NOTE ON THE CRYSTAL STRUCTURE OF COBALTITE

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Early X-ray studies showed that the crystal structure of cobaltite must be closely related to that of pyrite. The space group of pyrite is Pa3, and the unit cell contains 8S. In cobaltite these must be replaced by 4As+4S, and this leads inevitably to the space group $P2_13$. MECHLING (1921) realized this, and it was consequently assumed that cobaltite (and gersdorffite) had the same crystal structure as ullmannite, whose external crystal form was known to agree with the point group 23. This symmetry could not, however, be taken as finally established for cobaltite and gersdorffite, as the indications of the available X-ray photographs were not conclusive. But it was adopted, more or less tentatively, by W. L. BRAGG (1937) and apparently by most crystallographers. It was abandoned by PEACOCK and HENRY (1948), who proposed a disordered arrangement of the As and S atoms so that a structure of strict pyrite type resulted; they used powder photographs only. Later ONORATO (1957) has studied the cobaltite structure by more refined X-ray methods. He re-established that the structure is not of pyrite type and proposed a particular kind of ordering of the As and S atoms which is possible only if the cubic symmetry is abandoned (see below). The pyrite type structure proposed by Peacock and Henry seems to have been adopted to some extent. Thus in the 1957 edition of Mineralogische Tabellen by H. STRUNZ the space group of cobaltite and gersdorffite is given as Pa3, that of ullmannite as $P2_13$. (Onorato's results were hardly available then).

Many years ago I spent a large amount of work on the crystal structure of cobaltite, but no report was published, since my main result was in principle a confirmation of the structure proposed by Mechling. However, since the inadequacy of the space group Pa3 is not yet generally recognized, it may be of interest to quote a few pertinent data from my early work. I had a number of powder photographs of cobaltite, gersdorffite and ullmannite and an excellent Laue photograph of cobaltite parallel to a cube face of a very perfect crystal from Skutterud (Fig. 1).

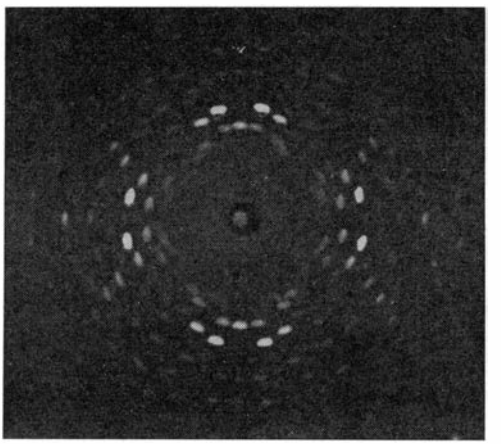

Fig. 1. Laue photograph of cobaltite || 100.
Taken by T. F. W. Barth 1925.

The indexing of the powder photographs according to the cubic unit cell ($a_0 = 5.570$Å for the cobaltite) showed definitely the presence of 301; it is represented by a very weak line in the photographs of cobaltite and gersdorffite and by a fairly strong line in those of ullmannite. Indices of this type — odd, 0, odd — exclude the space group Pa3 and indicate $P2_13$. The Laue photograph contains several spots with similar indices (301, 031, 501, 051), but these are not conclusive, since they include the corresponding second orders (602, etc.). The same applies to 401, which is represented by fairly strong spots and which is not compatible with Pa3; it may in reality be 802. In addition the Laue photograph shows indices like 061, 702, 902, but not 601,

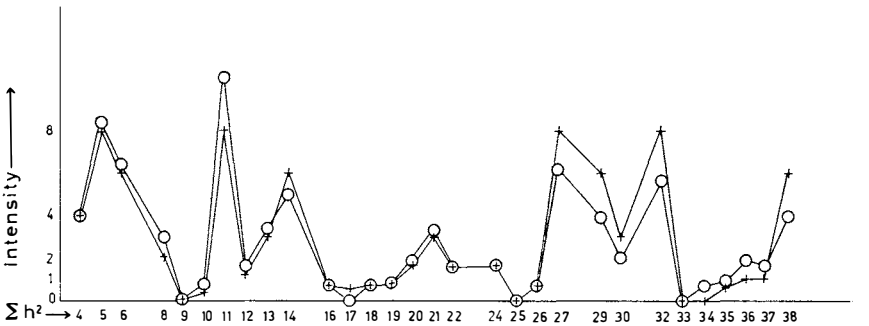

Fig. 2. Comparison of calculated (rings) and estimated (crosses) intensities for powder photographs of cobaltite (and gersdorffite).

072, 092, and this is in favour of Pa3. On the whole it is certainly no easy matter to discover in the Laue photograph features which will definitely exclude the space group Pa3.

Therefore the relationship between the structures of cobaltite and pyrite must be very close indeed. Assuming, according to the space group $P2_13$, As—S pairs of similar dimensions and positions as the S--S pairs in pyrite, the parameters can be adjusted so as to make the observed and calculated intensities agree very well for powder photographs of cobaltite (and gersdorffite) (Fig. 2). But this does not mean that the correct parameter values have been found, for the Laue photograph contains many finer details which I have not been able to explain. It is possible that a satisfactory set of parameter values may be found, so that the structure proposed first by Mechling is in principle correct. On the other hand my material of observations contains nothing which would exclude a solution of the kind proposed by Onorato. At any rate it appears that some kind of order must exist in the mutual arrangement of the As and S atoms.

It has been shown by SCHNEIDERHÖHN (1922), and is easily observed by anyone, that cobaltite exhibits anisotropy under the ore microscope. Thus the mineral is not strictly cubic in spite of the evidence of X-ray photographs. ONORATO (l.c.) was able to show that also X-ray studies indicate a non-cubic symmetry; he arrived at the result that cobaltite must be monoclinic. P. CHR. SÆBØ, now working in this Institute, found in powder photographs of cobaltite that some lines with high indices were split into several very close (overlapping)

components. He will report on his work later. It is evident that though cobaltite is not cubic (at room temperature) the deviation of the unit cell from cube shape must be exceedingly small.

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