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STRUCTURAL DISORDER IN NATURAL CUBIC HGS

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ABSTRACT

Cubic HgS crystals (loc.: Róka-hegy, Budapest, Hungary) were examined from the crystallographic point of view. The SAED patterns revealed structural disorder. The measure of the disorder, namely the ratio of the hexagonal close packed lamellae in the cubic close packed host was determined by using the Pandey-Lele method (1986). The sample examined can be characterised by low fault concentrations and relatively high growth probability by the calculations. The ratios of the hexagonal layers vary between 30-50%. The traces of structural deformation were observed on etched surfaces.

INTRODUCTION

The sphalerite-wurtzite system has the best-known structural properties among the sulphide compounds of II.B elements (MARDIX, 1986; FLEET, 1976, 1983; AKIZUKI, 1983; PÓSFAI et. al., 1988). The representatives of the close packed structure types are the common forms of ZnS, sphalerite (fcc) and wurtzite (hcp). The different stacking orders in the polytype modifications imply different physical properties too.

Other II.B sulphides are less investigated. There is one mentioned polytypic form of cubic CdS without description of its symmetry, and there were no traces of structural disorder found in the case of HgS (RAI et al., 1972). The structural disparities can be deduced from the different electron configurations. While the stable form of ZnS is the tetrahedrally co-ordinated sphalerite, the cubic HgS because of the presence of the 4f electrons results metastable. The cinnabar has distorted NaCl structure that is common in the nature.

In this paper we report the structural disorder of the cubic HgS and the calculated hexagonality of the sample.

THE SAMPLE AND THE EXPERIMENTAL METHODS

The sample is from a hydrothermal ore bearing carbonate vein, from Róka-hegy, Budapest, Hungary. The specimen was obtained by acidic solution, it was ground and mounted in suspension onto a Cu grid covered with graphite film. The SAED patterns were obtained by using a JEOL JEM 100U microscope at 100 kV and 120 mA. High rate of damaging caused by the electron beam was characteristic.

The X-ray data were obtained on a Siemens D5000 powder diffractometer (Bragg-Brentano geometry, scan mode: 4.8 sec/0.02°).

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The etched surface (30% c. aqua regia, 1 min) was observed with ore microscope and a Hitachi S-2300N scanning electron microscope operating at 20 kV, 100 mA.

For the calculation of the diffracted intensity with known input parameters a C program was used.

RESULTS AND DISCUSSION

Disorder in face-centered cubic HgS

The orientation of the crystals on the electron diffraction patterns (Fig. 1.) is the same: the electron beam is parallel to the zone axis [110]. This is the adequate orientation for examining the sequence of the layers of the fcc structure perpendicular to [111] direction (Fig. 2.). The electron diffraction patterns reveal through the presence of cinnabar, metacinnabar also the disordered metacinnabar phase as it can be seen on Fig. 1.

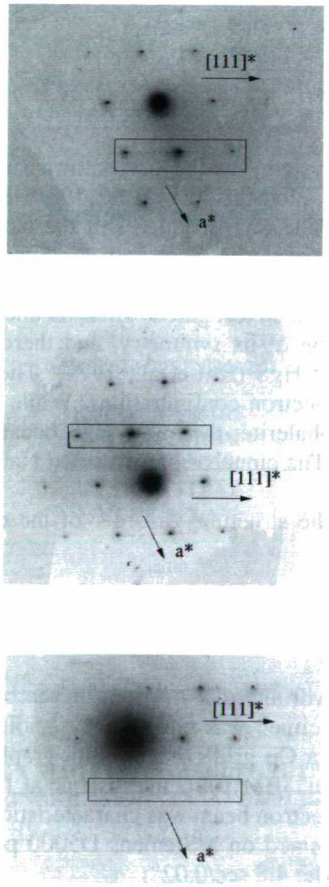

Fig 1a-c. SAED patterns of disordered metacinnabar. Intensifying diffuse streak in direction a → b → c along the 111* axis. Satellite reflections appear on the third pattern.

On the SAED patterns a diffuse streak is observable parallel to the 111* axis. It's intensity increases in the direction a → b → c. On Fig. 1c. nor yet separate satellite reflections arise in the vicinity of the 11$\bar{1}$ 220 113 and 002 reflections. That is indicative of the disruption of the fcc's characteristic stacking sequence ABCABC.... , and at the same time the condensation of hexagonal close packed lamellae (Fig. 3.).

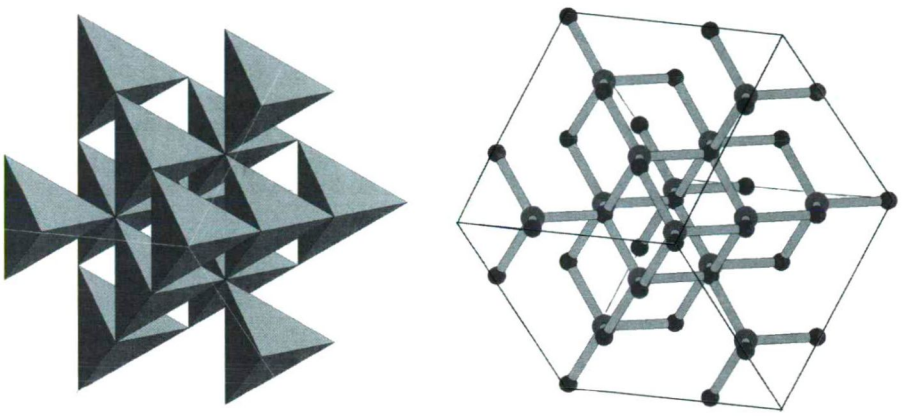

Fig. 2. Crystal structure of metacinnabar, face centered cubic structure viewing from the [111] direction.

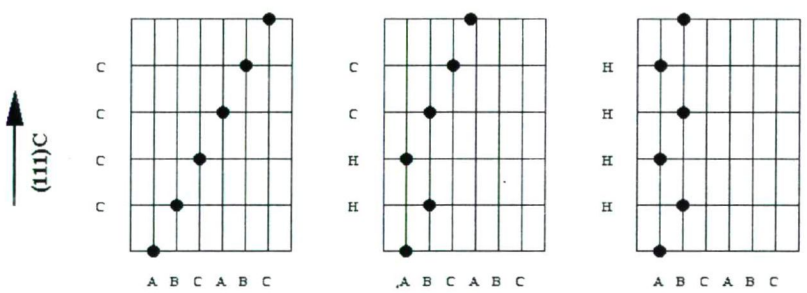

Fig. 3. Relationship between the fcc and hcp structures, appearance of the stacking fault. After Bollmann (1970.), modified.

Method for characterising the disorder

The PANDEY and LELE's (1986.a, 1986.b) model applied to determine the observed disorder's degree of cinnabar-metacinnabar crystals. Although the hcp modification of HgS is unknown in the nature, several aspects account for it's use: the structural analogy between the sphalerite and metacinnabar, the observed phenomena on the diffraction pattern and the reference to a natural γ-modification of HgS (hypercinnabar), with hexagonal symmetry, but without the exact space group determination (POTTER and BARNES, 1978.).

The model describes the different transition stages between the two close packed structures with two probability variants: the fault concentration (α) and the fault's growth probability (β). These two parameters can be calculated by measuring the diffracted

intensity along a given direction. The measurement was made along the direction 111* in the surroundings of the marked reflections on Fig. 1. The measured intensity is shown on Fig. 4.

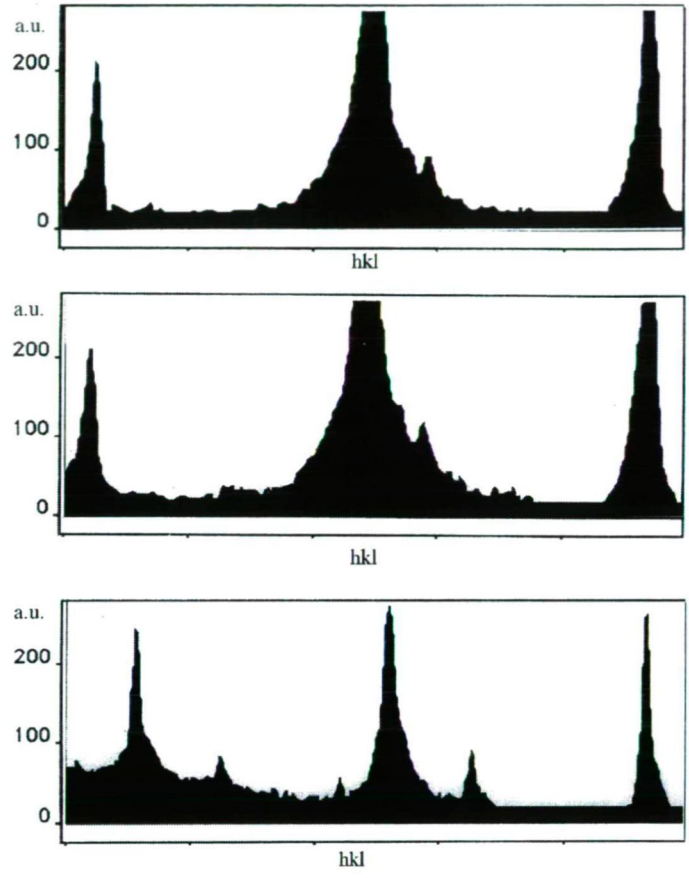

Fig. 4a-c. Measured diffracted intensity in the surroundings of the marked reflections of Fig. 1.

On the first intensity profile (Fig.4.a) a moderate asymmetric broadening of the reflections can be seen, which intensifies in the next profile (Fig. 4.b) where a small additional shoulder appears too in the vicinity of the reflection 113. Fig. 4.c shows a completely separated satellite near the main reflection 113 (or 1$\bar{1}$1) and both of them are considerably sharper than the profiles of the same reflections on Figs. 4.a and 4.b. With the appearance of the well defined satellite there is also observable the tendency of a slight shifting of the reflection maximum 113 (or 11$\bar{1}$) and 002 (or 220).

Degree of the disorder

Supposing different default conditions characterised with known fault concentration and growth probability data, a set of calculated intensity curves was traced. The best fitting curves and the corresponding input data are shown in Fig. 5.

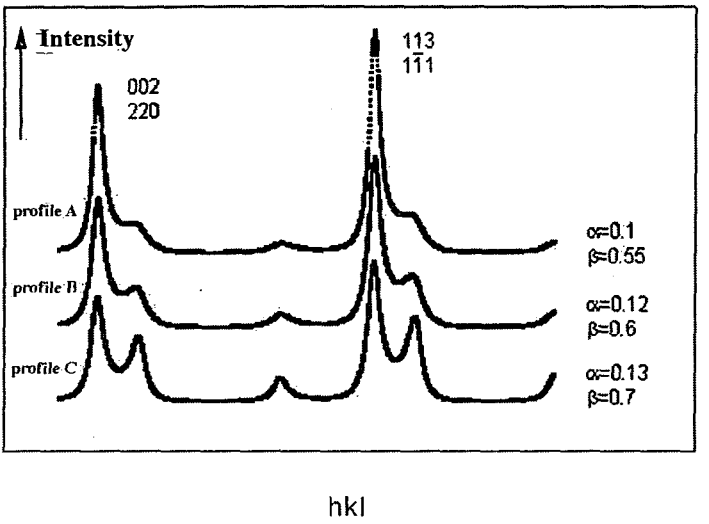

Fig. 5. Calculated diffracted intensity best fitting to the measured one. Parameters are given for all the curves.

All the examined samples are characterised typically with low fault concentration and relatively high growth probability. In the direction profile a.→profile b.→profile c. parallel with the observed intensifying reflection broadening and satellite separating both of the parameters are growing, although the growth rate is different. In spite of the growth the fault probability α in all cases it remains low, it's value varies between 0.1 and 0.13, that means the nucleation rate is moderated. The growth probability's β value is considerably higher, it is between 0.55 and 0.7.

The probability of the appearance of one stacking fault in the cubic structure of the HgS is not significant, but once the fault appeared the growth of the faulted region begins with an elevated probability in average 60-65 %. Basing on this we can deduce that the microstructure of the sample shows thick alternating lamellae of hexagonal and cubic close packing.

The Pandey-Lele's model with known α and β values allows the calculation of the ratio of hexagonal and cubic close packed lamellae using the following equations (PANDEY and LELE, 1986.a):

$$f_C = \frac{1-\beta}{1+2\alpha-\beta},$$

$$f_H = \frac{2\alpha}{1+2\alpha-\beta}$$

where f_C stands for the ratio of the cubic, and f_H for the ratio of the hexagonal layers. Considering the calculated α and β values the resulting data are the following:

f_C (a) = 0.6923	f_H (a) = 0.3077
f_C (b) = 0.6250	f_H (b) = 0.3750
f_C (c) = 0.5357	f_H (c) = 0.4643

The evidency of increasing hexagonality — which means the formation of stacking fault in the cubic host — with increasing fault concentration and growths probability is clearly seen.

The stacking fault arises with the decomposition of partial dislocations. The partials bordering the faulted region repel each other. The shove between them depends on the stacking fault energy. The appearance of the stacking faults is indicative of the enough low stacking fault energy during the crystallisation that allowed the formation of stable partials.

The anomalous profile-distortion on X-ray powder diffraction patterns caused by the structural disorder, because of the close intergrowth of the two HgS phases – the cubic and the trigonal (see Fig. 6.), – doesn't provide facilities in the identifying of hexagonality.

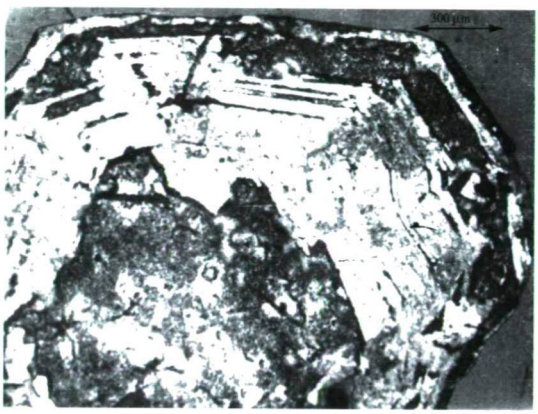

Fig 6. Etched surface of a strongly zoned grain. The core of the grain is homogeneous metacinnabar with resorbed margin. The core is surrounded by thick inclusion-hole rich cinnabar bands and thin inclusion-hole free metacinnabar stripes. Traces of structural inhomogenity are observable in the isotropic core. Ore-microscope photograph || N.

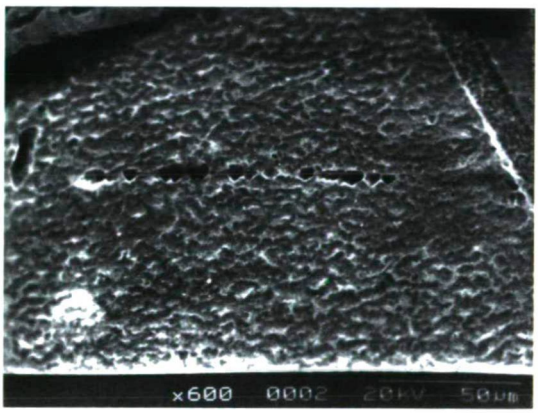

Fig. 7. Traces of structural inhomogenity: narrow stark point-lines and wider shallow bands in the core of the grain in *Fig.6.* SEM photograph.

Etched surface examination

Because of the etching first dissolves the unstable part of the crystal, different structural deformations and partial dislocations which boarder the stacking faults become more conspicuous on etched surfaces. For etching it was used 30% concentration aqua regia during 1 minute. The observed etching traces which origin sometimes is doubtful are shown on Figs. 6. and 7.

SUMMARY

Cubic HgS crystals (loc.: Róka-hegy, Budapest, Hungary) were examined from the crystallographic point of view. The main aim of the work was to observe structural disorder, stacking faults, and/or polytypic stacking. Our results can be summarised in the followings.

The SAED (Selected Area Electron Diffraction) method proved to be the most adequate method for the observation of the structural feature. By the diffraction patterns the sample examined consists of cinnabar, metacinnabar, and disordered metacinnabar. Disorder was not observable with X-ray powder diffraction method.

The disorder revealed to be hexagonal close packed lamellae in cubic close packed host. The stacking faults are supposed to be traces of dislocation reactions. By the calculations the sample can be characterised by low fault concentration and relatively high growth probability. The ratios of hexagonal layers vary between 30-50%. By increasing of the two probabilities variable increase the density of the hexagonal close packed layers.

Scanning electron microscopy and ore microscopy was applied to observe partial dislocations at the vicinity of the faulted regions.

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