

SOME NEW ASPECTS OF POLYTYPIC STRUCTURES IN $ZnS_{1-x}Se_x$ MIXED CRYSTALS

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Results of the investigation of the structures formed in mixed $ZnS_{1-x}Se_x$ crystals in the entire range from $x = 0$ to $x = 1$ are presented. The existence of the following poly-, typical structures: 3C+DS, 6H(33), 4H(22), 10H(222211) was found. The type of predominant polytypic structures with appropriate stacking faults was identified as "intrinsic 2h". The dependence of the hexagonality of $ZnS_{1-x}Se_x$ crystal structures on their composition was examined and its interpretation presented. Based on a theoretical estimation of stacking fault energy (SFE) for the basic polytype structures: 6H(33), 4H(22) and 10H(222211), the succession of their occurrence was argued. Moreover, for the 10H(222211) structure not observed till now in ZnS crystals, the possibility of the substantiation of layer ordering based on Schneer's theory was considered.

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1. Introduction

Results of the investigations of polytypic and disordered structures formed in ZnS and ZnSe crystals doped with Al, Cd, Mn and In were presented by Kozielski (1975, 1976), Michalski et al. (1979) and Demianiuk et al. (1979). For these crystals it was found that in some range of dopant concentration there exist changes in a layer stacking resulting in the occurrence of polytypic and disordered structures. The kind of layer ordering in these structures and the shape of hexagonality vs dopant concentration were examined. Kozielski (1975, 1976) interpreted these results introducing into Schneer's (1959) statistical theory the linear for Cd and square for Al dependences of the potential difference of hexagonal and regular layers on the dopant concentration. On the other hand, Michalski et al. (1979) used the theoretical analysis of the structure stacking faults energy for an entire range of their changes, that is, from 3C to 2H structures. They used a method that was based on the model of Hirth and Lothe (1968) of elastic spheres and adopted for polytypic structures by Tiwary et al. (1974), Pandey and Krishna (1975). Moreover, the occurrence of complex polytypic structures in $ZnS_{1-x}Se_x$ was found by Kozielski (1976). This observa-

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tion is especially interesting because both ZnS and ZnSe structures are very sensitive towards the dopant concentration. This problem needs additional investigation and the interpretation of the formation of these structures.

2. Experimental results

The mixed $\text{ZnS}_{1-x}\text{Se}_x$ crystals used for these studies were grown from the melt phase under a pressurized argon atmosphere (Demianiuk and Žmija (1979)). Their structures were examined by rotating crystal methods using DKK-60 cameras. Samples were prepared by chipping-off small crystals (0.3 mm thick and 3 mm long), oriented approximately along the c -axis. The starting compositions taken for crystallization were: ZnS+3% ZnSe, ZnS+10% ZnSe, ZnS+20% ZnSe, ZnS+50% ZnSe, ZnS+90% ZnSe. Because of changes in the dopant concentrations along crystals there exists the possibility of samples with intermediate compositions.

The 10.l and 11.l rows of X-ray diffraction photographs for chosen samples of $\text{ZnS}_{1-x}\text{Se}_x$ crystals are shown in Fig. 1. The selenium concentration was determined by chemical methods (Wieteska (1979)) and for the samples examined they were: a) 0.88, b) 1.96, c) 2.18, d) 2.44, e) 5.43, f) 7.15, g) 8.42, h) 9.16, i) 9.61, j) 46.35 (in weight %).

The high level of background observed in Fig. 1 was caused by the X-ray luminescence of $\text{ZnS}_{1-x}\text{Se}_x$ crystals.

3. Identification of the observed structures

The structures observed were identified using the method of "model analysis" described by Pałosz (1977), Michalski et al. (1979a) and Demianiuk et al. (1979). The starting point for our investigations was an initial analysis of X-ray diffraction photographs to determine the basic structures and type of stacking faults which cause the characteristic reflex broadening observed.

X-ray diffraction photographs in Fig. 1a, b, c show the 3C structure with twin stacking faults. The increasing broadening shifts and the splitting-off of the maximum of the broadened reflexes for 3C structures is shown. For this distribution of intensities theoretical curves correspond to the models of the 3C+DS structures presented by Demianiuk et al. (1979).

Reflections in Fig. 1d are situated so that they correspond to the 6H structure. However, the intensity distribution does not correspond to any one of those computed for the two possible stackings of layers in the 6H structure. The theoretical reflex intensities for the two 6H structures with Zhdanov's symbols (33) and (2211) are shown in Table I.

TABLE I

Table of relative reflex intensities $I_{10,l}$ for two 6H polytypes							
	10.0	10.1	10.2	10.3	10.4	10.5	10.6
33	0	53	100	58	20	12	0
2211	60	52	33	100	7	11	22

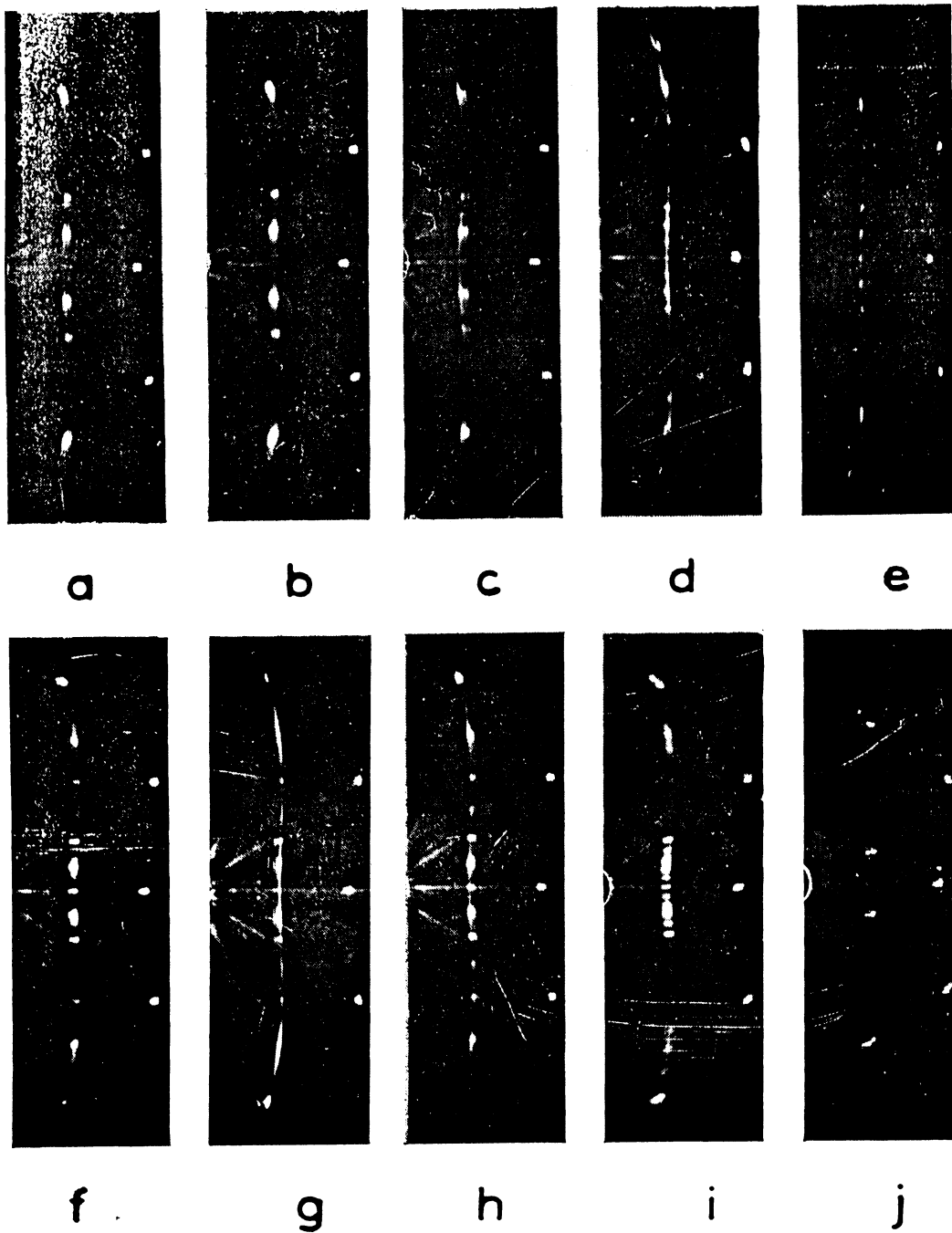


Fig. 1. The $10.l$ rows of the X-ray diffraction photograph of rotary crystals for the samples of $ZnS_{1-x}Se_x$ examined

Here it can be seen that the observed intensity distribution shows a small increase for 10.0, 10.3 and 10.6 reflexes with respect to that computed for the 6H(33) structure. That is, enhancements in places correspond to the reflexes of the 2H structure. That is why we have formed models composed of the 6H polytype and a small quantity of the 2H polytype (Fig. 2b).

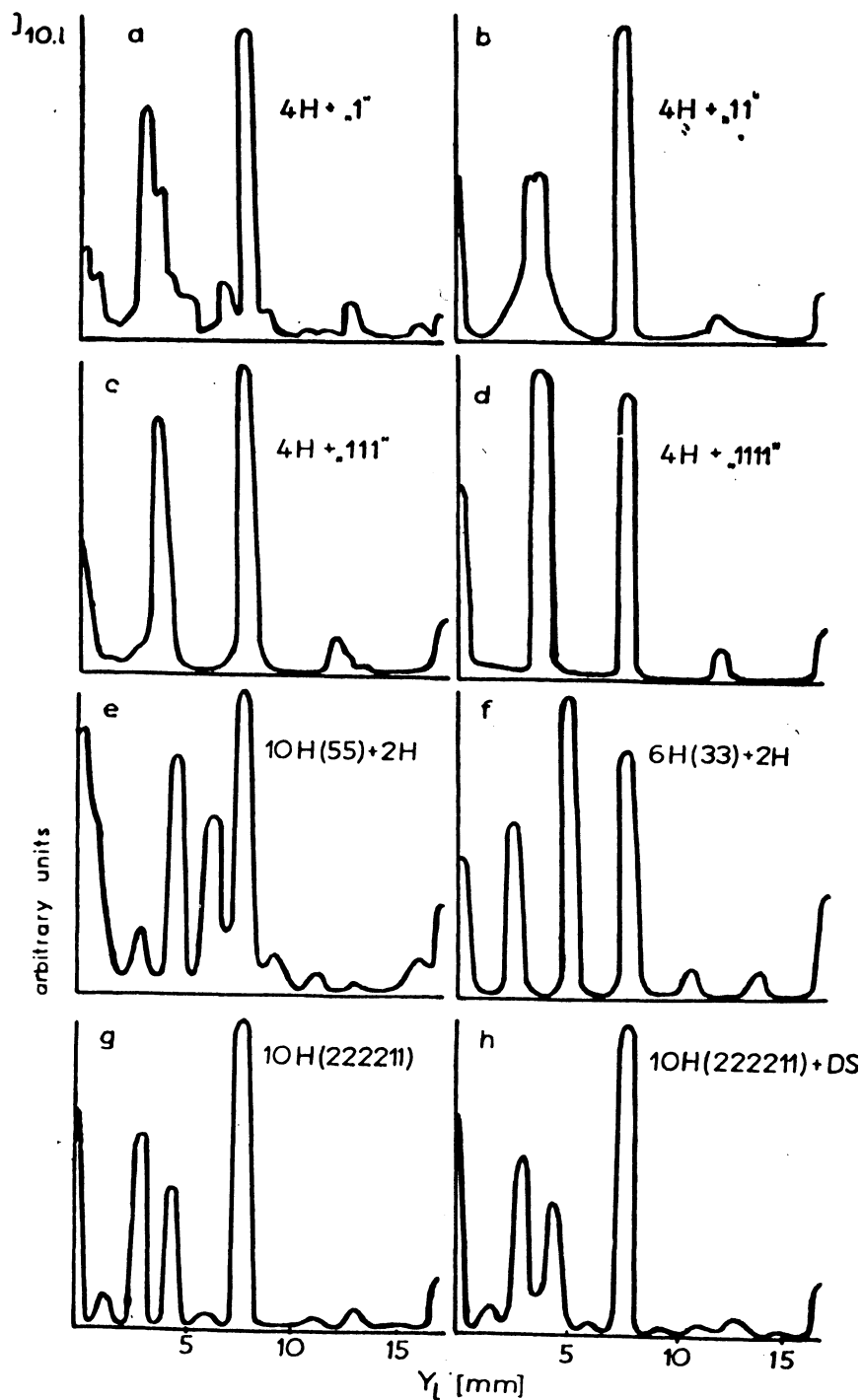


Fig. 2. Theoretical curves of the intensity distribution along the 10.1 row obtained from model analysis. They are representative for the effects on the diffraction photograph observed

The X-ray diffraction photograph shown in Fig. 1e corresponds to the nearly quite ordered 4H(22) structure. The negligible broadening of only the 10.1 and 10.3 reflexes is seen. This broadening occurs very clearly in Figs. 1f, g and h. For the interpretation of the changes in structures which cause this reflex broadening we have used the results of Prasad and Lele (1970). They considered the diffraction effects from all stacking faults in the 4H(22) structure. According to their results an effect of reflex broadening of the 10.1 and 10.3 reflexes, with sharp 10.0, 10.2 and 10.4 reflexes, proceeds from the "intrinsic 2h" type of stacking faults, that correspond to occurrence of the "11" (to single cells of 2H structure) in Zhdanov's symbol. This reflex broadening is not caused by structures with single cells, "1", or groups "111", "1111" in Zhdanov's symbol. This is clearly seen in the theoretical curves shown in Fig. 2a, b, c, and d. All four models of

TABLE II

Table of relative $I_{10.1}$ reflex intensities for all possible 10H polytypes

	10.0	10.1	10.2	10.3	10.4	10.5	10.6	10.7	10.8	10.9	10.10
55	8	3	22	100	71	4	15	9	3	0	2
4411	40	11	52	47	100	22	20	4	7	2	14
3322	10	23	51	100	24	78	5	9	7	5	3
331111	59	84	27	52	86	100	18	4	3	19	20
4312	13	33	72	73	100	52	21	6	10	7	4
232111	44	53	31	55	28	100	6	5	4	12	15
222211	65	10	58	43	4	100	0	4	8	2	22
231121	13	89	51	28	74	100	15	2	7	20	4
311311	11	85	31	7	100	58	21	0	4	19	3
221221	44	31	79	19	37	100	7	1	11	7	15
22111111	100	21	18	13	8	90	1	1	2	5	34
21121111	65	69	8	6	27	100	5	0	1	16	22
82	6	6	7	100	46	11	9	9	1	1	2
7111	44	33	8	86	100	24	20	8	1	7	15
6121	9	31	41	38	100	15	20	3	5	7	3
5131	7	22	47	13	100	4	21	1	6	5	2
4141	29	0	61	0	100	0	21	0	8	0	9

the structures contain 0.1 layers with stacking faults which form the appropriate type of faults.

The next X-ray diffraction photograph (Fig. 1i) shows 10.1 reflexes which are situated in positions corresponding to the 10H polytypic structure. To identify the stacking of polytype layer sequences in a unit cell we have computed the relative intensities of 10.1 reflexes for all possible unit cells with 10-hexagonal layers. Our calculations were based on formulas given and discussed by Demianiuk et al. (1979) and Verma and Krishna (1966). Using the condition fulfilled by hexagonal polytypes: $n_+ - n_- = 3r$, 10-layer unit cells were chosen, where n_+ and n_- are the numbers corresponding to signs of Hegg's symbol and $r = 0, \pm 1, \pm 2, \dots$

Table II contains the numerical results obtained. The first 12 models of 10H structures we have obtained for the condition of $n_+ - n_- = 0$. For the others the $n_+ - n_- = 6$ apply. Models of structures with $n_+ - n_- = -6$, which differ from the last by the sign (of + ; —) in Hegg's symbol, but in respect to it in enantiomorphic relation, leads to an identical X-ray diffraction pattern for the rotating crystal. Thus, the table contains the theoretical reflex intensities for all possible models of 10-hexagonal layers of unit cells. The measurements of intensities carried out on the X-ray diffraction photograph of 10.l reflexes gives:

$I_{10.0}$	$I_{10.1}$	$I_{10.2}$	$I_{10.3}$	$I_{10.4}$	$I_{10.5}$	$I_{10.6}$	$I_{10.7}$	$I_{10.8}$	$I_{10.9}$	$I_{10.10}$
60	20	60	50	20	100	15	5	10	5	20

When comparing these intensities with those from Table II we see that they are very close to those obtained theoretically for the (222211) polytype. On the other hand, the observed broadening (as for the 4H structure) along the 10.2 and 10.3 reflexes and between them, proceeds from some disordering in the distribution of the single 2H(11) cells. Corresponding theoretical curves, descending for a model of "pure" (222211) poly-type and with some disordering (DS) are shown in Figs. 2g and h. However, according to literature data (Kozielski (1975), Michalski et al. (1979), Pandey, Krishna (1975), Verma, Krishna (1966), Prasad (1976) and Kliflawi et al. (1976)), it was not found until now any occurrence of the 10H(222211) polytype structure in $A^{II}B^{VI}$ compounds. Instead, the most frequently met polytype structure of 10H was the (55). In connection with the above and also taking into account some disordering of the structure, it was indispensable to check whether it is possible to obtain the theoretical curves for an intensity distribution based on the 10H(55) type of polytype similar to the experimental ones. This was shown to be impossible. The theoretical curve which is the most close to the experimental one (Fig. 2c) comes from the model of 10H(55) and 2H(11) polytype structures and the single "2" in Zhdanov's symbol and differs significantly from the observed distribution. This difference is especially clearly seen in the mutual ratios of 10.2, 10.3 and 10.4 reflex intensities.

The last X-ray diffraction photograph (Fig. 1j) exhibits the 3C polytypic structure with microscopic defects. The broadening does not occur along 10.1 row, however the scattering of both 10.1 and 11.1 rows is caused by the presence of low-angle boundaries.

4. Interpretation of the observed results

The sequence of the occurrence of basic polytypic structures of 6H(33), 4H(22), 10H(222211) with increasing contents of Se can be argued in a simple way by comparing their stacking faults energies which are equal to:

$$\begin{aligned} \text{SFE}_{6\text{H}(33)} &= \frac{1}{3} \Psi_2 + \frac{2}{3} \Psi_3 + \frac{1}{3} \Psi_4, \\ \text{SFE}_{4\text{H}(22)} &= \frac{1}{2} \Psi_2 + \Psi_3 + \Psi_4, \quad \text{SFE}_{10\text{H}(222211)} = \frac{6}{10} \Psi_2 + \Psi_3 + \frac{8}{10} \Psi_4. \end{aligned}$$

For further interpretation we have plotted detailed results of model analysis on the diagram of the dependence of structure hexagonality on a structure constitution (Fig. 3). This diagram exhibits a similarity to our results of the stacking faults energy vs the hexagonality function and to Michalski et al. (1979) as well as to the results for Al, Cd and Mn dopants obtained by Kozielski (1975), (1976) and Michalski et al. (1979) only in the initial range. Above $c = 6\%$ of Se this relationship is shifted towards the lower hexagonal direction (below $\alpha = 0.6$). This behaviour can be explained assuming that structures in mixed $\text{ZnS}_{1-x}\text{Se}_x$

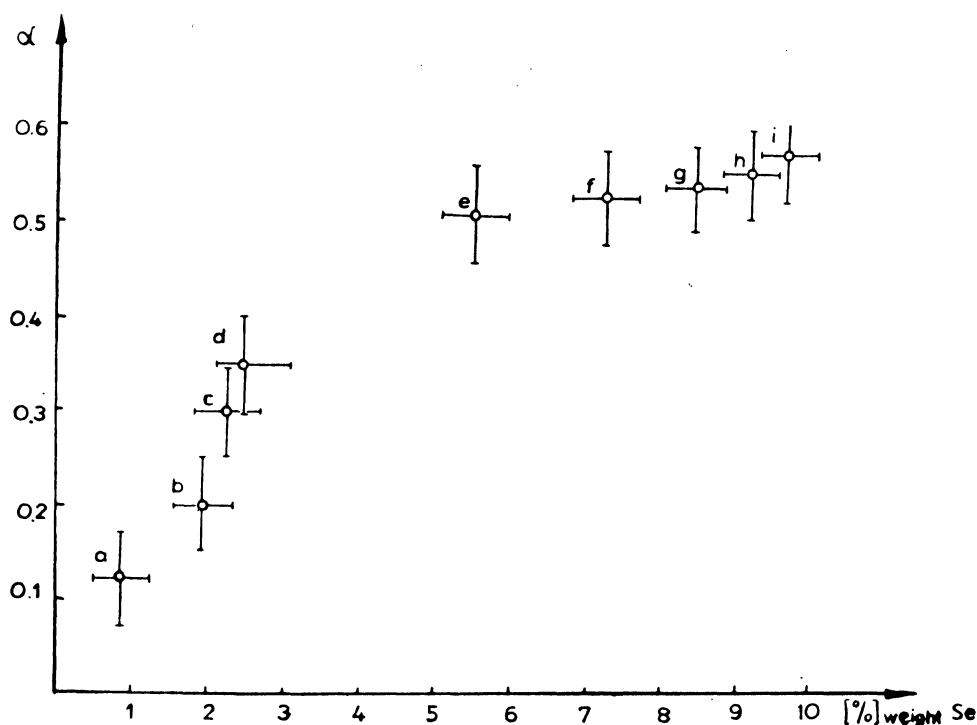


Fig. 3. Experimental dependence of structure hexagonality on constitution (on Se dopant concentration) in $\text{ZnS}_{1-x}\text{Se}_x$ crystals

crystals can be formed in some range of constitution (above $c = 6\%$ Se) on the basis of two lattices, ZnS and ZnSe. A change of constitution will have an opposite influence, here, on a structural hexagonality which forms based neither in ZnSe the basis nor ZnS. This results from the fact that the increase of a dopant content in ZnS means a simultaneous drop in the structure hexagonality formed on the basis of ZnSe lattice. For this interpretation we mention also the drop in structure hexagonality up to 3C (Fig. 2j), observed with the further increasing of ZnSe contents in mixed crystals. For the 10H(222211) structure which was not yet observed in ZnS crystals, we have considered the possibility of explaining the occurrence of layer ordering based on Schnee's theory (Schnee (1959), Rai and Krishna (1963)). According to these theories the energy of interactions between the layers of polytypic structure is minimum if

$$\phi = \frac{n_{kh} - (n_{kk} + n_{hh})}{n_{kh} + n_{kk} + n_{hh}}$$

achieves the maximum value of Φ_m , where Φ is the contacts distribution of the mutual interaction of layers, n_{ij} is the contact number between corresponding layers. Then $\Phi_m = 3 - 4D$ for

$D > 1/2$ and $\Phi_m = 4D - 1$ for $D < 1/2$,) where:

$$D = \frac{n_k}{n_k + n_h}$$

For the 10H(222211) structure, the values of Φ and D are: $\Phi = 6/10$, $D = 4/10$. Thus, it is on the straight line $\Phi_m = 4D - 1$, (Fig. 4). At this same point, however, there is also the 10H(221221) structure. The computations of potential effects from the long range interaction according to formulae:

$$\varepsilon = \sum_n \varepsilon_{n_{ij}}$$

(where $\varepsilon_{nhh} = \varepsilon_{nkk} = + \frac{\varepsilon_0}{nr}$, $\varepsilon_{nkh} = - \frac{\varepsilon_0}{nr}$) gives the result $\varepsilon_{(222211)} > \varepsilon_{(221221)}$

In accord with this, the more privileged structure should be the 10H(221221) and not 10H(222211).

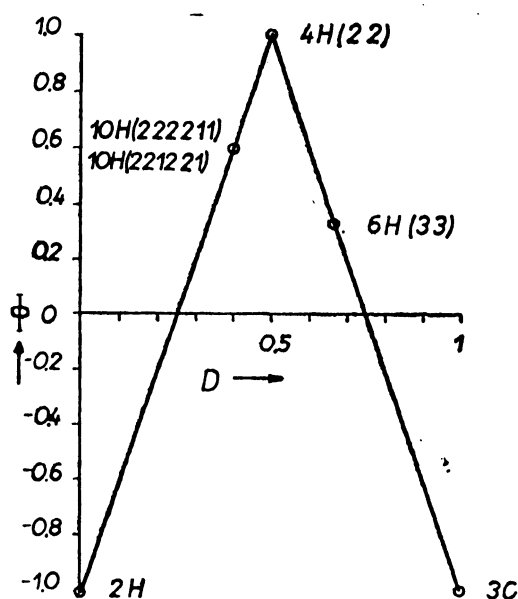


Fig. 4. The run of $\Phi_m = f(D)$ dependence obtained according to Schneer's theory (Schneer (1959)). They are determining the structures in $ZnS_{1-x}Se_x$ crystals

These results suggest that long range Schneer's potentials are not responsible neither for the structure ordering nor for the type of dominant faults. Probably the influence on the formation of single 2H cells (the grouping of 3 hexagonal layers) have local effects. Perhaps the 2H cells are formed on the basis of another lattice instead of the rest of the structure. It seems interesting, if it is possible to explain these interactions based on the statistical models given by Kozielski and Tomaszewicz (1977a, b).

REFERENCES

- Demianiuk, M., Zmija, J., Biul. WAT **24**, 105 (1975).
 Demianiuk, M., Kaczmarek, S., Michalski, E., Zmija, J., Biul. WAT **28**, 91 (1979).
 Hirth, J. P., Lot he, J., Theory of Dislocation, Me Grow-Hill Inc. 1968.
 Kozielski, M. J., J. Cryst. Growth **30**, 86 (1975).
 Kozielski, M. J., Reports of the Institute of Physics, Warsaw Technical University 1976, p. 16.
 Kozielski, M., Tomaszewicz, A., Bull. Acad. Pol. Sci. Ser. ScL Math. Astron. Phys. 25, 313 (1977).
 Kozielski, M., Tomaszewicz, A., Bull. Ac-ad. Pol. Sci. Ser. Sci. Math. Astron. Phys. 25, 321 (1977).
 Kozielski, M., Tomaszewicz, A., Bull. Acad. Pol. Sci. Ser. Sci. Math. Astron. Phys. 25, 321 (1977).

- Kiflawi, J., Kalman, Z. H., Sonnenblick, Y., *J. Cryst. Growth* **34**, 145 (1976).
- Michalski, E., Demianiuk, M., Kaczmarek, S., Żmija, J., *Acta Phys. Pol.* **A56**, 333 (1979).
- Michalski, E., Demianiuk, M., Kaczmarek, S., Żmija, J., *Electron Technology* (1980) (in print)
- Pałosz, B., Dissertation, Warsaw Technical University (1977).
- Pałosz, B., *Acta Cryst.* **A33**, 172 (1977).
- Pandey, W., Krishna, P., *Philos. Mag.* **31**, 1113 (1975).
- Prasad, B., Lele, S., *Acta Cryst.* **A26**, 54 (1970).
- Prasad, B., *Phys. Status Solidi* **38**, 11 (1976).
- Rai, K. N., Krishna, P., *J. Cryst. Growth* **34**, 741 (1963).
- Schneer, C. J., *Acta Cryst.* **8**, 279 (1959).
- Tiwari, R. S., Rai, A. K., Srivastava, O. N., *Phys. Rev.* **B9**, 5155 (1974).
- Verma, A. R., Krishna, P., *Polymorphism and Polytypism in Crystals*, John Wiley and Sons Inc. 1974
- Wieteska, E., unpublished results 1976.