STUDIES OF NATURAL AND ARTIFICIAL SELENIDES: I—KLOCKMANNITE, CuSe[1]

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ABSTRACT

CuSe prepared by dry fusion and by hydrosynthesis is physically and structurally identical with klockmannite from Sierra de Umango, Argentina. Pyrosynthetic CuSe gave $G=5.99$. Minute greenish black hexagonal plates of hydrosynthetic CuSe show $c(0001)$, $n(10\bar{1}2)$, $r(10\bar{1}1)$, $m(10\bar{1}0)$; the unit cell with space group $C6/mmc$, $a=3.93$, $c=17.22$ kX, contains 6[CuSe]. A superstructure has $a'=12a$, $c'=c$. Klockmannite is clearly isostructural with covellite.

Klockmannite (Ramdohr, 1928) is a rare copper selenide which occurs intimately associated with umangite, clausthalite, eucairite, and chalcomenite at Sierra Umango (Argentina), and sparingly with other selenides at Lerbach and Tilkerode (Harz Mts.) and Skrikerum (Sweden). Unlike umangite (Klockmann, 1891), which is reddish violet on fresh surfaces, klockmannite is slate-grey; but since both minerals finally tarnish to a dull bluish black color they were not distinguished by Klockmann and the slate-grey mineral was actually first recognized and described by Ramdohr on a specimen which had been labelled "umangite" by Klockmann. Analyses of somewhat impure materials have indicated the compositions Cu_3Se_2 for umangite and CuSe for klockmannite. Ramdohr (1928, 1931) has added a wealth of microscopic observations on both minerals and also brief crystallographic observations on crystals said to be artificial CuSe. These data all tend to establish klockmannite as a distinct species, CuSe, analogous to covellite, CuS; but the evidence for the composition of the selenide is hardly adequate and further work on natural and artificial material are needed to confirm the individuality and properties of the mineral.

Only one authentic specimen of klockmannite could be obtained, Royal Ontario Museum, M 17025, from Sierra de Umango, Argentina. This specimen had been supplied by Professor Paul Ramdohr in an exchange of minerals and it was kindly lent for study by Dr. V. B. Meen. On this specimen the somewhat scanty klockmannite is tarnished and not very different from umangite in appearance, and it is intergrown by much chalcomenite. For lack of material further observations on the mineral were limited to obtaining the x-ray powder pattern, which proved to

be quite unlike that of umangite. The remaining observations were made on artificial CuSe.

Preparation of CuSe. Pyrosynthetic CuSe was prepared by fusing copper and selenium metals in equal atomic proportions in evacuated silica glass tubes at 1125° C. Two fusions were prepared in this way; one was quenched in cold water from 1125° C., the other was cooled slowly to room temperature. In polished sections the products are homogeneous, and they yielded x-ray powder patterns identical with the pattern given by the available specimen of klockmannite. The pattern of the material which was cooled slowly is sharper, due probably to better crystalline development.

Crystals of artificial klockmannite were also produced by hydrosynthesis from a 0.5 molar solution of copper sulphate in contact with copper and selenium metal in a steel bomb at about 400° C. The bomb is of the same design as that used by Smith (1947) for the hydrosynthesis of vein minerals. The synthetic crystals are greenish black plates showing hexagonal outline, seldom more than 0.1 mm. wide. The x-ray powder pattern of these crystals is also identical with the pattern of klockmannite.

Physical Properties. Six determinations of specific gravity, made with the Berman balance on fragments of the pyrosynthetic material gave an average value 5.99. The mineral specimen did not yield fragments of sufficient size or purity for specific gravity determinations, but Ramdohr (1928) gives the specific gravity as >5. In the natural specimen, klockmannite is finely granular and cut by veinlets of chalcomenite. In reflected light a polished section of klockmannite shows strong reflection pleochroism varying from bluish green to white. It is strongly anisotropic with four extinction positions and polarization colors from brownish blue to fiery orange, giving a mottled appearance to the section. The Talmadge hardness is C, estimated with a needle. Etch tests: HNO_3 fumes tarnish; HCl negative; KCN stains black rapidly; $FeCl_3$ negative, KOH stains differentially brown; $HgCl_2$ stains differentially blue. These reactions agree with those reported by Short (1940, p. 136).

Structural Crystallography. Cleavage fragments suitable for single-crystal measurements were not obtainable from the natural specimen or the artificial material made by dry fusion. A hydrosynthetic crystal plate (0.1 mm. in width) was adjusted to rotate about an edge of the hexagonal plate, an a-axis, for x-ray measurements. Later the crystal was readjusted to rotate about the normal to the plate, the c-axis. Good rotation and Weissenberg photographs were obtained with CuK radiation. Measurements on the films gave the hexagonal cell dimensions:[3]

$$a = 3.94 \pm 0.01 \text{ kX}, \ c = 17.26 \pm 0.05 \text{ kX}; \ c/a = 4.38$$

[3] Using λ CuK$\alpha_1 = 1.5374$ kX.
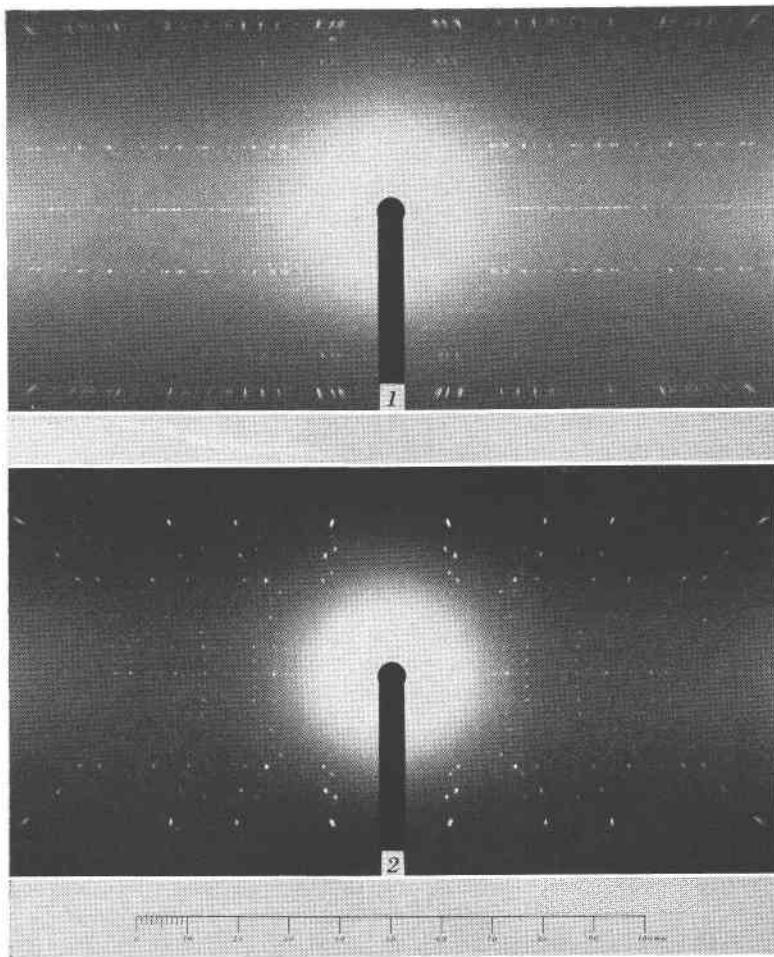
FIGS. 1, 2. Artificial CuSe: X-ray rotation photographs with CuK radiation (long exposure); camera radius $90/\pi$ mm. FIG. 1. Rotation about a-axis, showing weak intermediate layer lines requiring a period of $12a$. FIG. 2. Rotation about c-axis.

A heavily exposed photograph about the a-axis (Fig. 1) shows very weak intermediate layer lines which indicate a 12-fold multiplicity of the a-length. The rotation about the c-axis (Fig. 2) shows a few weak lines of nearly continuous diffraction parallel to the Bernal curves.

The Laue symmetry is $6/mmm$ and the systematically missing spectra are $(h \cdot h \cdot \overline{2h} \cdot l)$ present only with $l = 2n$. These conditions are characteristic of the space-group D_{6h}^4—$C6/mmc$. An additional condition, $(hk\bar{i}5)$ all absent, is due to a structural peculiarity.

Geometrical Crystallography. Klockmannite occurs in granular aggre-

gates and no recognizable crystals are developed. Cleavage is not visible in our hand specimen of the natural material, although reported by Ramdohr as (0001), perfect. The material made by dry fusion shows one perfect cleavage but the hydrosynthetic crystals are too small to permit the observation of cleavage. On the reflecting goniometer such crystals show platy development of $c(0001)$ and six-sided outlines due to the intersections of this plane with $n(10\bar{1}2)$, $r(10\bar{1}1)$, and $m(10\bar{1}0)$. The edge-faces are very narrow but give fair reflections. The following measured angles were obtained from two crystals:

$$n(10\bar{1}2) \quad \rho=67°\ 51'—68°\ 30' \quad (9) \quad \text{av. } 68°\ 13'$$
$$r(10\bar{1}1) \quad \rho=77°\ 38'—79°\ 23' \quad (8) \quad \text{av. } 78°\ 33'$$

These angles yield the axial ratio $c/a=4.31$ which agrees roughly with the structural lattice ratio, $c/a=4.38$, the axial ratio, $c/a=4.382$, given by Ramdohr (1931, p. 317) for artificial crystals. Thus the x-ray measurements confirm the symmetry and setting chosen by Ramdohr.

Composition and Cell Content. The cell dimensions and measured specific gravity on artificial CuSe, with the mass factor 1.650, give the molecular weight of the cell contents M = 836.2. This molecular weight

TABLE 1. KLOCKMANNITE FROM SIERRA DE UMANGO, ARGENTINA
ANALYSIS AND CELL CONTENT

| 1		2		3		4	
Cu	35.37	Cu	24.14	Cu	43.58	Cu	5.73
Se	45.73	Se	31.67	Se	56.42	Se	5.98
Pb	0.84	$CuSeO_3 \cdot 2H_2O$	40.25				
Ag	0.73	Pb	0.84				
Fe_2O_3	0.74	Ag	0.73				
Quartz	1.34	Fe_2O_3	0.74				
H_2O+	6.84	SiO_2	1.34				
H_2O-	0.48	H_2O-	0.48				
	[92.07]		100.19		100.00		

1. Anal. Geilmann, in Ramdohr (1928). 2. Anal. 1, as recast in Ramdohr (1928), showing chalcomenite ($CuSeO_3 \cdot 2H_2O$) determined by solution in ammonia. 3. Recast analysis recalculated to 100 per cent after deducting $CuSeO_2 \cdot 2H_2O$, PbSe, Ag_2Se, Fe_2O_3, SiO_2. 4. Empirical cell content.

combined with the analysis given by Ramdohr (1928) (Table 1), recalculated to 100 per cent after deducting chalcomenite ($CuSeO_3 \cdot 2H_2O$), clausthalite (PbSe), naumannite (Ag_2Se), Fe_2O_3, and SiO_2, indicates the structural cell content Cu_6Se_6.

The empirical formula CuSe is confirmed by the fact that homogeneous artificial material identical with klockmannite was formed by fusion of

the elements in equal atomic proportions in a closed system. The specific gravity calculated for the unit cell containing 6[CuSe] is 6.12, in fair agreement with the measured value 5.99.

X-Ray Powder Photographs. Identical patterns are given by natural klockmannite (Fig. 3), pyrosynthetic CuSe (Fig. 4), and hydrosynthetic crystals of CuSe (Fig. 5). Table 2 gives the observed relative intensities
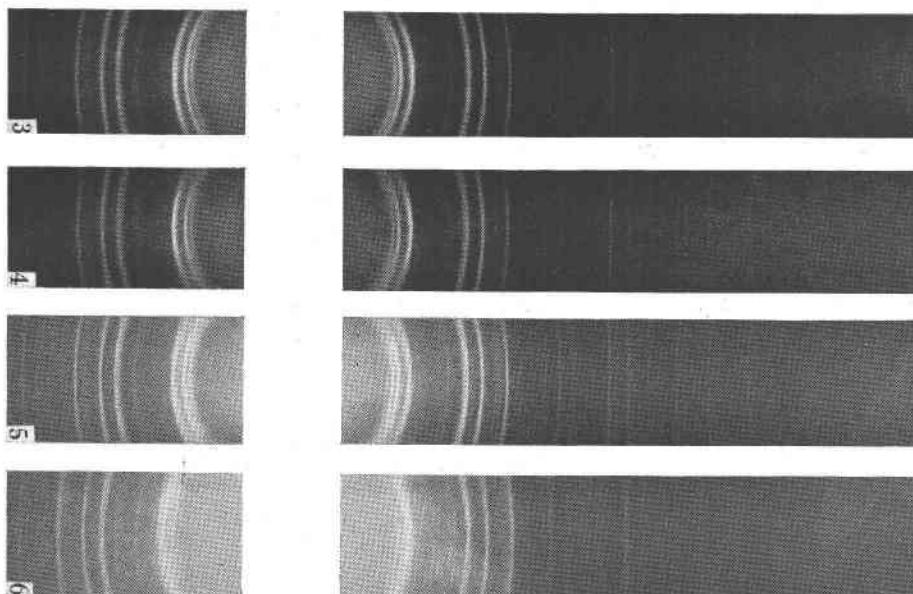
FIGS. 3–6. X-ray powder photographs with Cu/Ni radiation; camera radius $90/\pi$ mm. ($1°\theta = 1$ mm. on film); full size reproductions of contact prints. FIG. 3. Klockmannite Sierra de Umango, Argentina. FIG. 4. Artificial CuSe formed by pyrosynthesis. FIG. 5. Artificial CuSe crystals formed by hydrosynthesis. FIG. 6. Covellite, Butte, Montana.

and glancing angles for Cu$K\alpha$ radiation, together with the measured spacings, the indices of the powder lines, and the calculated spacings, using the cell dimensions, $a = 3.93$, $c = 17.22$ kX, which are slightly smaller and more accurate than the values obtained from the single-crystal measurements. The measured spacings given by Harcourt (1942) for klockmannite from Sierra de Umango agree fairly well with the stronger lines of our pattern.

The close similarity in lattice dimensions, crystal form and structural formula between klockmannite and covellite confirms the already inferred isostructural character of the two minerals. The close structural similarity is further borne out by comparing the powder patterns of the two minerals (Figs. 3–6).

TABLE 2. KLOCKMANNITE—CuSe: X-RAY POWDER PATTERN

Hexagonal, $C6/mmc$; $a=3.93$, $c=17.22$ kX, $Z=6$

I	θ(Cu)	d(meas.)	(hkīl)	d(calc.)	I	θ(Cu)	d(meas.)	(hkīl)	d(calc.)
6	13.33	3.34	$(10\bar{1}1)$	3.339	½	39.59	1.206	$(2.0.\bar{2}.10)$	1.210
9	14.03	3.17	$(10\bar{1}2)$	3.165	½	40.89	1.174	$(21\bar{3}6)$	1.174
1	15.23	2.93	$(10\bar{1}3)$	2.928	4	41.69	1.156	$(1.0.\bar{1}.14)$	1.157
10	15.53	2.87	(0006)	2.870	2	42.59	1.136	$(30\bar{3}0)$	1.135
3	20.54	2.19	$(10\bar{1}6)$	2.194	3	44.20	1.103	$(21\bar{3}8)$	1.104
½	20.95	2.15	(0008)	2.152	½	45.20	1.083	$(1.0.\bar{1}.15)$	1.088
4	22.65	1.996	$(10\bar{1}7)$	1.994	½	45.60	1.076	$(0.0.0.16)$	1.076
8	23.05	1.963	$(11\bar{2}0)$	1.965	1	46.90	1.053	$(30\bar{3}6)$	1.055
½	23.75	1.909	$(11\bar{2}2)$	1.916	3	50.41	0.997	$(2.0.\bar{2}.14)$	0.997
6	25.05	1.815	$(10\bar{1}8)$	1.819	1	51.51	0.982	$(22\bar{4}0)$	0.982
½	25.56	1.782	$(11\bar{2}4)$	1.788	½	51.92	0.977	$\begin{cases}(22\bar{4}2)\\(30\bar{3}9)\\(1.1.\bar{2}.16)\end{cases}$	0.976 0.976 0.944
1	26.96	1.695	$\begin{cases}(20\bar{2}0)\\(20\bar{2}1)\end{cases}$	1.702 1.694	3	54.52	0.944	$\begin{cases}(31\bar{4}0)\\(31\bar{4}1)\end{cases}$	0.944 0.943
1	27.36	1.673	$\begin{cases}(20\bar{2}2)\\(10\bar{1}9)\end{cases}$	1.669 1.668	½	55.72	0.930	$(22\bar{4}6)$	0.930
5	28.36	1.619	$(11\bar{2}6)$	1.621	½	59.03	0.896	$(31\bar{4}6)$	0.897
½	30.07	1.534	$(1.0.\bar{1}.10)$	1.536	4	59.83	9.889	$\begin{cases}(3.0.\bar{3}.12)\\(2.1.\bar{3}.14)\end{cases}$	0.890 0.889
½	31.57	1.468	$(20\bar{2}6)$	1.464	2	62.74	0.865	$(31\bar{4}8)$	0.865
½	32.37	1.436	$(0.0.0.12)$	1.435	½	63.74	0.857	$(2.1.\bar{3}.15)$	0.857
½	32.77	1.420	$(1.0.\bar{1}.11)$	1.422	1	67.15	0.834	$\begin{cases}(1.0.\bar{1}.20)\\(3.0.\bar{3}.14)\\(2.0.\bar{2}.18)\end{cases}$	0.834 0.834 0.834
1	33.37	1.398	$(20\bar{2}7)$	1.399	½	68.55	0.826	$(2.1.\bar{3}.16)$	0.826
3	35.28	1.331	$(20\bar{2}8)$	1.335	¼	74.66	0.797	$\begin{cases}(1.0.\bar{1}.21)\\(2.1.\bar{3}.17)\end{cases}$	0.797 0.796
½	36.78	1.284	$\begin{cases}(21\bar{3}0)\\(21\bar{3}1)\end{cases}$	1.286 1.283	2	79.27	0.782	$(0.0.0.22)$	0.783
1	37.08	1.275	$\begin{cases}(21\bar{3}2)\\(20\bar{2}9)\end{cases}$	1.272 1.272					
¼	37.78	1.255	$(21\bar{3}3)$	1.255					
¼	38.58	1.233	$\begin{cases}(1.0.\bar{1}.13)\\(21\bar{3}4)\\(0.0.0.14)\end{cases}$	1.234 1.232 1.230					

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