

# INVESTIGATIONS OF ZnS CRYSTALS STRUCTURE DEPENDENCE ON THE MANGANESE DOPANT CONTENTS

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## SUMMARY

THIS work presents the results of investigations of polytype structure crystals with stacking faults occurring in zinc sulfide due to introduction of manganese impurities during crystal growth. The changes in layer settings were observed from the starting 3C structure through the 6H(33) and 4H polytypes and the not completely ordered structures to the final 2H structure. The theoretical analysis was made of structure stacking faults energy SFE run as a function of their hexagonality. The qualitative agreement was found between the observed structures run as a function of impurity concentration and the one anticipated on the basis of SFE considerations. Founded on the above considerations is a new interpretation of structure hexagonality dependence on impurity concentration.

## 1. INTRODUCTION

THE CORRELATION between the impurity contents and the type of polytype structures appearing in crystals was found, among others, in the following works [1, 2, 3, 4, 5]. First results of circumstantial investigations of the whole range of structure changes (from 3C to 2H) of ZnS crystals under the influence of Al and Cd impurities were given in [6] and [7]. The interpretation of results obtained was based on statistical theory. The HIRTH and LOTHE method [13] of counting the energy of particular stacking faults based on the model of elastic spherulite by central forces was developed in works [8, 9, 10, 11, 12] and used for polytypism phenomenon considerations. The investigations presented in this paper are the continuation of the above mentioned works.

## 2. RESULTS OF INVESTIGATIONS

The manganese-doped zinc sulfide crystals under investigation were obtained from melt phase under the pressure of argon atmosphere [14]. The samples to be used in tests were selected by splicing pieces of crystal 0.3 mm thick and about 3 mm long having the longer edge orientation approximately following the *c* axis. Manganese concentration

was determined by means of chemical analysis [15]. The structure repeatability for the same manganese concentrations was satisfactory. Fig. 1 shows composed rows of 10.1 X-ray diffraction photographs of crystal samples rotated around their  $c$  axes in the increasing sequence of Mn concentration. This picture gives ground to reasoning that with the increase of manganese contents the concentration of hexagonal layers increases too.

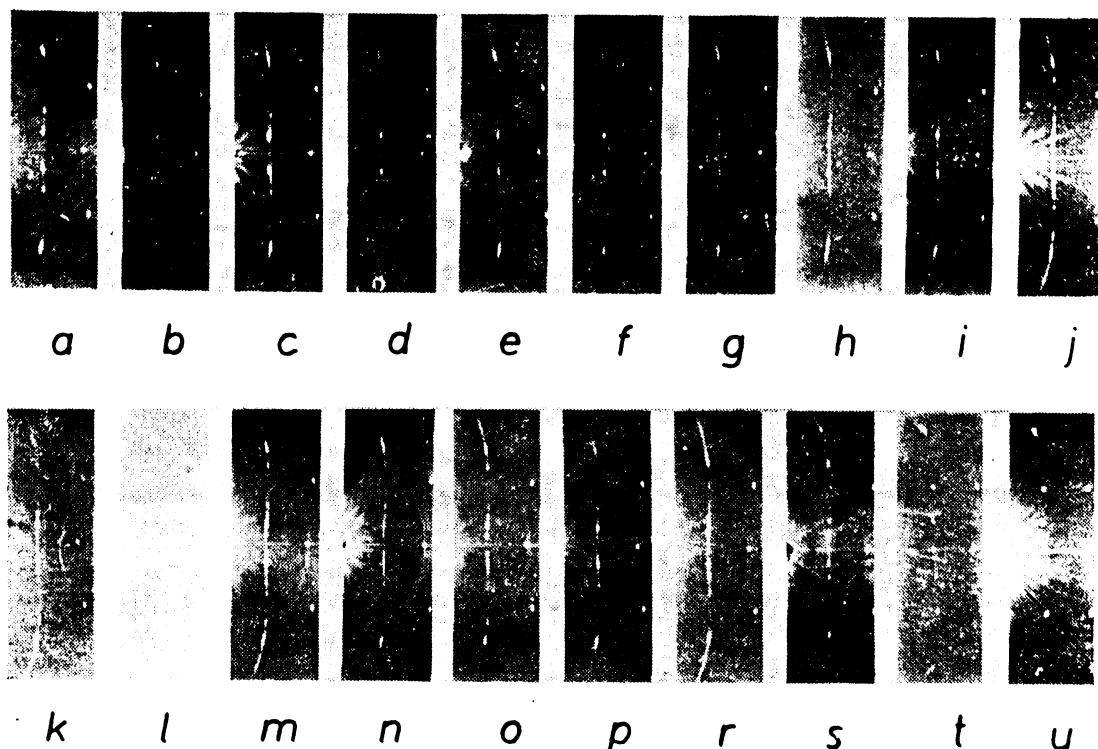


FIG. 1. Rows of 10.1 X-ray diffraction photographs of crystal rotated around the  $c$  axis of ZnS samples with the following Mn concentrations expressed in molal %: a) 0.1, b) 0.65, c) 0.74, d) 0.83, e) 1.10, f) 1.21, g) 1.22, h) 1.26, i) 1.79, j) 1.76, k) 1.78, l) 1.88, m) 2.16, n) 2.17, o) 2.36, p) 2.39, r) 2.50, s) 2.59, t) 3.23, u) 6.25.

With the increase of manganese contents the following structures appeared sequentially: **3C+DS**, **6H (33)+DS**, **4H+DS**, **2H**. The dependence of investigated structures hexagonality on the impurity concentration was determined by using the model analysis method which was described in detail in [16]. The results obtained were plotted on the graph with the axes  $c$  (manganese concentration) and  $a$  (hexagonality) (Fig. 2), on which for comparison purposes the experimental points from the work by KOZIELSKI [7] were marked (for Al and Cd impurities). This graph gives evidence that the results obtained by these authors take similar run as those obtained by Kozielski. Some authors [8, 9, 10, 11] have observed a very good agreement of transformation directions in some politype structures with the stacking faults energy for those structures. In order to compare the changes observed in structures of doped ZnS crystals with their stacking faults energy an analysis of the SFE run as a function of hexagonality was performed.

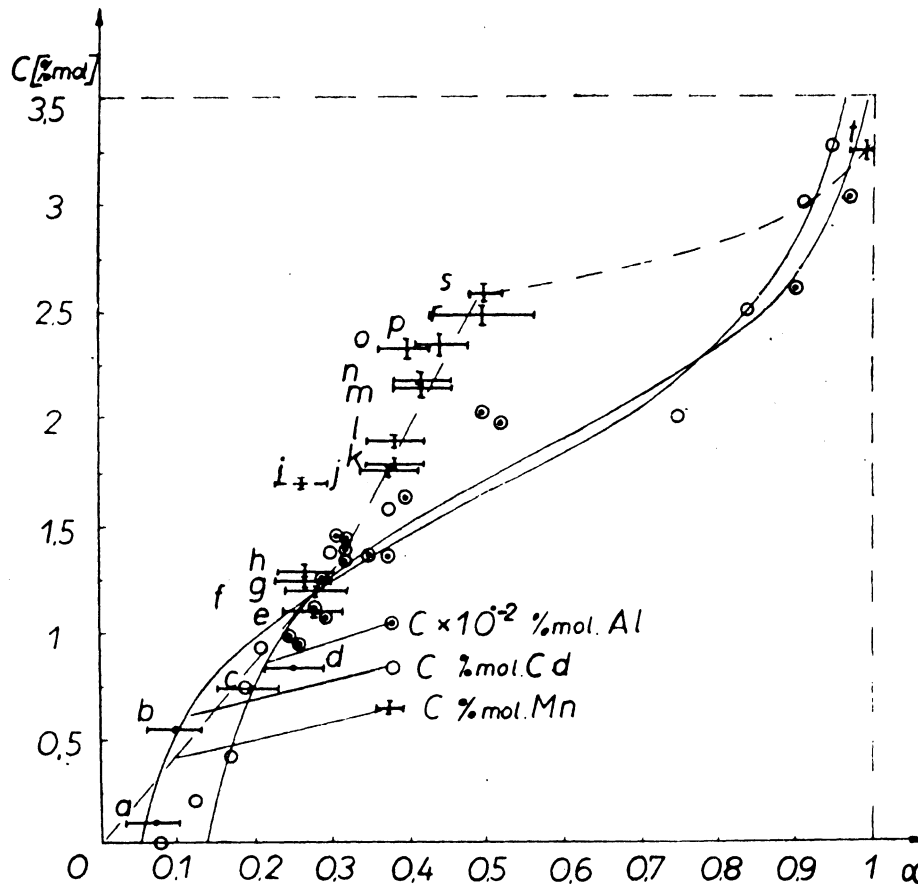


FIG. 2. Experimental dependence of structures hexagonality on Al and Cd impurity concentration obtained by Kozielski and on Mn concentration obtained by these authors.

### 3. ANALYSIS OF SFE RUN AS A FUNCTION OF HEXAGONALITY

According to results given in [8, 9, 10, 11, 12, 13] the stacking faults energy may be presented as a sum of products of the number of defective layer pairs  $n$  layers away from each other and the corresponding distortion energies of those layer pairs  $\psi_n$  (as defined in [13]). Neglected in this calculation are layer pairs more than 4 layers away due to small value of distortion energy. The number of defective layer pairs is determined by summing up all pairs that appear in settings other than the ones proper for the nondefective structure. The distortion energy of particular pairs is calculated as the absolute value of difference between the sum of "bonds" (as defined in [13]) between particular spheres of layer pair in a defective structure and that of a proper  $3C$  structure. Calculation of bond length and expression of distortion energy of layer pairs by means of spheres "bonds" energy is made by considering the projection of all spheres above the selected layer surface on this layer surface and on the surface perpendicular to it. Detailed considerations and drawings are given in [8, 12]. It is impossible however, to make quantitative estimation of SFE without introducing to the model an accurate dependence of "bond" energy on the distance between spheres. At the same time it follows from the model that this dependence concerns intersphere interactions (interactions between atom pairs), the character

of which is not known well. One only knows that the values of spheres "bonds" energy  $\phi$  (and thus the values of layer pairs distortion energy  $\psi$ ) decrease as the distance between spheres increases. For the sake of straightforwardness in the following considerations, that lead towards quantitative conclusions, it was determined for example that the values of  $\psi_2$ ,  $\psi_3$  and  $\psi_4$  are inversely proportional to layer distance, i.e.

$$\psi_2 = 3/2\psi_3 = 2\psi_4$$

This assumption, as will be shown later, does not limit the generality of obtained conclusions. With such assumption all politype and not completely arranged structures were shown on a plot with coordinates SFE and  $\alpha = 1/x$  (where  $\alpha$  is hexagonality and  $x$  is average number of layers in areas where all layers are of the same stacking sequence) (Fig. 3).

Along the 0-1-2-3 curve lay the structures containing in their Zhdanov symbols numbers equal to the average number of layers in areas exhibiting the same sequence of layer stackings  $x = 1/\alpha$ , or, in case when  $x$  is not an integer, numbers being an integer closest to  $x$ . Other structures may be located either to the left or to the right from the curve, depending on the estimate of their stacking faults energy. Basing on the analysis of the

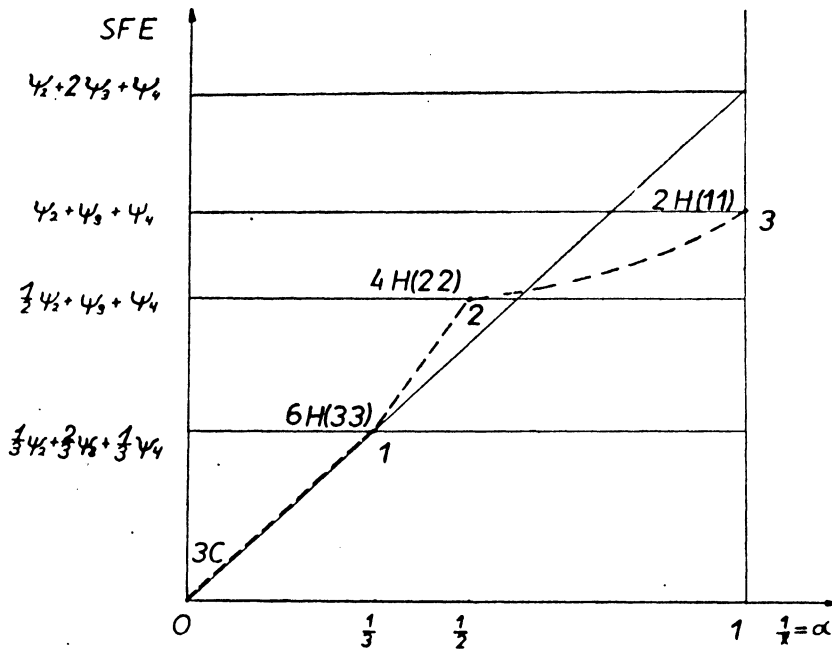


FIG. 3. Settings of politype and not completely arranged structures on the plot with coordinates SFE and  $\alpha = 1/x$  under the assumption of  $\psi_2 = 3/2\psi_3 = 2\psi_4$ . The curve 0-1-2-3 is described by the following formulas:

$$\text{SFE} = \frac{2\psi_2 + 4\psi_3 + 2\psi_4}{2x} \quad \text{on the } 0-1 \text{ distance;} \quad \text{SFE} = \frac{2\psi_2 + 4\psi_3 + 2\psi_4}{2x} + \left(\frac{1}{x} - \frac{1}{3}\right) 3\psi_4 \quad \text{on the } 1-2$$

$$\text{SFE} = \frac{2\psi_2}{2x} + \psi_3 + y\psi_4 \quad \text{on the } 2-3 \text{ distance, where } y \text{ is } 1 \text{ at the points } 2 \text{ and } 3 \text{ and between these points}$$

distance;  
 $0 < y < 1$ .

0-1-2-3 curve one can state that its characteristic shape will be preserved independently on the interrelation between the values of  $y_2$ ,  $y_3$  and  $y_4$ . This shape will be linear on the 0-1 distance, which is a plot of a sum of equal energies of single twin-type stacking faults as a function of the number of those faults.. On the 7-2 distance appearance of a larger number of layer pairs 4 layers away requires an additional SFE increment besides the one necessary for hexagonality increase as compared to the distance 0-1, due to the occurrence of the stacking faults of the intrinsic type (number 2 in the Zhdanov symbols). This is expressed by the following formula, what was shown in paper [12]:

$$\text{SFE} = \frac{2\psi_2 + 4\psi_3 + 2\psi_4}{2x} + \left( \frac{1}{x} - \frac{1}{3} \right) 3\psi_4.$$

This causes an upward bend of the 7-2 distance. On the ground of similar reasoning an explanation may be obtained for a comparably characteristic plot of the 2-3 distance. Besides, one may notice that the legitimacy of neglecting the distortion energy of layer pairs more than 4 layers away, since all purely polytype structures 6H, 4H, 2H found on the plot do not exhibit layer pairs 5 layers away that would be situated erroneously relative to the basic 3C structure.

By comparing the Figures 2 and 3 one may state that the runs of experimental points obtained both by the authors of this paper and by KOZIELSKI are qualitatively in accordance with the 0-1-2-3 curve.

Hence our investigations allow for a new interpretation of polytype and not completely arranged structures hexagonality dependence on the impurity concentration.

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#### STRESZCZENIE

### BADANIA ZALEŻNOŚCI STRUKTURY KRYSZTAŁÓW ZnS OD KONCENTRACJI DOMIESZKI MANGANU

W pracy przedstawiono wyniki badania kryształów o strukturach politypowych i zawierających błędy ułożenia, powstałe w siarczku cynku na skutek wprowadzenia podczas wzrostu domieszek Mn. Zaobserwowano zmiany w ułożeniu warstw od wyjściowej struktury 3C poprzez politypy 6H (33) i 4H oraz struk-

tury nie w pełni uporządkowane do końcowej 2H. Przeprowadzono teoretyczną analizę przebiegu energii błędów ułożenia struktur (SFE—stacking faults energy) w funkcji ich heksagonalności. Stwierdzono jakościową zgodność przebiegu obserwowanych struktur w funkcji koncentracji domieszek z oczekiwanym na podstawie analizy SFE. Opierając się na tym podano nową interpretację zależności heksagonalności struktur od koncentracji domieszek.

РЕЗЮМЕ

**ИССЛЕДОВАНИЕ ЗАВИСИМОСТИ СТРУКТУРЫ КРИСТАЛЛОВ ZnS ОТ  
КОНЦЕНТРАЦИИ ПРИМЕСИ МАРГАНЦА**

В работе представлены результаты исследований кристаллов с полигиновой структурой и содержащих ошибки упаковки, которые возникли в сульфиде цинка из-за введения примесей Mn во время нарастания. Наблюдено изменения в упаковке слоев начиная с выходной структуры 3С через поли типы 6Н (33) и 4Н а также структуры не вполне упорядочные до конечной 2Н. Проведено теоретический анализ пробега энергии ошибок упаковки структур (SFE— stacking fault energy) в функции их гексагональности. Установлено качественное согласие пробега, наблюдаемых структур в функции концентрации примесей, с теоретическим анализом. Опираясь на выше указанных данных сделано новую интерпретацию зависимости гексагональности структур от концентрации примесей.