

X-RAY EXAMINATION OF COLUSITE,
(Cu, Fe, Mo, Sn)₄(S, As, Te)₃₋₄

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Through the courtesy of Professor R. E. Landon I was given the opportunity to make an *x*-ray examination of the newly discovered mineral colusite.

From the material placed at my disposal I was able to select a fragment of a crystal showing two faces. With this crystal fragment a series of oscillation photographs were taken. In addition I examined the crystal by means of the powder method. The oscillation as well as the powder photographs were taken with MoK α radiation. For the powder photographs a camera of radius 20.32 cm. was used. The powder of colusite was mixed with rock salt and the sample placed in a thin glass capillary. In this manner the $\alpha_1\alpha_2$ doublet was resolved over almost the entire range of angles and the displacement of the colusite diffraction lines with respect to the closest rock salt lines were measured. All measurements were made on the α_1 lines. In the oscillation photographs the crystal was rocked through an angle of 15°. The distance from the crystal to the photographic plate was 5.00 cm.

The observations show that the crystal is cubic. No deviation from holohedral symmetry could be detected in the oscillation photographs. The translation lattice is face centered. Long exposure photographs (both oscillation and powder photographs) were taken in order to determine whether very weak reflections might be obtained indicating either a larger unit cell or another type of translation lattice. No positive evidence of the presence of additional lines could, however, be found.

The edge of the unit cell was found to be:

$$a = 5.304 \pm .001 \text{ \AA}$$

This value was found on the basis of 5.628 Å for the edge of the unit cube of rock salt and a wave length of .7078 Å for the MoK α_1 line.

For the density Professor Landon gave the value $4.2 \pm .1$. Hence the average molecular weight of the atoms associated with each unit cell is 380 ± 9 .

On the basis of the chemical analysis given by Professor Landon

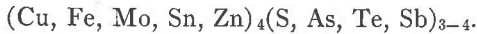
we are now in position to calculate the average number of atoms per unit cell. We find:

Sn	0.22 atoms per unit cell		
Mo	0.35 " " " "	Sb	0.02 atoms per unit cell
Zn	0.05 " " " "	Te	0.09 " " " "
Cu	2.13 " " " "	As	0.12 " " " "
Fe	1.24 " " " "	S	2.85 " " " "
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	3.99		3.08

In the above list atoms which are capable of replacing each other isomorphously have been grouped together.

The fact that the translation lattice has been found to be face centered requires that the number of equivalent atoms per unit cell be divisible by 4. This requirement is fulfilled as far as the metal atoms are concerned, but not by the sulphur atoms. As the possibility of a larger unit cell or of a different type of translation lattice has been fairly definitely ruled out, it becomes necessary to assume that the sulphur atoms are arranged in fourfold positions. Since there are only 3.08 atoms per unit cell and four available positions, it means that there is about one vacant position per unit cell. These vacant positions must be distributed in a random way throughout the lattice.

According to the above discussion it appears that the logical way of writing the chemical formula would be:



Because of the face centered translation lattice the atomic arrangement must be derived either from the normal rock salt type of structure or from the normal sphalerite structure. On the basis of the observed intensities the first possibility can be ruled out quite definitely. The sphalerite type of structure, however, accounts satisfactorily for the observed intensities. The structure amplitudes of Table 2 and the intensities of Table 1 have been calculated on the following basis: For the metal atoms I have used the scattering power for Cu calculated by means of Thomas' method.¹ The F-curve for sulphur is given by James and Brindley² and by Pauling and Sherman.³ These values have been reduced by 25 per-

¹ L. H. Thomas, *Proc. Cambridge Phil. Soc.*, **23**, 5, 542, 1927.

² James and Brindley, *Zeit. f. Krist.*, **78**, 470, 1931.

³ Pauling and Sherman, *Zeit. f. Krist.*, **81**, 1, 1932.

cent in order to take into account the fact that about 25 percent of the sulphur positions in the sphalerite lattice are vacant in colu-site.

TABLE 1. OBSERVATIONS FROM A POWDER PHOTOGRAPH^a

$\sin^2 \theta = (h^2 + k^2 + l^2) \times \lambda^2 / 4a^2$	<i>hkl</i>	<i>Int. obs.</i>	<i>Int. calc.</i>
.01346 = $3 \times .004487$	111	vs	31.2
.01778 $4 \times .004445$	200	m	5.2
.03569 $8 \times .004461$	220	vs	19.1
.04901 $11 \times .004455$	311	s+	14.1
.05359 $12 \times .004466$	222	w-	1.3
.07138 $16 \times .004461$	400	m	3.3
.08441 $19 \times .004443$	331	s-	5.8
.08923 $20 \times .004462$	420	w-	1.8
.10685 $24 \times .004452$	422	s	6.5
.11991 $27 \times .004441$	511, 333	m	4.2
.14215 $32 \times .004442$	440	w	1.9
.15582 $35 \times .004452$	531	m	3.9
.16028 $36 \times .004452$	442, 600	vw--	0.7
.17807 $40 \times .004452$	620	w+	2.5
.19121 $43 \times .004447$	533	vw	1.3
.19590 $44 \times .004452$	622	vvw	0.4
.21343 $48 \times .004446$	444	vw	0.6
.22695 $51 \times .004450$	711, 551	w-	1.8
	640	nil	0.3
.24954 $56 \times .004456$	642	w+	2.4
.26304 $59 \times .004458$	731, 553	vw	2.0

$$\lambda^2/4a^2 = .004451_3 \pm .000001_6$$

$$a = 5.304_2 \pm .000_9 \text{ \AA}$$

^a Concerning calculation of limits of error see: E. Broch, *Zeit. f. phys. Chem.*, **127**, 446, 1927.

TABLE 2. OBSERVATIONS FROM OSCILLATION PHOTOGRAPHS

<i>hkl</i>	<i>Int. obs.</i>	<i>F calc.</i>
111	s	24.4
200	m	13.3
220	s+	25.9
311	s	18.6
400	s+	21.9
331	s-	16.1
420	w-	9.1
422	s-	19.4
511	w+	14.4
440	m+	17.7
531	w	13.2

The observed intensities from the oscillation photographs are compared directly with the calculated structure amplitudes in the absence of any knowledge of the amount of secondary extinction. The calculated intensities for the powder photographs have been obtained with the usual relation:

$$\text{Intensity} \propto \frac{(F)^2 p(1 + \cos^2 2\theta)}{\sin^2 \theta \cdot \cos \theta}$$

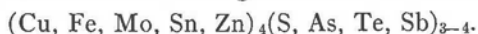
The distance from metal atom to that of sulphur was determined to be 2.298 Å. This value compares very well with the distance calculated from Goldschmidt's radii for atomic binding.⁴ It is to be remarked, however, that the effect of the missing sulphur atoms would be to reduce the interatomic distance.

Cases like the present one in which there are too few atoms to fill all the points in a set of equivalent positions have been established previously for other minerals. The most striking examples from the mineralogical point of view are those of hornblende, $(\text{Ca}, \text{Na}, \text{K})_{2-3}(\text{Mg}, \text{Fe}, \text{Al})_5(\text{Si}, \text{Al})_8\text{O}_{22}(\text{OH})_2$ and pyrrhotite, Fe_{1-x}S .

SUMMARY

X-ray examinations show that the new mineral colusite is cubic, with a length of the edge of the unit cube = $5.304 \pm .001$ Å.

The correct manner of writing the chemical formula is:



The atomic arrangement is essentially the same as in sphalerite; however, with about $\frac{1}{4}$ of the sulphur atoms removed at random. Accordingly the mineral should be classified as a new member of the sphalerite group.

⁴ V. M. Goldschmidt, *Geochemische Verteilungsgesetze der Elemente*, VII, Oslo, 1926.