ZnS MINERAL WITH ZnS-3R CRYSTAL STUCTURE

By

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Some years ago a new rhombohedral crystal modification of ZnS was found by *Buck* and *Strock* [1] in applying a heat treatment on sphalerite crystal powder in vacuo at temperatures between 600—1100° C. The new modification appeared mixed up with sphalerite and could be identified by the splitting of the reflection (111) of the latter. According to the above authors, the new modification is brought about when at higher temperatures (above 600°C) a greater temperature expansion occurs in the direction of one of the body diagonals of the cubic unit cell of sphalerite than in the other three directions and the cubic symmetry decreases therefore to a rhombohedral one. The close packed atomic planes remain essentially unchanged after the structural transformation, only their distances increase a little and at the same time the atomic distances within the planes decrease to a certain degree. An interpretation for this phenomenon is given by *Buck* and *Strock* in the elongation of the electron distribution of the S atoms in the favoured direction [111] in the temperature interval given above.

Disregarding deformations of a smaller degree the unit cell of the rhombohedral lattice is the rhombohedron which can be drawn into the unit cell of the sphalerite lattice. Since in this three closed-packed atomic planes are present, according to *Buck* and *Strock* this new modification is designated by ZnS—3R.

The hexagonal cell corresponding to this rhombohedral lattice can be given with the axes a_1, a_2, a_3 of the cubic cell of sphalerite expressed by the following axes transformations:

$$\bar{a}_H = \frac{1}{2}(-\bar{a}_1 + \bar{a}_2)$$

$$\bar{b}_H = \frac{1}{2}(-\bar{a}_2 + \bar{a}_3) \qquad (1)$$

$$\bar{c}_H = \bar{a}_1 + \bar{a}_2 + \bar{a}_3$$

On the basis of this, the axis of the hexagonal unit cell calculated from the undistorted sphalerite lattice ($a_1 = a_2 = a_3 = 5{,}412$ Å) are

$$a'_H = 3{,}827 \text{ Å}$$
$$c'_H = 9{,}374 \text{ Å}$$

On the other hand, the authors have obtained

$$a_H = 3,82 \text{ Å}$$
$$c_H = 9,42 \text{ Å}$$

by a rotation x-ray diffraction photograph of a single crystal grown between 800 and 850° C.

According to *Buck* and *Strock,* the ZnS—3R crystal modification occurs above 600° C and remains in this structure up to 1020° C. In the meantime the structure shows a monotonous expansion with temperature in the direction of the axis *c* and a contraction along the axes *a* which lead to a monotonous variation of the axial ratio. This variation is the most rapid between 900 and 1000° C. After cooling, this structure remains in a metastable form even at room temperature and, by a mechanical effect, it is reversed to sphalerite in the same way as wurtzite (ZnS—2H). It is inverted to sphalerite also when cooling occurs very slowly. According to *Buck* and *Strock* the quicker the cooling the greater is the amount of the remaining metastable ZnS—3R and the axes lengths show the best approximations to those which have been convenient at the temperature before cooling. In their samples, sphalerite has been always present on account of the incomplete transformation or reversion, respectively, during cooling. At temperatures above 1020° C ZnS—3R is inverted into wurtzite (ZnS—2H). In the latter case, because of incomplete transformations in the samples, all three ZnS crystal modifications were obtained. The reflexions (003) and (101) of ZnS—3R as well as the reflexion (002) of ZnS—2H appeared superimposed on the reflexion (111) of sphalerite on the x-ray photograph of this material and corresponding to this four peaks emerged from the interference.

Koch [2] found yellowish-brown coloured ZnS—crystals embedded in the quartz and calcite of *Gyöngyösoroszi* (Hungary). A considerable part of these are crystal agglomerates grown to hexagonal pyramidal formations (the crystal needles show an inclination about 5—6° to each other), in smaller amounts, however, they form needle-shaped hexagonal prismatic single crystals. According to *Koch* the major part of ZnS is anisotropic. The single crystal needles themselves are isotropic in some sections in the direction of the needle axis, and on the other places anisotropic. The latter sections have to be cosidered as being crystal modifications different from sphalerite.

Crystal needles about 0,1 mm thick and 1 mm long obtained from *Prof. Koch* have been investigated. The needles showed between crossed nicols a double refraction on their whole length. With two needles the brightening was uniform and of medium intensity along the whole length during rotation. The third needle, however, shows also a section at which, with a sudden transition, a brightening of multiple intensity could be observed.

From oscillation x-ray photographs obtained for the crystal needles and the pyramidal crystal agglomerates we found that, in every case, the crystallographical identity was 9,4 Å in the direction of the axis of the needles, while perpendicularly to this in the direction through the opposite edges it was 3.8 Å. This corresponds to the
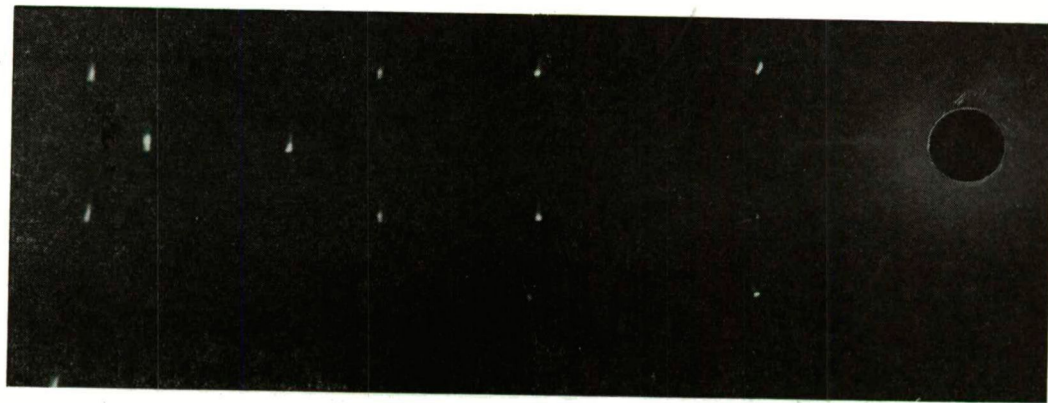
Fig. 1. Oscillation X-ray photograph of ZnS—3R, axis of oscillation c_H.

hexagonal cell which could be placed into the sphalerite lattice and has to say that, in their natural occurrence any crystal needles showing anisotropy belong to the ZnS—3R modification, which has been artificially prepared by *Buck* and *Strock.* This was the first case in which it has been possible to indentify the ZnS—3R crystal modification in natural occurrence.

After having indexed the x-ray reflexions appearing on the oscillation x-ray diffraction photographs on the basis of the hexagonal cell, these indexes were transformed according to equation (1) into the cubic cell. In this way it could be shown, that there exist many of reflexions which on the basis of the hexagonal indexes do not correspond to rational planes of the cubic cell. Since the hexagonal cell is not a rational one, we cannot expect that all its rational planes should also be rational ones of the cubic cell, but all apparent reflexions must belong to a rational plane of the cubic cell. The previous anomaly is suspended as soon as the sign of the hexagonal index l will be changed for all reflexions of which the transformation do not lead to rational cubic indexes since then also for these hexagonal indexes the transformation gives rational cubic indexes. The crystal needles are therefore twinned crystals with oppositely directed c axis.

Considering the external appearance of the x-ray reflexions they are found to show an elongated diffuse ground perpendicularly to the equator and beside this, parallel to the equator and sometimes perpendicularly to it they desintegrate into multiple reflexions which can be particularly well observed in the direction of greater angles. (Fig. 1.) This phenomenon is much better evident on the original film than on the reproduction.

As it was already stated, the crystals show on some spots a medium, on others a strong double refraction with a sudden transition. An interpretation for this may be the presence of pure anisotropic modification at places where the strong double refraction occurs, while at the spots of medium brightenings isotropic and anisotropic portions are alternating. This, however, takes place in form of so small volume elements that only uniform brightenings with less intensity are observable. This follows from the observations of *Koch* [2] too, who was able to detect, betwen crossed nicols, very strong brightened as well as entirely dark crystal sections with sudden transitions on considerably smaller crystal needles as mentioned above.

In the latter case the conditions of originating or structural transformation, resp., have been such that the crystal was entirely transformed in some spots in one or another direction, in the other section it remained in its previous modification. This kind of transformation was realized for every varying volume element of our somewhat greater crystals investigated by X-rays. ZnS—3R and sphalerite modifications could be found alternately in the crystal and show identical orientation with regard to closely packed planes building up the lattice, since no change in the direction of this close packed planes takes place during transformation. On account of the dilatation in the direction of the axis c of ZnS—3R and the contraction perpendicularly to it, stresses occur

in the complex crystal. Koch, however, found some very fine crystals with medium double refraction too which probably show an anisotropic core with a sphalerite sheet grown around it. If this crust has grown later, then, beside the above mentioned, also a desorientation of the two crystal modifications has to be assumed to a certain extent. By the joint effect of stress and desorientation the elongated diffuse ground of the reflexions, which apparently sometimes also shows an inclination to follow the direction of the interference rings, may be explained.

The occurrence of sphalerite and ZnS—3R side by side in almost identical direction but with slightly deviating crystallographical axes, referred to the same kinds of unit cells, may also serve as an explanation for the doubling of interferences in the direction parallel to the equator.

In the rhombohedral modification of ZnS—3R the identity perpendicular to the close packed atomic planes is three times as long as the distance of two adjacent close packed atomic planes and therefore the sequence of the atomic planes could only be as ABCABC..., i.e. the same as it is known with the cubic close packing. Thus ZnS—3R may not be regarded as being a lattice with a one-dimensional defective order according to *Jagodzinski* [3, 4, 5], but on the basis of our present knowledge the appearance of the rhombohedral symmetry has to be considered as being the consequence of the deformation of sulfur atoms according to *Buck* and *Strock*. For a more definite decision in this question, our investigations will be continued.

The author wishes to express his thanks to *Professor Alexander Koch who* has drawn his attention to this investigation and who furnished the crystals.

SUMMARY

The yellowish-brown ZnS crystal needles grown together with sphalerite in identical orientation belonging to the collection of *Prof. Koch* (Szeged, Hungary) and coming from *Gyöngyösoroszi* (Hungary) are the first natural occurences of the ZnS—3R crystal modification which has been artificially prepared by *Buck* and *Strock*. In hexagonal prismatic crystal needles two crystal modifications in alternation appear, in most cases always in the same direction bringing about a stress in the macroscopical crystal and causing a diffuse ground at the X-ray reflexions. To explain the appearance of all the reflections on the oscillation photographs one has to suppose a twinning with oppositely directed *c* axis.

LITERATURE

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