40.4	0	1
00.16	41	36	20.3	64	58	40.5	6	9
00.18	29	13	20.4	4	3	40.6	0	6
00.20	33	31	20.5	24	−22	40.7	16	14
00.22	43	−33	20.6	17	16	40.8	27	−24
00.24	24	−9	20.7	35	−33	40.9	0	7
00.26	10	−9	20.8	58	−57	40.10	15	−8
00.28	21	17	20.9	17	−18	40.11	16	−16
			20.10	25	−17	40.12	0	−3
10.0	31	−35	20.11	37	38	40.13	7	−5
10.1	28	−29	20.12	0	−8	40.14	20	19
10.2	46	54	20.13	18	12	40.15	7	4
10.3	103	−88	20.14	37	40	40.16	7	3
10.4	8	5	20.15	14	−9	40.17	7	11
10.5	31	32	20.16	13	−24			
10.6	24	23	20.17	14	−24	50.0	0	−5
10.7	46	44	20.18	0	5	50.1	0	4
10.8	69	−75	20.19	0	7	50.2	0	8
10.9	23	25	20.20	8	−14	50.3	15	13
10.10	27	−22	20.21	15	11	50.4	0	1
10.11	40	−49				50.5	0	−5
10.12	4	−10	30.0	94	89	50.6	0	4
10.13	18	−15	30.2	0	−6	50.7	10	−8
10.14	34	50	30.4	14	−6	50.8	16	−14
10.15	17	12	30.6	65	−62	50.9	0	−4
10.16	13	9	30.8	24	27	50.10	0	−4
10.17	26	29	30.10	0	−5	50.11	10	10
10.18	0	6	30.12	11	15	50.12	0	−2
10.19	6	−9	30.14	24	−30	50.13	0	3
10.20	18	−18	30.16	20	20	50.14	15	11
10.21	22	−13	30.18	15	7			
10.22	0	4	30.20	9	17	60.0	17	16
10.23	0	−6	30.22	14	−19	60.2	0	−1
10.24	7	−5	30.24	10	−5	60.4	0	−1
10.25	7	12				60.6	16	−12

Structure factors, calculated for $000l$ and $10\bar{1}l$ reflections over a small range of the z parameters (z_{Cu} 0.107 to 0.110 and z_{S} 0.0625 and 0.064), gave the best agreement with $|F_o|$ in terms of the reliability index, $R=\sum[|F_o|-|F_c|]/\sum|F_o|$, when

$$z_{Cu}=0.107 \quad \text{and} \quad z_S=0.064.$$

Structure factors for all $h0\bar{h}l$ reflections within the range of observation, calculated with these parameters, were then corrected by a temperature factor. The temperature factor ($B=1.84$) was found by plotting log $|\overline{F_c}|/|\overline{F_o}|$ as a function of $(\sin\theta/\lambda)^2$. The resulting F_c values are given in Table 1. The reliability index, $R=0.22$, indicates fairly satisfactory agreement between observed and calculated structure factors, considering the unsuitable shape of the cleavage fragment used for obtaining the intensity data. The data here confirm Oftedal's structure but indicate that a slight change in z_S parameter is desirable.

KLOCKMANNITE

The lattice dimensions and possible space group of artificial CuSe are given by Earley (1949)

$$\text{Hexagonal,} \quad D_{6h}^4\text{—}P6_3/mmc; \qquad a=3.938, \quad c=17.25\ \text{Å}$$

who also found that the x-ray powder patterns of klockmannite and artificial CuSe are identical. The natural material is unsuitable for single crystal study. The similarity of lattice dimensions and symmetry suggest that covellite and klockmannite are possibly isostructural. Earley's films show evidence of the existence of a superstructure in CuSe. A heavily exposed rotation film about the a axis shows weak diffuse rows requiring a twelve-fold a axis and the rotation about the c axis shows a few weak lines of nearly continuous diffraction parallel to the Bernal curves. No further information about the nature of the superstructure could be obtained.

In 1951 several students cooperated in calculating intensities for the $000l$ reflections of klockmannite, using Oftedal's atomic positions for covellite, over a range of values for the two variable z parameters. The observed intensities were estimated visually on Earley's original zero layer Weissenberg film, $h0\bar{h}l$ (using CuK radiation and a small thin hexagonal plate of CuSe). On a graph of z_{Cu} against z_{Se} areas were eliminated in which the relation between each pair of calculated intensities is opposed to the relation between the corresponding pair of observed intensities. This procedure leaves a small area in which the order of calculated intensities in decreasing magnitude is the same as the order of observed intensities, here the parameter values are $z_{Cu}=0.109$ and $z_{Se}=0.068$. The work was laid aside at that time when it was found that these parameters result in rather poor agreement between calculated and observed intensities for $10\bar{1}l$ reflections.

TABLE 2. KLOCKMANNITE: STRUCTURE FACTOR DATA FOR THE $h0\bar{h}l$ ZONE

$h0\cdot l$	$\|F_o\|$	F_c	$h0\cdot l$	$\|F_o\|$	F_c	$h0\cdot l$	$\|F_o\|$	F_c
00.0	378	378	10.9	17	7	20.8	74	−103
00.2	11	−8	10.10	36	−31	20.9	20	−5
00.4	0	8	10.11	34	−37	20.10	33	−25
00.6	>67	−235	10.12	36	−6	20.11	21	29
00.8	40	40	10.13	37	−29	20.12	30	−5
00.10	46	−53	10.14	86	90	20.13	27	24
00.12	55	65	10.15	48	25	20.14	59	73
00.14	28	−47	10.16	35	26	20.15	32	−20
00.16	81	78	10.17	0	23	20.16	35	21
00.18	0	8	10.18	0	17			
00.20	20	33	10.19	0	−2	30.0	67	137
00.32	61	−64	10.20	50	−36	30.2	41	−3
			10.21	34	−22	30.4	42	4
10.0	46	12				30.6	56	−101
10.1	59	−56	20.0	46	9	30.8	21	19
10.2	>69	110	20.1	50	39			
10.3	44	−62	20.2	51	77	40.0	24	4
10.4	0	−17	20.3	29	42	40.1	0	−17
10.5	13	8	20.4	16	−12	40.2	23	33
10.6	39	−6	20.5	0	−6	40.3	19	−18
10.7	54	67	20.6	37	−5	40.4	0	−5
10.8	70	−135	20.7	56	−50	40.5	0	2
						40.6	13	−2

The crystalline CuSe, made by Earley in 1946, now consists of subparallel aggregates of tiny six-sided plates. It is not possible to segregate a single plate large enough to mount. In breaking up a group, the individuals inevitably split or bend. The crystal used by Earley, a clean hexagonal plate (0.1 mm. in width), has unfortunately been lost. The present appearance of the material suggests that the process of ordering which produced the superstructure indicated by Earley's films has now proceeded further.

The intensities, re-estimated from Earley's $h0\bar{h}l$ Weissenberg film (CuK radiation) by comparison with a series of graded exposures and converted to structure factors, $|F_o|$, are given in Table 2. Several apparently reasonable arrangements of copper and selenium were considered. One trial arrangement, with 2Cu in $(00\frac{1}{4})$, 4Cu in $(\frac{1}{3}, \frac{2}{3}, z)$, 2Se in $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$ and 4Se in $(00z)$ which gives better agreement in the $hki0$ intensities, results in peaks on the $h0\bar{h}l$ Fourier map essentially similar in position to those found for CuS. A Fourier synthesis, using the observed structure factors with signs determined for the covellite arrangement, gives a map with major peaks at $(0, -, \frac{4}{60})$, $(\frac{1}{3}, -, \frac{7}{60},)$, $(\frac{1}{3}, -, \frac{1}{4})$, $(\frac{2}{3}, -, \frac{1}{4})$ and some minor peaks. The first and third peaks are probably due to selenium and correspond closely in position to the sulphur peaks in the Fourier map of covellite, while the second and fourth are due to copper atoms. The minor peaks are probably ripples due to termination of the series at $\sin\theta/\lambda = 0.63$. The peak positions lead to the parameters $z_{Cu} = 0.114$ and $z_{Se} = 0.068$ agreeing closely with those found earlier and slightly larger than the values for covellite. Structure factors, calculated over a range of z values first for copper, then for selenium agree best with the observed values for

$$z_{Cu} = 0.10_7, \qquad z_{Se} = 0.06_6.$$

These values, however, can hardly be considered accurate beyond the second decimal place.

The calculated structure factors (F_c) corrected by a temperature factor ($B = 1.68$) obtained in the same way as for covellite are given in Table 2. The agreement, indicated by the reliability index ($R = 0.46$) is much poorer than for covellite. This is to be expected since data the were obtained from only one film and for a smaller range of reflections. The observed structure factors for some of the strongest reflections are much lower than the calculated values.

TABLE 3. INTERATOMIC DISTANCES IN COVELLITE AND KLOCKMANNITE

Covellite CuS		Klocknannite CuSe	
S_{II} —S_{II}	2.09, 3.80	Se_{II} —Se_{II}	2.28, 3.94
Cu_{I} —S_{I}	2.19	Cu_{I} —Se_{I}	2.27
Cu_{II}—S_{II}	2.30	Cu_{II}—Se_{II}	2.38
Cu_{II}—S_{I}	2.34	Cu_{II}—Se_{I}	2.46
Cu_{I} —Cu_{II}	3.21	Cu_{I} —Cu_{II}	3.35
S_{I} —S_{II}	3.75	Se_{I} —Se_{II}	3.90

The structural data here obtained result in the interatomic distances shown in Table 3. Cu_I has coordinated to it three S_I or Se_I in a plane parallel to 0001 and Cu_{II} is surrounded by three S_{II} or Se_{II} and one S_I or Se_I in nearly perfect tetrahedral coordination. S_I or Se_I is coordinated to three Cu_I in a plane perpendicular to c and two Cu_{II} on a line parallel to c in a trigonal bipyramid arrangement with the latter distance about 8% larger. S_{II} or Se_{II} is surrounded by three Cu_{II} and one S_{II} or Se_{II} in a nearly tetrahedral arrangement. The interatomic distances lead to the following atomic radii:

$$S = 1.05, \qquad Se = 1.14, \qquad Cu = 1.23 \text{ Å}.$$

The same average value for copper results from both CuS and CuSe structures using the above radii for S and Se. The S—S and Se—Se distances are in almost exact agreement with the values for the tetrahedral covalent radii given by Pauling (1948). This agreement confirms the values for the z_S and z_{Se} parameters established in this study.

The variation in the Cu—S and Cu—Se distances in the trigonal bipyramid is greater for Cu—Se, where the difference between Cu_I—Se_I and Cu_{II}—Se_{II} is 0.19. A larger value for the z_{Cu} parameter in klockmannite would reduce this difference slightly (to 0.14 with $z_{Cu}=0.11$, Cu_{II}—$Se_I=2.41$ and Cu_{II}—$Se_{II}=2.40$) McCullough (private communication) points out that this difference is comparable to that found in the di-*p*-tolylselenium dihalides (McCullough & Marsh, 1950) where the Se—*X* distance along the vertical axis of a nearly trigonal dipyramid yields a selenium radius of 1.40 Å while the Se—C distance yields a Se radius of 1.17 Å.

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