

THE CRYSTAL STRUCTURE OF SKUTTERUDITE AND RELATED MINERALS

A PRELIMINARY PAPER

BY
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WITH ONE PLATE

In the following pages are given briefly the results of an investigation, which will be treated more completely in a future publication.

The minerals considered are skutterudite and smaltite-chloantite. Thanks to the kindness of the Director of the Min.-Geol. Museum of Oslo, Professor J. SCHETELIG, I was able to select my samples in the beautiful collection of the Museum. For the excellent X-ray photographs I am indebted to my teacher of X-ray investigation, Professor Dr. V. M. GOLDSCHMIDT and his two assistants Cand. real. TOM. BARTH and Stud. real. HOLMSEN.

The formulæ of skutterudite and smaltite-chloantite are noted as $CoAs_3$ and $(Co, Ni)As_2$ respectively. The analyses, however, agree only approximately with these formulæ. The analyses of skutterudite give $Co:As \approx$ about $1:2^{3,4}$ (see for inst.: BJARNE SAMDAHL: Analyse des Skutterudits, N. G. T. Bd. VIII. H. 1 2, p. 68, 1925), and in smaltite-chloantite the ratio metal:arsenic is varying within wide limits on both sides of the mean value 1:2. The varieties richest in arsenic show a composition very similar to that of skutterudite, and the opposite extremes are approaching strongly the composition of $(Co, Ni)As$. It therefore looks clear that these minerals are in some manner mixtures, and the true chemical formulæ of the crystallized substances forming them cannot be said to be known. The well-known zonary structure of smaltite shows the variation in composition within the same crystal. VOLKHARDT (Zs, Kr., 14,

407, 1888) found one part of an inhomogenous smaltite to be more easily soluble in acid than the rest of it, and the less soluble part proved to be almost as rich in arsenic as skutterudite. He also found skutterudite to be less soluble than smaltite-chloantite. This may point in the direction that skutterudite is a more well defined mineral than smaltite-chloantite.

For my X-ray-investigation I had prepared several powder-photographs of skutterudite from Skutterud, smaltite from Riegelsdorf, and chloantite from Schneeberg, mostly with Cu-radiation. I also succeeded in preparing a serviceable Laue-photograph of skutterudite \perp 111. The crystals of smaltite and chloantite, on the other hand, proved to be aggregates not fit for the Laue-method; this also may indicate that they are not well defined mineral species.

The first statement is that the powder photographs of skutterudite and of smaltite-chloantite show such a perfect likeness to each other in proportions and intensities, that it is impossible to distinguish between them. See Fig. 1. Only in the dimensions there are slight differences, as will be seen below. This fact already makes it likely that we are dealing with only one crystallized substance, apart from the *Ni*, that partly replaces *Co* in smaltite and chloantite, and which will be unable to bring about any important difference in crystal structure and diffraction pattern, its properties being very nearly like those of *Co*. The varying ratio of metal: arsenic we then have to explain as a result of intermixing with other *Co*, *Ni*, *As*-compounds to varying amounts, and in some irregular manner, so that they do not give rise to particular diffraction patterns.

Careful measurements and calculations of the powder photographs show that all the visible lines (about 40) are perfectly explained by a cubic arrangement of the atoms, as it is also to be expected from our crystallographic knowledge of the minerals. The minimal unit length is $8,17 \text{ \AA}$ for skutterudite and a little larger (about $8,25 \text{ \AA}$) for smaltite and chloantite. The reality of this difference has been proved by means of powder photographs of the minerals in mutual mixture and in mixtures with *Na Cl*. The Laue-photograph states that the unit found for

skutterudite is also the correct one. As mentioned the crystals of smaltite and chloantite proved not fit for the Laue method; but in view of the perfect agreement between the powder photographs it must be permissible to treat the found unit cells of smaltite and chloantite as the correct ones also. Calculating the number of molecules in a unit one finds that 8 Co As_8 and 16 Co As give good agreements, while Co As_2 (resp. Ni As_2) is not at all fit for a cubic cell of the size mentioned (provided that the atoms were not equivalent, which is, of course, a possibility). We consequently now have to try the cubic space groups, which allow equivalent positions of 8 *Co* (resp. *Ni*), 24 *As*, and those which allow 16 *Co* (*Ni*), 16 *As*. A limitation of the number of possible space groups is reached by means of the following facts. For every one of the lines of the powder photographs the sum of $(h^2 + k^2 + l^2)$ is an even number; consequently we have to deal with body centered cubic lattices (Γ_c''). (Assuming the "reflecting" powers of *Co*, *Ni*, and *As* to be nearly equal, there is the possibility of simple lattices centering each other; this, however, looks rather improbable). Then there is the symmetry of the Laue photograph, which is prominently hemihedric. After combination of these facts there remain the following possibilities:

$$T^3 (8 \text{ Co}, 24 \text{ As}); T^5 (8 \text{ Co}, 24 \text{ As}); T_h^5 (8 \text{ Co}, 24 \text{ As}); \\ T_h^5 (16 \text{ Co}, 16 \text{ As}),$$

T^3 and T^5 belonging to the cubic tetartohedry (Tetrahedral pentagonal dodecahedral class) and T_h^5 to the paramorphic hemihedry of the cubic system (Diacisdodecahedral class). An examination of T_h^5 for the special case of 16 *Co*, 16 *As* (only possibility: 16 *d*; see R. W. G. WYCKOFF: The analytical Expression of the Results of the Theory of Space-Groups, Washington 1922) shows that this arrangement must always give rise to a holohedric Laue photograph; and thus this possibility is eliminated. So there remains Co As_8 , resp. $(\text{Co}, \text{Ni}) \text{ As}_8$ or Ni As_8 , as the only formula of the lattice-forming substance of skutterudite and smaltite-chloantite to be tried. The possible space-groups are

still T^3 , T^5 and T_h^5 , and we have to place 8 *Co* (*Ni*) and 24 *As* in the unit cell. To prove strictly the impossibility of two of these space groups is a hopeless task, because of all the variable parameters one has to deal with. In T^3 and T^5 the positions of the metal atoms are defined by (u), and those of the *As* atoms by (x, y, z), x, y and z being all different from each other. The only thing one can do to limit the problem is to make the space groups in question more or less probable by means of geometrical and mechanical considerations. As the space group T_h^5 is simplest and gives a very harmonic picture when looked at directly, it was natural to try at first if it would explain the observed facts.

The only set of positions to be tried is then (WYCKOFF: op. cit.):

8 *Co* (*Ni*)

$$(8e) \begin{array}{cccc} \frac{1}{4} \frac{1}{4} \frac{1}{4}; & \frac{1}{4} \frac{3}{4} \frac{3}{4}; & \frac{3}{4} \frac{1}{4} \frac{3}{4}; & \frac{3}{4} \frac{3}{4} \frac{1}{4}; \\ \frac{3}{4} \frac{3}{4} \frac{3}{4}; & \frac{3}{4} \frac{1}{4} \frac{1}{4}; & \frac{1}{4} \frac{3}{4} \frac{1}{4}; & \frac{1}{4} \frac{1}{4} \frac{3}{4}. \end{array}$$

24 *As*.

$$(24d) \begin{array}{l} 0u\nu; \bar{\nu}0u; \frac{1}{2}, u + \frac{1}{2}, \nu + \frac{1}{2}; \frac{1}{2} - \nu, \frac{1}{2}, u + \frac{1}{2}; \\ 0\bar{u}\bar{\nu}; \nu0\bar{u}; \frac{1}{2}, \frac{1}{2} - u, \frac{1}{2} - \nu; \nu + \frac{1}{2}, \frac{1}{2}, \frac{1}{2} - u; \\ 0u\bar{\nu}; u\nu0; \frac{1}{2}, u + \frac{1}{2}, \frac{1}{2} - \nu; u + \frac{1}{2}, \nu + \frac{1}{2}, \frac{1}{2}; \\ 0\bar{u}\nu; \bar{u}\bar{\nu}0; \frac{1}{2}, \frac{1}{2} - u, \nu + \frac{1}{2}; \frac{1}{2} - u, \frac{1}{2} - \nu, \frac{1}{2}; \\ \nu0u; u\bar{\nu}0; \nu + \frac{1}{2}, \frac{1}{2}, u + \frac{1}{2}; u + \frac{1}{2}, \frac{1}{2} - \nu, \frac{1}{2}; \\ \bar{\nu}0\bar{u}; \bar{u}\nu0; \frac{1}{2} - \nu, \frac{1}{2}, \frac{1}{2} - u; \frac{1}{2} - u, \nu + \frac{1}{2}, \frac{1}{2}. \end{array}$$

It is seen that the positions of the metal atoms are fixed, while those of the *As* atoms are defined by two variable parameters. The structural amplitude is most simply expressed as follows:

$A =$

$$\begin{aligned} 2 \text{Co}(\text{Ni}) & \left[e^{\frac{\pi}{2} i(h+k+l)} \left(1 + e^{\pi i(k+l)} + e^{\pi i(h+l)} + e^{\pi i(h+k)} \right) \right] + \\ & + 4 \text{As} [\cos 2\pi(ku + lv) + \cos 2\pi(ku - lv) + \\ & + \cos 2\pi(h\nu + lu) + \cos 2\pi(h\nu - lu) + \cos 2\pi(hu + kv) + \\ & + \cos 2\pi(hu - kv)], \end{aligned}$$

where *Co*(*Ni*) and *As* stand for their atomic numbers respectively. In search for a serviceable set of parameters it proves useful

to notice that the diffraction effect corresponding to (400) is invisible in all the photographs. Putting the amplitude of (400)

0, there result the following values (among others) of the parameters:

$$u \quad 0,1079, \quad v \quad 0,1421.$$

This value of u would claim extremely small atomic radii; we therefore go to the next larger value satisfying our condition, the value of v being fixed, which is

$$u = 0,3579.$$

It will be noticed that the sum of these values of u and v is exactly $= \frac{1}{2}$. A look at a model or drawing makes it highly probable that $u + v$ is really $= \frac{1}{2}$, for the structure contains groups of four neighbour arsenic atoms, forming the corners of rectangles, and only when $u + v = \frac{1}{2}$ these rectangles become squares, and only in this case the equilibrium of the lattice is quite simply explained. For the actual calculation of intensities were therefore chosen the values of

$$u \quad 0,35, \quad v = 0,15.$$

The corresponding atomic distances are: $As \quad As = 2,44 \text{ \AA}$, $Co \quad As = 2,34 \text{ \AA}$. The calculation of the intensities of the powder photographs was carried out by means of the usual formula

$$I = \frac{A^{2*}}{h^2 + k^2 + l^2} \cdot S \cdot \frac{1 + \cos^2 \vartheta}{2 \cos \frac{\vartheta}{2}}$$

With the above values of u and v was reached a very good agreement with the observed intensities all over the photographs. Also a considerable number of Laue-spots were fit for intensity comparisons, and a satisfactory agreement with the calculated intensities was found in all cases. Especially the comparison of spots corresponding to $(h \ k \ l)$ and $(l \ k \ h)$ was striking. Thus the

* In this special case no imaginary amplitudes are present, as shown in the common expression of the structural amplitude.

diffraction effects of skutterudite and smaltite-chloantite are perfectly explained by the atomic arrangement described, and even with the above values of the parameters. A comparison of certain intensities in the Laue photograph shows that the correct values of the parameters must be very nearly equal to those mentioned, a small change in the third place being already sufficient to spoil the agreement in these particular cases.

To be mentioned is a matter concerning the "reflecting power" of *Co*. V. M. GOLDSCHMIDT and his collaborators have in some cases observed that the *Cu-K α* -radiation does not interact in the usual manner with *Co*-lattices (and also *Fe*-lattices.) The intensities of the diffraction effects have been diminished, and the common blackening increased, an effect which is also to be expected theoretically. The properties of this effect are not sufficiently known; but in the case of skutterudite and smaltite-chloantite it is obviously present. In spite of the good agreement of the observed and the calculated intensities, the lines containing *Co*-diffraction effects show a tendency in the direction to be expected, whether the amplitude of the *Co*-lattice is to be added to that of the *As*-lattice, or it is to be subtracted from it. Also the common blackening of the films is unusually intense. A comparison with a *Fe*-radiation photograph to some amount confirms the existence of this effect of the *Cu-K α* -radiation.

From the results reached we have to conclude that the crystallized substance forming the lattice of skutterudite and smaltite-chloantite is *CoAs₈*, or *NiAs₈*. But as the natural minerals are never sufficiently rich in arsenic to satisfy these formulæ they must always be more or less intermixed with a non-crystalline, or anyhow non-diffracting, substance, it may be pure metal or lower arsenides. To find out the true nature of this "foreign" substance will probably be very difficult; one might possibly reach a result through a modification and refinement of the above mentioned experiment of VOLKHARDT. This would be of interest in order to find out the rôle of *Ni* in different varieties of smaltite and chloantite. At present we cannot tell to which amount *Ni*-atoms are placed in the lattice

of $(Co, Ni) As_3$ in different cases, the composition of the "foreign" substance being unknown. Yet the larger unit lengths of smaltite-chloantite varieties compared with that of skutterudite makes it probable that *Ni*-atoms are playing an important part in the lattices of the former ones, the "atomic radius" of *Ni* being empirically a little larger than that of *Co*. On the other hand we have to take account of the possibility, that the large amount of "foreign substance" in many smaltite-chloantite varieties may in some manner be able to expand the lattice. This question may perhaps be answered through a calculation if the unit lengths of a large number of carefully analyzed and examined samples.

LEWIS S. RAMSDELL (The American Mineralogist., Vol. 10, No. 9, september 1925. p. 296) recently published a paper, among other things also dealing with the crystal structure of smaltite-chloantite. Because of his maintaining of the formula $(Co, Ni) As_2$ he reached no final result, for he then met with the very same difficulty as I did myself. He states that his samples of skutterudite are giving the $Co As_2$ pattern, and so he concludes that they are really smaltite. My own result is, as shown, the directly opposite, that the pure crystallized substances of smaltite and chloantite must be analogous to that of skutterudite, which must be again $Co As_3$.

It will be seen that the crystal structure of this group of minerals is entirely different from that of pyrite, a fact which is also stated by RAMSDELL.

Summary.

The diffraction effects of skutterudite are in perfect agreement with the following crystal structure:

Cubic. Unit length $8,17 \text{ \AA}$. A unit containing 8 molecules $Co As_3$.

Space group: T_h^5 , belonging to the diacisdodecahedral class.

Positions: 8 *Co* (8*e*), 24 *As* (24*d*). Parameters fixing the positions of the arsenic atoms: $u = 0,35$, $v = 0,15$, ($u + v = \frac{1}{2}$).

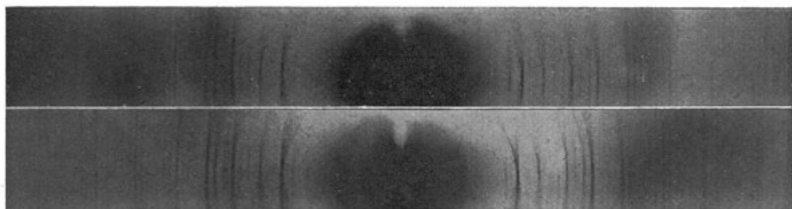


Fig. 1. Powder Photographs of Skutterudite (above) and Smaltite. *Cu*-radiation. The diameters of the two cameras used are nearly equal.

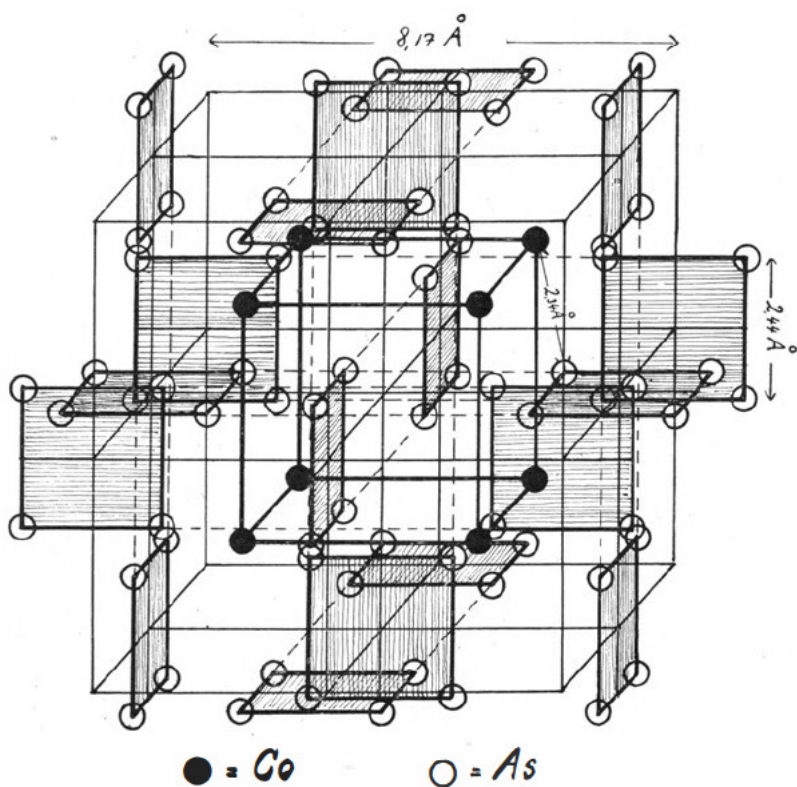


Fig. 2. Unit Cell of Skutterudite. In order to show the groups of arsenic atoms and their symmetry a number of arsenic atoms belonging to the neighbour cells are included.

Atomic distances: $As-As$ 2,44 Å; $Co-As$ 2,34 Å.

Structure composed of body centered cubic lattices.

The diffraction effects of smaltite-chloantite being in every detail analogous to those of skutterudite, there must also be a perfect analogy as to the crystal structures. The unit lengths of the smaltite-chloantite-minerals are a little larger than that of skutterudite about 8,25 Å. This structure necessitates the conclusion that the general formula of the pure smaltite-chloantite-minerals is $(Co, Ni) As_3$; the existence of cubic compounds $(Co, Ni) As_2$ is then made highly improbable. Smaltite and chloantite thus really are skutterudites, in which various amounts of Ni are replacing Co . The natural minerals always contain more or less of pure metal or lower arsenides in solid solution, or at least in a state not giving rise to diffraction effects.
