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Application of Theoretical Intensity Distribution Curves to the Analysis of Disordered ZnS–CdS and ZnS–ZnSe Crystals*

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The possibility is discussed of applying the theoretical intensity distribution formulae to the structural analysis of solid solution crystals of ZnS–CdS and ZnS–ZnSe with stacking faults. It is pointed out that the irregular shape of the photometric curves, the appearance of intensity maxima connected with areas of disordered type structure, and splitting of the diffuse reflexions, renders impossible the application of theoretical intensity formulae. Theoretical intensity curves, obtained for the model of a structure with stacking faults, are proposed for structural analysis.

Introduction

The ZnS crystals can be divided into two structural groups: polytypes, and structures with stacking faults. The structural analysis of polytypes consists of establishing the layer sequence periodicity in the unit cell thus determining completely the structure. The analysis of structures with stacking faults is much more complicated and calls for the introduction of parameters describing the degree of disorder in the arrangement of layers. The analysis of such structures can be of an approximate nature only, since it describes an infinite, statistically repeatable, sequence of layers forming the crystal. Polytypes usually occur in small areas of larger crystals or in the form of single crystals of macroscopic size (Brafman & Steinberger, 1966; Brafman, Alexander & Steinberger, 1967; Mardix, Kalman & Steinberger, 1968; Alexander, Kalman, Mardix & Steinberger, 1970; Rai, 1971a, 1972). Polytypes are usually accompanied by areas with stacking faults (Singer, 1963a; Rai & Krishna, 1968). In the investigated ZnS–CdS and ZnS–ZnSe crystals, areas of about 5 mm² showing similar stacking faults were found.

Polytype formation mechanisms suggested in the literature (Daniels, 1966; Mardix *et al.*, 1968; Alexander *et al.*, 1970; Rai, 1971a, b) are based on the analysis of known pure polytypes. Structures with

stacking faults may be considered as probable transition stages between pure polytype structures; hence the analysis of these structures may serve to explain the polytype growth mechanism.

Experimental results

Crystals of ZnS–CdS and ZnS–ZnSe solid solutions were investigated by the oscillating-crystal method in a range of 15° around the *c* axis with Cu *K* α radiation. The selected samples consisted of needles cut parallel to the *c* axis, measuring 2–4 mm in length and about 0.5 mm in diameter. The X-ray beam was of 0.5 mm diameter. On the *c* axis oscillation photograph a 10.*L* row of spots was obtained and subsequently in the intensity–*L/m* coordinate system the photometric curve was plotted, where *m* denotes the number of layers in the unit cell; e.g. the reflexion 10.1 for the structure 3C remains in the position $\frac{1}{3}=0.333$, the reflexion 10.1 of the structure 15H in position $\frac{1}{15}=0.0667$ etc. On the photometric curves broadened maxima were found in positions corresponding with 10.*L* reflexions of the 2H, 3C, 4H, 6H and 10H structures indicating that the latter polytype structural fragments appear in the crystal. The background observed on the photometric curves originates from disordered structure fragments. The analysis of the photometric curves of 10.*L* rows of spots of X-ray pattern for crystals oscillating around the *c* axis showed the occurrence of the following structures: 2H+disorder (Fig. 1), 3C+disorder (Fig. 2), 4H+disorder (Fig. 3), 6H+disorder (Fig. 4), 10H+disorder, 2H+4H+

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disorder, $4H+6H$ +disorder (Fig. 5), $6H+10H$ +disorder and disordered structure (Fig. 6).

Apart from simple polytype reflexions, maxima [marked by arrows on Figs. 1(d), 2, 4(a), (b), (c), (d), 6] and double reflexions [Figs. 1(b), (c), 3, 4(e)] not corresponding to any type of simple multilayer polytypes, were observed on the photometric curves.

The occurrence of similar additional maxima on the intensity curves of ZnS crystals was earlier stated by Farkas-Jahnke (1973). We have tried to determine the structure of the investigated crystals by comparing photometric curves with theoretical curves, calculated on the basis of the formulae of Kakinoki & Komura (1965) and Kakinoki (1967) for $s=4$ (s is 'Reichweite' according to Jagodzinski, 1949). The curves and parameters used for the calculations in the present paper are on Fig. 7.

Similar curves calculated from Jagodzinski's (1949) formula for $s=3$ (this formula being a particular case of the formula of Kakinoki, 1967) illustrating changes in the curves together with the changing degree of disorder are quoted by Farkas-Jahnke (1973).

In our more extended description of disorder the theoretical and experimental distribution curves do not agree, as is also the case in the paper of Farkas-Jahnke (1973).

Discussion

Comparison between the theoretical and experimental curves shows that the real structure of crystals with stacking faults is more complicated than structures described by theoretical intensity formulae. The theoretical curves are of quite regular shape, whereas experimental curves are irregular with additional maxima occurring between the reflexions characterizing simple polytypes. A regular shape for experimental intensity curves was observed only in exceptional cases with low degrees of disorder and prevailing ordering of the layers in simple polytype cells [Figs. 1(a), 4(e), 5].

Several applications of the theoretical intensity distribution formulae of Wilson (1942), Hendricks & Teller (1942), Jagodzinski (1949), Paterson (1952), Kakinoki & Komura (1965) and Kakinoki (1967) to crystal structure analysis were carried out; see Müller (1952), Singer (1963b), Ebina & Takahashi (1967) and Farkas-Jahnke (1973). Singer found good agreement between a single experimental and the corresponding theoretical curve calculated from Jagodzinski's formula for $s=3$. At the same time he stated that no agreement could be achieved for other experimental curves. Ebina & Takahashi, calculating with Paterson's (1952) formula for $s=2$, found agreement between theoretical and experimental curves with respect to the reflexion broadening but not with respect to general behaviour of the curves. They did not observe the peak displacement as predicted by Paterson's formula.

Apart from the disagreement in the type of broadening and the intensity distribution of theoretical and experimental curves obtained on the basis of Kakinoki's (1967), formula serious differences occur between the reflexion intensity calculated from this last formula and the experimental intensities. For illustration, in Table 1 intensities of $10.L$ reflexion are shown, calculated from the classical intensity formula given by Brafman, Alexander & Steinberger (1967) and by Kakinoki's formula for $s=4$. The calculations of the intensity $I(\varphi)$ according to the formula of Kakinoki were carried out for the values of disorder parameters shown in Fig. 7.

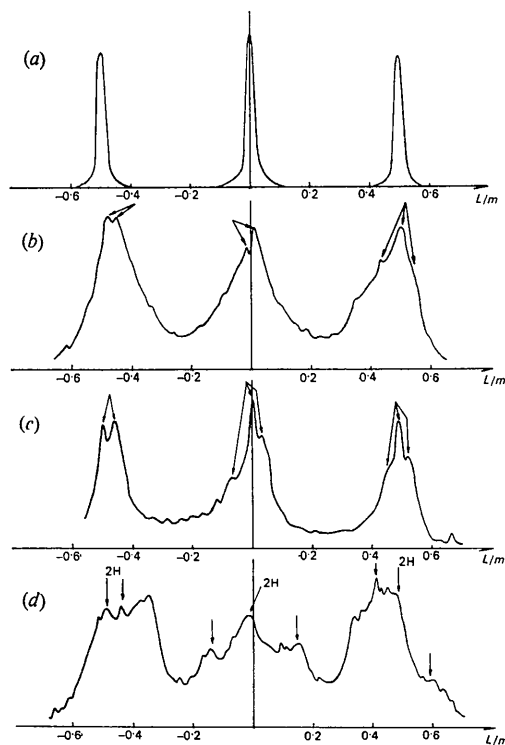


Fig. 1. Photometric curve for structure $2H$ +disorder.

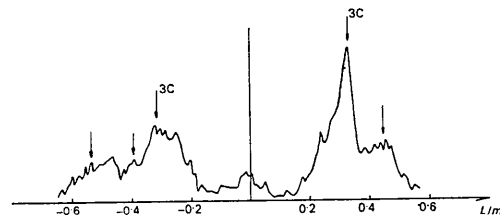


Fig. 2. Photometric curve for structure $3C$ +disorder.

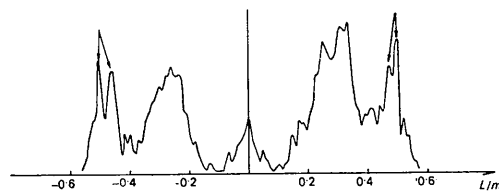


Fig. 3. Photometric curve for structure $4H$ +disorder.

Table 1. Comparison of observed and calculated intensities of 10 . L reflexions

Poly-type	HK.L	I calculated from			I calculated from Kakinoki's formula for $s=4$	I observed ZnS
		ZnS	ZnSe	CdS		
2H	10.0	100	100	100	30	100
	10.1	52	37	87	100	70-80
4H	10.0	49	51	38	10	45
	10.1	100	100	83	32	100
	10.2	78	56	100	100	90
6H	10.3	12	4	21	32	10-20
	10.0	0	0	0	0	0
	10.1	58	61	51	28	50-60
	10.2	100	100	100	76	100
	10.3	48	36	69	100	40-50
	10.4	12	1	32	76	15-30

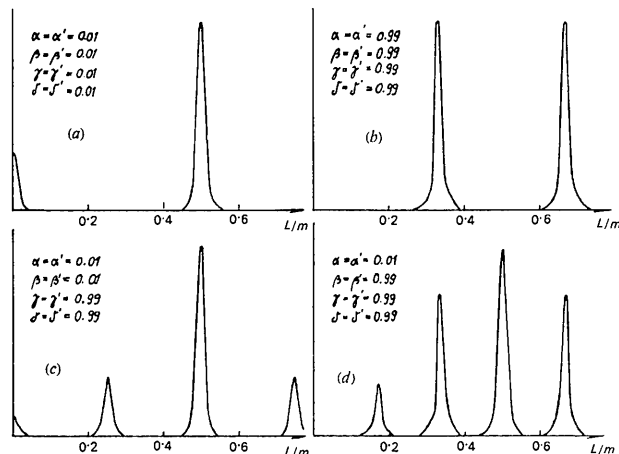
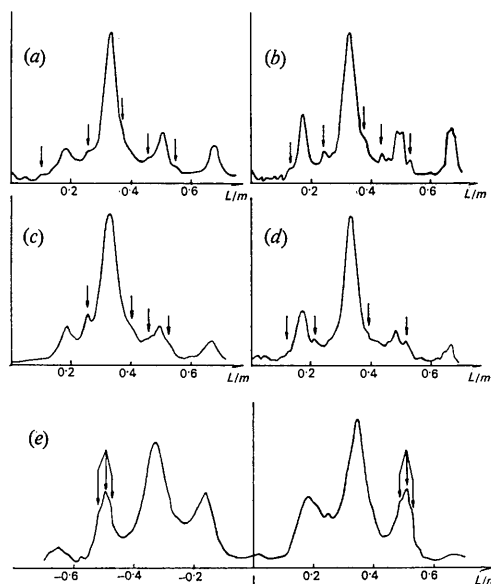
Fig. 7. Theoretical intensity distribution curves calculated on the basis of J. Kakinoki's (1967) paper for $s=4$ ($N=40$) for structures similar to simple polytypes: 2H(a), 3C(b), 4H(c), 6H(d).

Fig. 4. Photometric curve for structure 6H+disorder.

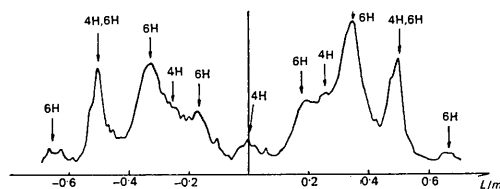


Fig. 5. Photometric curve for structure 4H+6H+disorder.

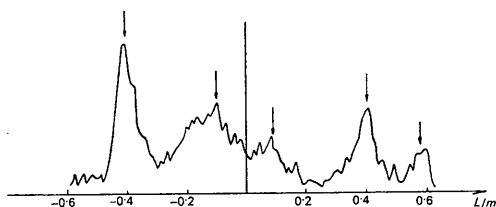


Fig. 6. Photometric curve for structure disordered.

These examples of the application by various authors of the existing general formulae to the determination of real crystal structures prove the deficiency of existing theoretical description. A more realistic approach is clearly desirable.

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