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Microhardness Anisotropy in Cubic and Hexagonal ZnS Single Crystals

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Microhardness anisotropy of hexagonal and cubic ZnS crystals grown from the vapour-phase has been investigated.

Experimental data have been analysed by statistical methods and it has been established that ZnS shows remarkable work-hardening.

Whatever the crystal structure, on close-packed planes, it was not possible to observe microhardness anisotropy in different crystallographic directions (type A anisotropy). However, in both cubic and hexagonal crystals, on prism planes, type A anisotropy could often be seen. In both types of crystal, between the close packed and prism planes, a remarkable microhardness anisotropy could be measured on different planes (type B anisotropy). The value of this type B microhardness anisotropy was dependent on the degree of contamination of the crystal.

On the basis of the measurements made it was established that the microhardness of ZnS follows the Meyer law.

1. Introduction

The measured values and anisotropy of the microhardness of a given material can give information on its plastic and other physical and chemical properties. Recently, several such measurements have been published, relating especially to metals and alkalihalides. Considerably less data are available concerning the hardness and hardness anisotropy of semiconductors and semiconducting compounds, i.e. the $A^{II}B^{VI}$ materials [1–4].

The literature available is insufficient and inconsistent compared with that on the metals and alkalihalides. Thus the present paper aims to investigate, using ZnS single crystals, the correlation between microhardness and parameters such as crystal structure, homogeneity, mechanical properties, contamination etc.

2. Experimental

The microhardness of the experimental material was measured by a microhardness tester attached to a Reichert Universal Camera Microscope MeF. The ZnS single crystals used were grown from the vapour-phase by two different methods [5–7] partly by the Research Institute for Technical Physics of the HAS and partly at the Lebedev Physical Institute of the Academy of Sciences of the USSR. As-grown, cleaved, polished, etched, and both etched and polished crystal surfaces were used for the measurements. The investigated surfaces were identified by the measurable interfacial angles, by X-ray methods and by selective chemical etching. Chromic acid, a suitable etchant for $A^{II}B^{VI}$ compounds was applied [8, 9].

The crystal was ground and polished by Al_2O_3 of different grain sizes. All measurements were carried out at room temperature. The load range varied between 8.0 to 170.0 lb, the loading time was 5 sec. Depending on the scatter of the observations each diagonal of indentation was determined as the mean of 20 to 50 observations $\bar{d}$. Under constant load, 8 to 15 indentations were made on every investigated surface. These measurements were reproduced under similar conditions on a series of crystals made and prepared in the same way. The microhardness values were determined from the $\bar{d}$ mean diameter.

A considerable spread of the microhardness values could be observed on identical crystal planes and on crystals of the same character.

Statistical methods [10, 11] were used to find out whether the spread is caused by random errors (i.e. small divergence in the deformation rate, errors in loading, etc.) or whether it is due to significant differences in the crystal itself. The data obtained from the above-mentioned analysis were classed into two groups. The first group contains data characterised by their distribution differing strongly from the normal one. This group contains, for instance, hardness anisotropy of type A, observed on certain ZnS crystals (differing hardness in different directions on a given crystal plane). Results obtained from data showing normal distribution belong to the second group. These data refer respectively to homogeneous crystal regions and to numerous crystals of the same character. Here we are concerned with the data on microhardness anisotropy of type B (hardness difference between different crystallographic planes) and data related to the load dependence of the microhardness.

3. Results

3.1. Effect of Surface Condition on H_v

According to our measurements, the microhardness of the ZnS single crystals, as in metals and ionic crystals, depends to a large extent on surface treatments, such as cutting, grinding etc. Measuring the adequate ranges of the crystals, it was observed that coarse preparation increases the hardness by 5 to 30%. This work-hardening is especially easy to observe on hexagonal {1210} and cubic {110} planes. On the {0001} and {111} planes of the same ZnS crystals the work-hardening is less, and generally it did not surpass 10%. As observed with metals [12] the mechanical polishing and short etching carried out after the cutting and grinding procedure decreases this effect. After diminishing the surface layer by ~ 0.5 μm by etching on cleaved surfaces and mechanically worked crystals, hardness values were obtained similar to those measured on as-grown ones. The data given below refer to surfaces prepared according to the latter method.

3.2. Type A Anisotropy

Anisotropies of type A have been observed on $A^{II}B^{VI}$ compounds especially when scratching CdS and in Knoop hardness measurements [13, 14]. The above results, however, could not be proved by the Vickers method.

Scratches made on certain materials appeared to be in contradiction with the results achieved by the Vickers measurements for the hardness anisotropy of type A. This is why some authors do not consider the difference of the diagonal of Vickers indentation as a real hardness anisotropy. This contradiction is due to slipping processes, causing distortion.

On ZnS, type A hardness anisotropy could not be observed either on cubic or on hexagonal close-packed planes. On the crystal planes perpendicular to the height of the Vickers pyramid the same indentation diagonals were obtained. ($d_1 = d_2$) in every case independently of the orientation of the diagonals. On hexagonal prism planes and cubic {110}, {112} planes a strong anisotropy was observed in the direction of the hexagonal c and cubic ⟨111⟩ axes in many cases. Especially strong anisotropy was observed in the neighbourhood of covering {0001} and {111} planes, as well as in the vicinity of microcracks directed towards ⟨1210⟩, ⟨1010⟩ or ⟨112⟩, ⟨110⟩ and at singular points of unknown origin. If the indentation diagonal parallel to the hexagonal c-axis and the cubic ⟨111⟩ axis is denoted d_{par}, whereas the diagonal perpendicular to these directions is denoted d_{per}, $d_{\text{par}} \neq d_{\text{per}}$ in the vicinity of the above-mentioned places.

The shortening of one of the diagonals is the consequence of the long range depression observable only by sensitive methods [15].

On hexagonal ZnS prism planes this depression is most probably due to {1010} ⟨1210⟩ type slip and dislocation pile-up. Since this phenomenon appears only in certain crystal regions, the latter process plays, most probably, an important role. The increase of the diagonal in direction ⟨0001⟩ seems to be fictitious; $d_{\text{per}} \neq d_{\text{par}}$ is characterising the anisotropy, but not in its original meaning. If we characterise the hardness anisotropy of the first kind with H_{par} and H_{per}, calculated by using values of d_{par} and d_{per} respectively, we obtain

$$\Delta H' = \frac{H_{\text{per}} - H_{\text{par}}}{\bar{H}} = \frac{d_{\text{par}}^2 - d_{\text{per}}^2}{d_{\text{par}} \cdot d_{\text{per}}} . \quad (1)$$

In many cases $\Delta H'$ in the directions of $\langle 0001 \rangle$ or $\langle 111 \rangle$ changes monotonically with l, distance measured from the above-mentioned singular places. A characteristic example is shown in fig. 1. The indentation becomes symmetric if the diagonals of the Vickers pyramid form an angle of 45° with the mentioned directions.

3.3. Type B Anisotropy

After having separated the data showing either strong anisotropy or extreme values, the microhardness measured on certain crystal planes showed a microhardness anisotropy of type B. This anisotropy occurs first of all between the close-packed and the so-called side planes. At a given cooling rate and medium load (38.25 kg) the analysis of H_v values measured on hexagonal $\{0001\}$, cubic $\{111\}$, hexagonal $\{1210\}$, $\{1010\}$ and cubic $\{110\}$, $\{112\}$ planes shows that the hardness values on close-packed and side planes independently of the crystal structure belong to two normal distributions obeying

$$\Phi(H_v) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(H_v - \bar{H}_v)^2}{2\sigma^2}\right] \cdot \quad (2)$$

The curves of the two distributions can be well separated. The $\bar{H}_v$ value depends on previous heat-treatments and on the impurity content of the crystal.

3.4. Effect of Purity

In the case of pure crystals (the total concentration of the heavy metal ions is less than 10^{-4} gMe/gZnS) the mean value of $\bar{H}_v/(\bar{H}_v{}^{B})$ on close-packed planes is 213.0 Kpmm^{-2}; on side planes ($\bar{H}_v{}^{S}$) is 149.0 Kpmm^{-2}. The measured variances are $\sigma_B = 13.3$ and $\sigma_S = 9.8$ respectively. Under the same conditions in the case of crystals highly doped with Cu (Cu concentration is about 10^{-3} gCu/gZnS) the hardness values shifted strongly. For $\bar{H}_v{}^{B}$ and $\bar{H}_v{}^{S}$ the values 196.0 and 156.0 Kpmm^{-2} were obtained (due to the precipitation of Cu_2S; the effect of higher Cu concentration has not been examined).

Fig. 2 shows the distribution curves. As can be seen, impurities, especially precipitates similar to other materials, increase the ZnS hardness on side planes (see fig. 2 and table I), whereas on close-packed planes an anomalous hardness decrease can be measured. This shows that crystals with high Cu-content are affected by new slipping systems, inactive in pure crystals.

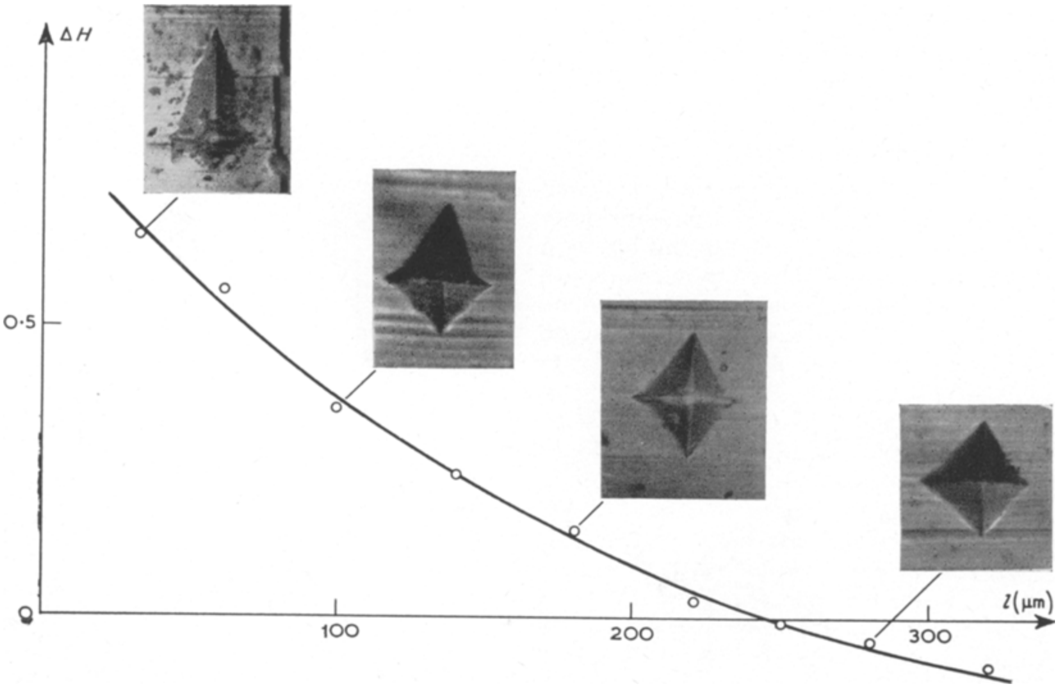

Figure 1 Microhardness anisotropy as a function of distance measured from a given place with extremely high microhardness.

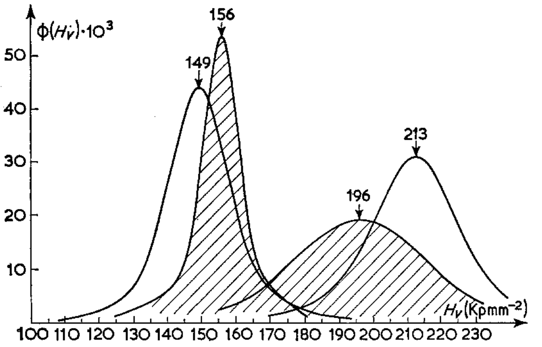

Figure 2 Microhardness distributions on different crystallographical planes of ZnS. The striated area belongs to ZnS crystals with very high Cu contamination.

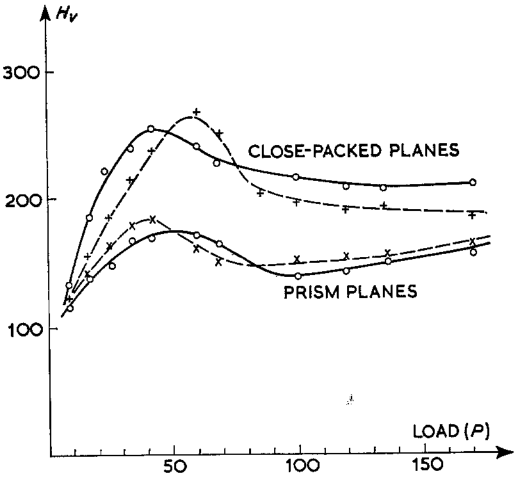

Figure 3 Load dependence of ZnS microhardness: full lines, pure ZnS crystals; dotted lines, Cu-activated crystals.

TABLE I

Rate of cooling ° C/min	On close-packed planes $\bar{H}_v{}^B$	On side planes $\bar{H}_v{}^S$
17.0	200.5	133.5
1.7	203.5	135.0
0.8	210.0	138.5
0.8 (high Cu content)	196.0	155.0
0.8 (heat-treatment)*	216.0	146.0

*The crystals were held at 900° C for 10 h in a neutral atmosphere. After this heat-treatment the crystals were cooled down with the cooling rate applied in the growth process itself.

3.5 Load Dependence

Because of the type B anisotropy the load dependence of H_v was measured on both close-packed and side planes. This anisotropy observed in ZnS single crystals differs from the anisotropy observed in materials with a diamond lattice (Si, C) [19, 20] since the close-packed planes are the hardest in ZnS. All H–P curves show a definite maximum at low loads. In the case of pure crystals the maximum value of H_v appears at the same load, whereas in highly doped crystals these maxima appear at different loads. The dispersion of the measuring data is of the same order of magnitude as previously (see fig. 3). Plotting log P versus log $\bar{d}$, the values obtained could be well approximated by a straight line. In the load range investigated the hardness of ZnS obeys the Meyer law well, according to the measuring data in fig. 4, i.e.

$$P = A\, d^n$$

where $n = 1.89$ independently of the crystal structure and orientation for pure crystals.

For doped crystals this exponent slightly increases with increasing cooling rate and impurity content.

On close-packed planes the A value was 4.80

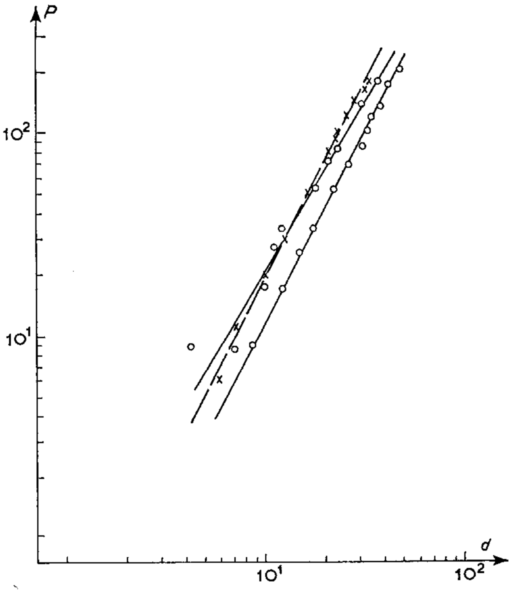

Figure 4 Log P versus log d dependence of ZnS crystals. The dotted line corresponds to the data measured on the basal plane of Cu-activated ZnS crystals. The full lines correspond to d-values measured on prism-planes. The left curve belongs to pure crystals and the right one to ZnS crystals of high Cu concentration.

to 4.95, on side planes it amounted to 7.85 to 8.00.

3.6. Effect of Cooling Rate and Heat-Treatment

According to our experiments the H_v value is considerably influenced both by the cooling rate in the final period of crystal growth and by any kind of subsequent heat-treatment. Table I shows some characteristic data, as described in the experimental method. These values were measured on crystals selected from the same batch.

In the case of both the close-packed and the so-called side planes (hex. {1210}, {1010}; cubic {110}, {112}) regions showing extremely high hardness values were frequently observed. In many cases these regions correspond to the singular places mentioned above. The frequency of their appearance shows a correlation with the cooling rate applied in the course of the crystal growth. Such ranges were measured at high cooling rates ($v = 1.0$ to $18.0°$ C/min) on close-packed planes, especially in the vicinity of the crystal edges, independently from the contamination of the crystals. Fig. 5 displays the hardness distribution measured in two different directions by medium load (38.25 kg) on the basal plane of a Cu-contaminated ZnS crystal of hexagonal morphology. In side planes at high cooling rates the frequency of appearance of places with high microhardness values increases with increasing cooling rate, whereas their distribution shows a random character. At low cooling rates ($v < 1.0°$ C/min) the frequency of their occurrence decreased on both close-packed and side planes.

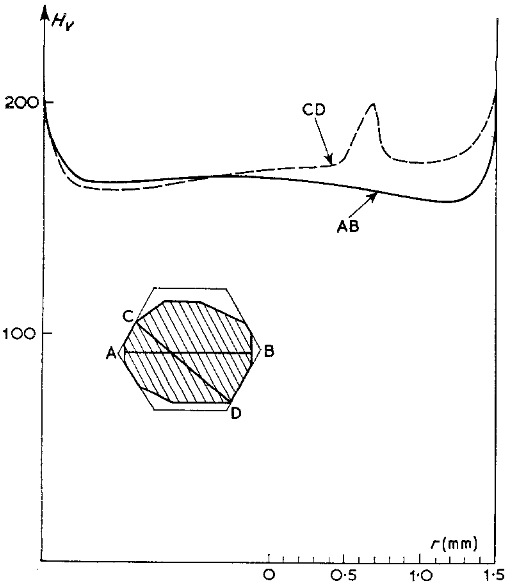

Figure 5 Regions with extremely high microhardness values measured on the basal plane of a hexagonal ZnS crystal in two (AB and CD)directions.

Regions in ZnS showing extremely high hardness values are probably due to high dislocation densities or dislocation pile-up. This phenomenon has been previously reported in other materials [16, 18]. The experiments show that with increasing dislocation density the hardness increases.

The phenomenon can be interpreted as a fixed dislocation network, developed as a result of the dislocation interaction in the vicinity of the indentation. The formation of this so-called Frank net – which hinders the plastic deformation – strongly depends on the density of the "as-grown" dislocations.

Selective chemical etching experiments show that on ZnS single crystals – similarly CdS [8] – just under the crystal planes the dislocation density is considerably higher than in the bulk. Probably this is the reason why in fig. 5 the hardness is higher in the vicinity of the bounding planes. This phenomenon is most probably due to the high mechanical stresses formed in the vicinity of the crystal boundaries during the cooling process after the crystal growth. Even in the case of ZnS these stresses might be so high as to move and generate the dislocations at certain temperatures.

The mean hardness might considerably increase, if no dislocation pile-up occurs in the vicinity of the surface. This is the reason why the mean hardness changes both with the cooling rate and the heat-treatment. Based on the above-described observations an explanation of this phenomenon can be given if it is assumed that extended dislocation networks develop in the bulk of the crystal.

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