

## X-ray Diffraction Study of One-Dimensional Disorder in Cadmium Iodide Crystals

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One hundred and eighteen crystals of cadmium iodide have been investigated by X-ray diffraction methods to verify the disorder theory of polytypism in these crystals. The degree of one-dimensional disorder has been evaluated for eighty-two polytypes by intensity measurements on oscillation photographs. The frequency distribution curve of relative abundance of polytypes *versus* their degree of disorder shows two maxima, one for  $\alpha_1 \approx 0.06$  and the other for  $\alpha_2 \approx 0.26$ . The results are in agreement with those obtained earlier by Jagodzinski in silicon carbide crystals and provide more information regarding the origin of polytypism in crystals. Fifty-three new polytypes of cadmium iodide, forty-four hexagonal and nine rhombohedral, have also been discovered during the investigation.

### Introduction

Among the various theories put forward to explain the phenomenon of polytypism (Zhdanov & Minervina, 1945; Lundqvist, 1948; Frank, 1951; Ramsdell & Kohn, 1952; Jagodzinski, 1954*a*; Schneer, 1955; Peibst, 1963), our attention has been mainly directed towards Jagodzinski's disorder theory, according to which the structure of a polytype is determined by thermodynamical considerations. Jagodzinski (1954*b*) has suggested a layer transposition mechanism based on the vibration entropy of the structure. The theory has been verified by Jagodzinski (1954*a*) himself, in the case of silicon carbide crystals, by evaluating the degrees of disorder of sixty-two one-dimensionally disordered crystals. The frequency distribution curve, obtained by plotting the relative abundances of polytypes *versus* their degrees of disorder, shows two maxima, one at  $\alpha_1 \approx 0$  corresponding to ordered polytypes and the second at  $\alpha_2 \approx 0.12$  corresponding to disordered polytypes, in accordance with the theory.

In recent years, experimental evidence has been steadily mounting against Frank's dislocation theory of polytypism, which provides a simple explanation for the creation of polytypes and which found support in the early work of Verma (1957). The expected direct correlation between the spiral step height, as measured by multiple-beam interferometry, and the height of the X-ray unit cell was observed by Verma in 9 silicon carbide crystals. However, in a similar extensive investigation of solution-grown cadmium iodide crystals, Trigunayat & Verma (1962) failed to establish such a correlation in practically all the 20 cases examined by them. So they concluded that the dislocation theory fails to explain the formation of cadmium iodide polytypes. Similar conclusions have been arrived at by Srivastava & Verma (1962, 1964, 1965) by working out the detailed atomic structures of four long period polytypes of cadmium iodide, *viz.* 22*H<sub>c</sub>*, 26*H<sub>c</sub>*, 26*H<sub>a</sub>* and 28*H<sub>c</sub>*. Recently Chadha & Trigunayat (1967*a*) have performed a combined optical and X-ray investigation

of a large number of vapour-grown cadmium iodide crystals, which are expected to be more pure than the solution-grown specimens. They, too, have failed to establish a correlation between the spiral step height and the cell height in practically all the 26 cases tested by them. They have also discovered (Chadha & Trigunayat, 1967*b*) for the first time two rhombohedral polytypes of cadmium iodide whose existence cannot be explained on Frank's (1951) theory. During their investigations of polytypism in cadmium iodide crystals, Trigunayat & Verma (1962) and Chadha (1967*c*) frequently observed 'streaking' on numerous X-ray photographs. The 'streaking' in which the reflexions on a layer line (or a row line) are seen to run into each other, is a direct manifestation of one-dimensional disorder inside a crystal. However, no quantitative measurements of the degrees of disorder were made by them. As cadmium iodide is a strongly polytypic substance (86 CdI<sub>2</sub> polytypes had been discovered before the present investigation) and has two types of atoms like silicon carbide, it was decided to verify Jagodzinski's theory in the case of CdI<sub>2</sub> crystals by an X-ray investigation similar to that carried out earlier by Jagodzinski (1954*a*) on SiC crystals. 196 CdI<sub>2</sub> polytypes have been examined out of which the degree of disorder has been evaluated in 82 cases. The results, presented in the following, find good qualitative agreement with Jagodzinski's theory.

### Experimental

The crystals used in the present investigation were all grown from a supersaturated solution, elevated to about 60°C, by slow evaporation at room temperature. The details of the method of growth have been described elsewhere (Jain & Trigunayat, 1968). The crystals were observed under a polarizing microscope for perfection and only those which showed uniform extinction were subjected to X-ray studies.

The degree of disorder of the crystals were measured upon their *c* axis oscillation photographs. The same

were also used for the identification of polytypes. Since the reciprocal lattices of different polytypes are all similar, except for a change in  $c^*$ , the X-ray diffraction photographs obtained from them are also very similar. On the X-ray oscillation photographs, the rows of  $10.l$  reflexions coincide for all hexagonal (or rhombohedral) polytypes of a substance. The oscillation photographs of the higher polytypes were compared with that of a type  $2H$  or type  $4H$  for identification purposes. The oscillation photographs about the  $c$  axis were taken in a range starting from the position when the  $a$  axis made an angle of  $31.5^\circ$  with the incident X-ray beam and went over to the position  $31.5 + 15^\circ = 46.5^\circ$ . This range of oscillation for any cadmium iodide polytype is found to be the most suitable as it records all the reflexions from  $10.0$  to  $10.X$  for an  $XH$  polytype. Only those crystals were chosen for final investigation which could be identified unambiguously. As examples, Figs. 1 and 2 show the  $15^\circ$   $c$  axis oscillation photographs of types  $4H$  and  $20H$ , respectively, taken in the above-mentioned range of oscillation.

#### Evaluation of the degree of disorder

The structural faults, consisting of random displacement of layers from their normal positions, occur during the growth of cadmium iodide crystals. The directions of the displacements being parallel to the layers, their effect is to destroy the regularity of the structure in  $[0001]$  direction, causing one-dimensional disorder in the crystals. Consequently only one Laue condition is violated. On an X-ray diffraction photograph, spots on a row with  $h-k \not\equiv 0 \pmod{3}$  are linked by a streak, the intensity of which depends on the degree of disorder and varies from crystal to crystal.

Jagodzinski (1954a) has developed a method for evaluating the degree of one-dimensional disorder of a crystal, with two types of atoms, by measuring the intensities of the sharp reflexions and the streak connecting them, on an oscillation photograph. The relation for the degree of disorder, as deduced by him for the case where the faults tend to occur at regular intervals and form a superstructure, is given by

$$\frac{\alpha}{1-\alpha} = \frac{\int_0^1 \frac{I_d}{|F|^2} dA_3}{\int_0^1 \frac{I_s}{|F|^2} dA_3} \quad (1)$$

where  $\alpha$  represents the degree of disorder,  $|F|$  is the theoretical value of the structure factor of a unit layer of structure, and  $I_d$  and  $I_s$  represent the intensities of the streak and the sharp reflexions, respectively. The integration is made over the range of the reciprocal lattice plane distance of a unit layer in the Fourier space.

#### Calculation of $\alpha$ in $\text{CdI}_2$ crystals

Cadmium iodide is a strongly polytypic compound with two types of atom. The relation (1) applies to this

case as well. However, for certain practical reasons, described below, we have employed relation (1) in evaluations of  $\alpha$  after changing the limits of integration from  $0 \rightarrow 1$  to  $1 \rightarrow 2$ , which leaves the values of the integrals unaffected in the relation. Thus the relation used by us is

$$\frac{\alpha}{1-\alpha} = \frac{\int_1^2 \frac{I_d}{|F|^2} dA_3}{\int_1^2 \frac{I_s}{|F|^2} dA_3} \quad (2)$$

where the integration is now made over the range of the reciprocal lattice plane distance of a basic unit layer,  $A_3$ , of cadmium iodide, in Fourier space.  $|F|$  is the theoretical value of the structure factor of the unit layer of cadmium iodide. As on the  $10.l$  row of an oscillation photograph the range distance, containing reflexions from  $10.0$  to  $10.X$ , for an  $XH$  polytype, is twice the reciprocal-lattice plane distance of the spacing between two consecutive unit layers of cadmium iodide. Thus out of the two ranges available,  $0 \rightarrow 1$  and  $1 \rightarrow 2$  (on the  $10.l$  row of reflexions), the latter has been used in the calculation of the degree of disorder.

The change in the limits of integration is necessitated for the following reason. The cadmium iodide crystals occur as flat hexagonal platelets with the  $c$  axis normal to the  $(0001)$  basal faces. Because of high absorption coefficients of both cadmium and iodine, a heavy absorption occurs near the zero layer line of the  $c$  axis oscillation photographs, seriously affecting the intensities of nearly one quarter of the reflexions recorded in the range 0 to 1. The reflexions in the reciprocal lattice range 1 to 2 remain unaffected by such an absorption. Therefore, they are particularly suitable for intensity measurements.

The value of the structure factor  $|F|$  of the basic unit layer of cadmium iodide has been calculated as follows. As determined by Bozorth (1922), the basic unit layer, usually referred to as minimal sandwich, of cadmium iodide, consists of two layers of hexagonal close-packed iodine ions with small cadmium ions nested between them. In the standard  $ABC$  notation the unit layer may be represented by  $(A\gamma B)$ ,  $(B\alpha C)$ , or  $(C\beta A)$ . Let  $zA, \alpha$ ,  $zB, \beta$  and  $zC, \gamma$  denote the  $z$  coordinates of the iodine and cadmium atoms on the  $A$ ,  $B$ , and  $C$  axes, respectively, passing through  $(0, 0, 0)$ ,  $(\frac{2}{3}, \frac{1}{3}, 0)$  and  $(\frac{1}{3}, \frac{2}{3}, 0)$ , respectively.

The intensity of a  $10.l$  reflexion from any cadmium iodide polytype can be written as

$$I \propto |F|^2 = A'^2 + B'^2$$

where

$$\begin{aligned} A' &= \sum_{zA, \alpha} f_{I, \text{ca}} \cos 2\pi lz + \sum_{zB, \beta} f_{I, \text{ca}} \cos 2\pi(lz - \frac{1}{3}) \\ &\quad + \sum_{zC, \gamma} f_{I, \text{ca}} \cos 2\pi(lz + \frac{1}{3}) \\ B' &= \sum_{zA, \alpha} f_{I, \text{ca}} \sin 2\pi lz + \sum_{zB, \beta} f_{I, \text{ca}} \sin 2\pi(lz - \frac{1}{3}) \\ &\quad + \sum_{zC, \gamma} f_{I, \text{ca}} \sin 2\pi(lz + \frac{1}{3}). \end{aligned}$$

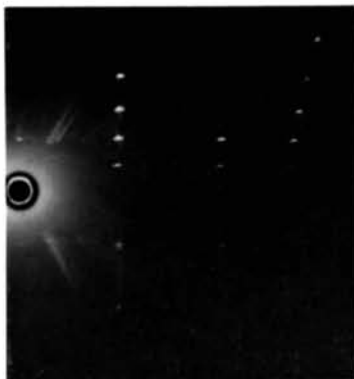


Fig.1. A  $15^\circ$   $c$ -axis oscillation photograph of the type  $4H$  (Crystal No. 25, Table 1); 3 cm camera;  $\text{Cu } K\alpha$  radiation.

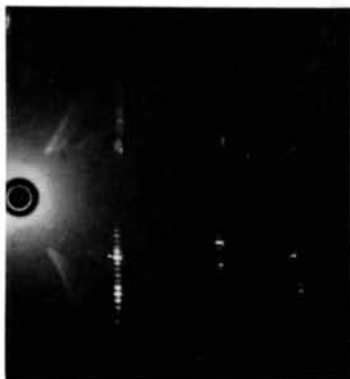


Fig.2. A  $15^\circ$   $c$ -axis oscillation photograph of the type  $20H$  (Crystal No. 51, Table 1); 3 cm camera;  $\text{Cu } K\alpha$  radiation. The photometric trace taken along the  $10.l$  row from the photograph is shown in Fig.3.

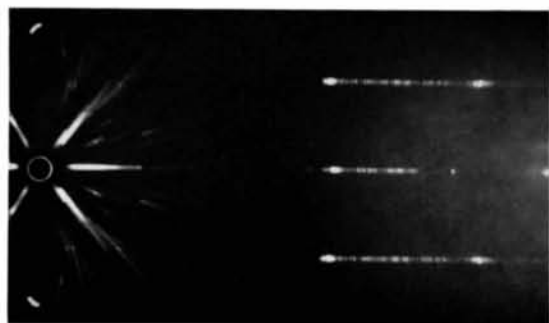


Fig.7. A  $15^\circ$  *a*-axis oscillation photograph of the type 46*H*.  
3 cm camera; Cu  $K\alpha$  radiation.

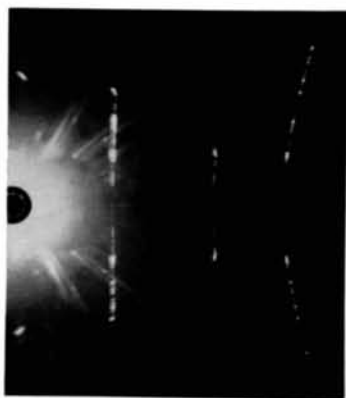


Fig.8. A  $15^\circ$  *c*-axis oscillation photograph of the type 108*R*.  
3 cm camera; Cu  $K\alpha$  radiation.

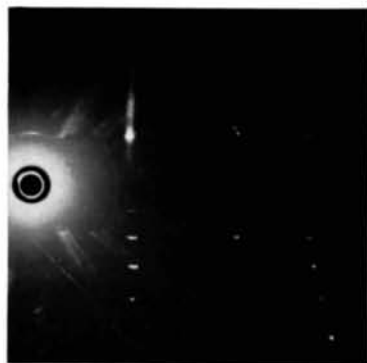


Fig.10. A  $15^\circ$  *c*-axis oscillation photograph of a  $\text{CdI}_2$  crystal  
showing a mixture of highly disordered polytypes. 3 cm  
camera; Cu  $K\alpha$  radiation.

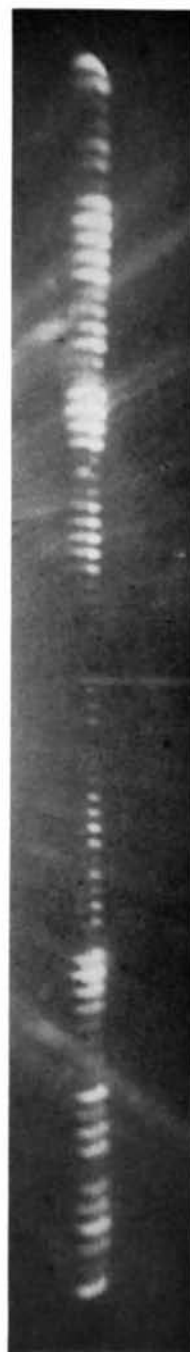


Fig.9. Enlargement of part of Fig.8 showing non-symmetrical  
diffraction spots on the 10.*l* row about the zero layer line.

$f_I, f_{Cd}$  represent the atomic scattering factors of iodine and cadmium atoms respectively.  $\sum_{zA,\alpha}$  means summation over iodine atoms at  $A$  sites and cadmium atoms at  $\alpha$  sites. Similarly for  $\sum_{zB,\beta}$  and  $\sum_{zC,\gamma}$ .

The intensity measurements were made with the help of a recording type microphotometer. The photometric traces along  $10.l$  row and of the background near the row were taken in each case. As a representative example Figs. 3 and 4 show the traces of the  $10.l$  row and of the background intensities for the polytype  $20H$ . For determination of intensities from photometric traces, a standard calibration curve of photographic density (of blackening) versus exposure time was drawn. The curve thus obtained was used to read the intensity values. All photometric traces always had the same distance of nearly 8.5 inches along the abscissa. Every inch of the chart consisted of 10 divisions. Therefore in all cases the intensity values at about 85 points along the trace were read with the aid of the calibration curve. The same procedure was repeated for the traces of background intensity. The measured intensity at any point was then taken to be the difference between the two values. *i.e.* the value for  $10.l$  row minus the corresponding value for the background intensity.

From the intensity values, measured experimentally, and the  $|F|^2$  values, calculated theoretically,  $I/|F|^2$  val-

ues for various reflexions were obtained. These were then plotted against the reciprocal lattice distance range or  $A_3$  values [equation (2)]. The intensity curve thus obtained was divided into areas pertaining to the sharp reflexions ( $I_s$ ) and the streak ( $I_a$ ) respectively. The ratio  $\int I_a / \int I_s$  of these integrated intensities gave the degree of disorder according to equation (2) as

$$\frac{\alpha}{1-\alpha} = \frac{\int I_a}{\int I_s},$$

or,

$$\alpha = \frac{\int I_a}{\int I_s + \int I_a}. \quad (3)$$

Fig. 5 shows the plot of  $I/|F|^2$  versus  $A_3$  values, obtained from the photometric traces of Figs. 3 and 4. The shaded area belongs to the streaking while the area covered by peaks belongs to sharp reflexions.

#### Experimental results

196 polytypes have been examined during the present investigation, out of which 82 have been found suitable

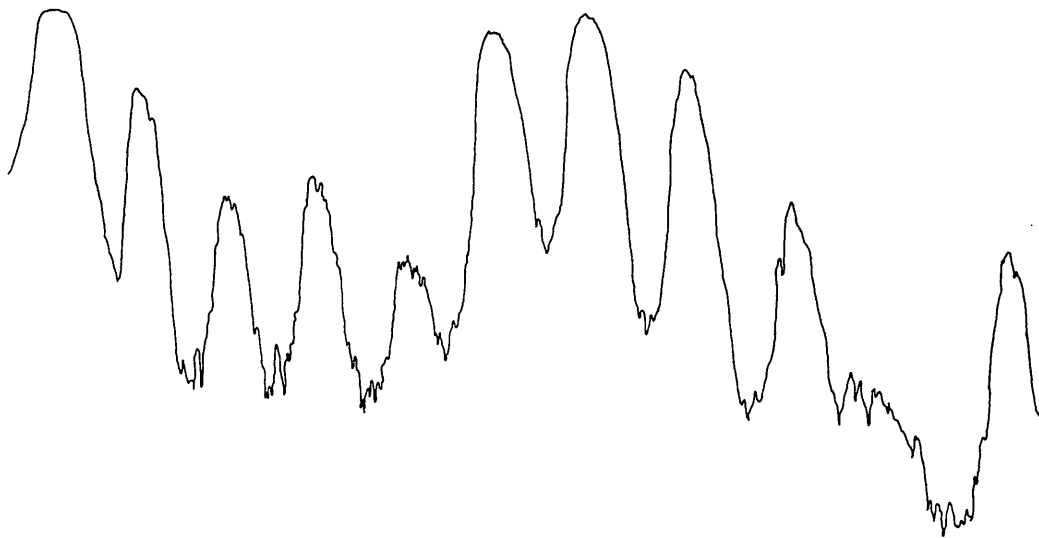


Fig. 3. Photometric trace along the  $10.l$  row, in the limits  $A_3=1 \rightarrow 2$ , of the type  $20H$  (Crystal No. 51, Table 1).

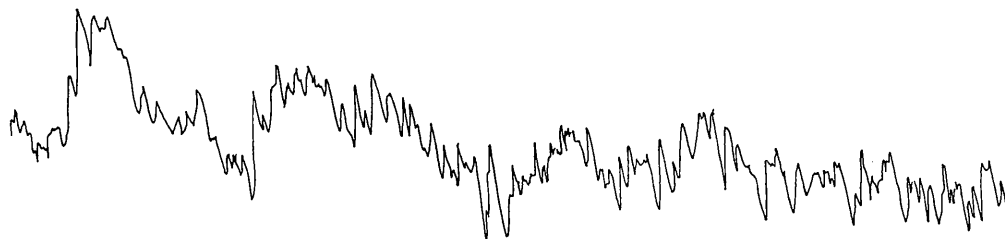


Fig. 4. Photometric trace of the background measured near the  $10.l$  row in the limits  $A_3=1 \rightarrow 2$  (Crystal No. 51, Table 1).

for calculating  $\alpha$ , the degree of disorder. The values of  $\alpha$ , calculated according to relation (3) are listed in Table 1. In addition, 16 polytypes have been found to be well-ordered ( $\alpha \approx 0$ ). The rest of the polytypes have shown a heavy streaking, streaking through a small part of the spots only, a very high identity period, or a mixture of several polytypes or unidentified types, thus rendering the calculation of  $\alpha$  impossible.

Table 1. Values of  $\alpha$  calculated according to relation (3)

Crystal			Crystal		
No.	Type	$\alpha$	No.	Type	$\alpha$
1	2H	0.06	42	8H	0.18
2	2H	0.06	43	8H	0.32
3	2H	0.08	44	10H	0.09
4	2H	0.09	45	12H	0.06
5	2H	0.11	46	12H	0.08
6	2H	0.15	47	14H	0.14
7	2H	0.29	48	16H	0.15
8	2H	0.29	49	18H	0.08
9	2H	0.49	50	20H	0.05
10	4H	0.04	51	20H	0.07
11	4H	0.05	52	20H	0.08
12	4H	0.06	53	20H	0.09
13	4H	0.06	54	20H	0.12
14	4H	0.07	55	20H	0.16
15	4H	0.08	56	22H	0.08
16	4H	0.09	57	22H	0.15
17	4H	0.10	58	24H	0.07
18	4H	0.10	59	26H	0.07
19	4H	0.12	60	26H	0.07
20	4H	0.12	61	26H	0.10

Table 1 (cont.)

Crystal			Crystal		
No.	Type	$\alpha$	No.	Type	$\alpha$
21	4H	0.13	62	28H	0.25
22	4H	0.13	63	30H	0.03
23	4H	0.14	64	30H	0.07
24	4H	0.16	65	30H	0.08
25	4H	0.17	66	30H	0.10
26	4H	0.17	67	34H	0.08
27	4H	0.20	68	34H	0.10
28	4H	0.21	69	36H	0.08
29	4H	0.21	70	36H	0.09
30	4H	0.23	71	36H	0.11
31	4H	0.24	72	36H	0.11
32	4H	0.24	73	38H	0.03
33	4H	0.25	74	40H	0.13
34	4H	0.27	75	40H	0.15
35	4H	0.27	76	42H	0.05
36	4H	0.28	77	42H	0.09
37	4H	0.31	78	42H	0.09
38	4H	0.33	79	42H	0.18
39	4H	0.35	80	44H	0.03
40	6H	0.10	81	44H	0.04
41	6H	0.20	82	44H	0.07

Fig. 6 shows the frequency distribution curve of the degree of disorder in  $\text{CdI}_2$  crystals. The relative abundance of polytypes, with their degrees of disorder lying within a fixed small range of  $\Delta\alpha$ , was obtained by counting the number  $\Delta N$  of the polytypes and forming

the product  $\frac{1}{N} \frac{\Delta N}{\Delta\alpha}$  [ $N=82$  (the total number of poly-

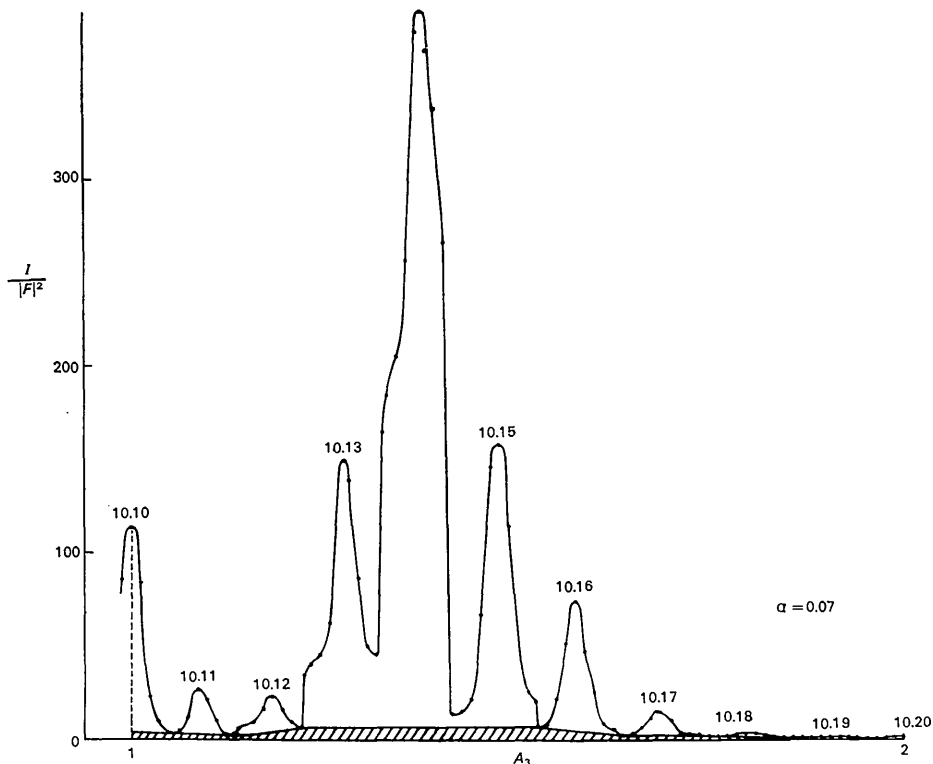


Fig. 5. The plot of  $I/|F|^2$  versus  $A_3$  of the photometric trace (Fig. 3).

types whose  $\alpha$  values have been calculated)+16 (the well-ordered polytypes for which  $\alpha \simeq 0$ )=98]. The curve shows two distinct maxima, the first near the value  $\alpha_1 \simeq 0.06$  and the second for  $\alpha_2 \simeq 0.26$ . The value of the interval  $\Delta\alpha$  chosen in plotting this curve has been 0.40. The frequency distribution curves were also plotted with  $\Delta\alpha=0.030, 0.035, 0.045, 0.050$  and in each case two distinct maxima were obtained. The values of  $\alpha_1$  and  $\alpha_2$ , corresponding to the two peaks of the maxima, in the different cases were found to vary within the limits  $\pm 0.008$  and  $\pm 0.015$ . The reason for finally choosing the value of  $\Delta\alpha=0.040$  has been twofold: (i) the  $\alpha_1, \alpha_2$  values obtained by plotting the curve with this interval very nearly coincides with the average values of  $\alpha$  obtained from the 5 cases mentioned above, (ii) this interval value provides a reasonably sufficient number of points (*viz* nine) to plot the curve. The value  $\alpha=0.49$  was left out while plotting the curve, because it was isolated from the other values and also it did not essentially influence the characteristic shape of the curve. In plotting the curve, the crystal No. 3 with  $\alpha=0.08$  has been included in the range 0.04–0.08 of  $\Delta\alpha$ ; similarly crystal No. 24 with  $\alpha=0.16$  has been included in the range 0.16–0.20 of  $\Delta\alpha$ . Such selections have been made from the knowledge of  $\alpha$  to the third place of decimals.

### New polytypes

This study has resulted in the discovery of 53 new polytypes of cadmium iodide in addition to the already

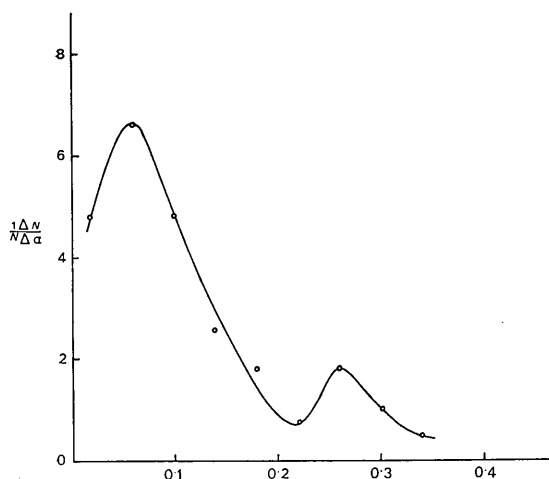


Fig. 6. Frequency distribution of the degree of disorder in  $\text{CdI}_2$  crystals.

known 86 polytypes of this compound. These have been listed below in two categories according to whether (i) their  $c$  dimensions are already known but structural sequences may be different and (ii) they have entirely new  $c$  dimension.

### Category (i)

Hexagonal		Hexagonal	
1	8H <sub>c</sub>	22	30H <sub>g</sub>
2	12H <sub>f</sub>	23	34H <sub>c</sub>
3	14H <sub>c</sub>	24	34H <sub>a</sub>
4	16H <sub>c</sub>	25	36H <sub>a</sub>
5	18H <sub>g</sub>	26	36H <sub>e</sub>
6	20H <sub>i</sub>	27	36H <sub>f</sub>
7	20H <sub>j</sub>	28	36H <sub>g</sub>
8	20H <sub>k</sub>	29	36H <sub>h</sub>
9	20H <sub>i</sub>	30	38H <sub>a</sub>
10	20H <sub>m</sub>	31	40H <sub>f</sub>
11	20H <sub>n</sub>	32	40H <sub>g</sub>
12	22H <sub>e</sub>	33	42H <sub>c</sub>
13	22H <sub>f</sub>	34	42H <sub>a</sub>
14	22H <sub>g</sub>	35	42H <sub>e</sub>
15	24H <sub>i</sub>	36	42H <sub>f</sub>
16	26H <sub>e</sub>	37	44H <sub>b</sub>
17	26H <sub>f</sub>	38	44H <sub>c</sub>
18	28H <sub>e</sub>	39	44H <sub>a</sub>
19	30H <sub>a</sub>	40	44H <sub>c</sub>
20	30H <sub>e</sub>	41	48H <sub>c</sub>
21	30H <sub>f</sub>	42	48H <sub>a</sub>
		43	54H <sub>b</sub>

### Rhombohedral

1 42R<sub>b</sub>

### Category (ii)

Hexagonal		Rhombohedral	
1	46H	1	24R
2	62H	2	36R <sub>a</sub>
3	66H	3	36R <sub>b</sub>
		4	48R
		5	60R
		6	108R

As representative examples, Figs. 7 and 8 show the  $15^\circ$   $a$  axis and  $c$  axis oscillation photographs of the new polytypes 46H and 108R, respectively. Fig. 9 is an enlarged photograph of a part of Fig. 8, showing unsymmetrical diffraction spots on the 10.1 row, about the zero layer line, characteristic of all rhombohedral polytypes.

With the addition of these new polytypes, the total number of cadmium iodide polytypes discovered up to this date becomes 139.

The percentages of the various polytypes observed in the present investigation are given in Table 2. The

Table 2. Percentages of the observed polytypes

	Crystal type	Ordered	Disordered	Total number of times observed		Percentage
1	Type 4H	4	48	52	26.53	
2	Type 2H	11	13	24	12.24	
3	Rare types	1	71	72	36.73	
4	Unidentified			48	24.49	
	Total			196	99.99	

authors present these data with some reservations, because these percentages do not seem to be the same for every batch of crystals.

### Discussion

The theory of one-dimensional disorder in crystals, as developed by Jagodzinski (1954*a*) explains the phenomenon of polytypism in terms of vibration entropy of crystals. The vibration entropy causes an ordering of faults in a disordered crystal, leading to the formation of a 'superstructure' of the faults. All polytypes of a substance can be derived from one or two basic structures, by postulating that stacking faults occur randomly in the structure during crystal growth and subsequently become ordered by the vibration entropy, giving rise to the new polytypic structure which naturally has a lesser degree of disorder. Thermodynamically it means that a coexistence of the ordered and disordered structures within a crystal is possible and can be interpreted as a metastable equilibrium. The nature of variation of the total entropy with different degrees of disorder, obtained theoretically, gives rise to two maxima in the frequency distribution curve of the polytypes, one for  $\alpha_1 \approx 0$  and the other for  $\alpha_2 \approx 0.12$ . This has been experimentally verified to be so for silicon carbide polytypes. The results obtained in this investigation for cadmium iodide polytypes find agreement with the above theoretical prediction. The frequency distribution curve drawn for the relative abundances of polytypes *versus* their degrees of disorder shows two maxima (Fig. 6). The first of these occurs at  $\alpha_1 \approx 0.06$  (relatively ordered polytypes) and the second at  $\alpha_2 \approx 0.26$  (disordered polytypes), with a continuous transition between the relatively ordered and disordered types. That means the polytypes with any degree of disorder may exist, but a large number of them will occur having the degree of disorder, either  $\alpha_1 \approx 0.06$  or  $\alpha_2 \approx 0.26$ . These  $\alpha$  values show a shift towards the higher side when compared with the corresponding values,  $\alpha_1 \approx 0$  and  $\alpha_2 \approx 0.12$ , in the case of silicon carbide. However, as all cadmium iodide polytypes are built up of various numbers of minimal sandwiches (each sandwich is a molecular sheet of cadmium iodide, consisting of a layer of Cd ions sandwiched between two close-packed layers of I ions) held together by weak van der Waals forces of attraction, they are far more favourably suited for layer displacements than silicon carbide, in which the layers are firmly secured in their positions because of interlinking of carbon and silicon lattices, with each Si atom in strong homopolar binding with four surrounding C atoms and *vice versa*. Therefore the cadmium iodide polytypes are generally expected to be more disordered than the silicon carbide polytypes. This is substantiated by the experimental observation that only rarely does one come across a completely ordered cadmium iodide crystal. Out of the 196 polytypes, found in 118 crystals, and studied during this investigation, only 16 have been found to possess

well-ordered structures. Excepting for the 16*H* polytype, all these happen to be one of the basic types, 2*H* or 4*H*. It is worth while comparing these results with those of Jagodzinski for silicon carbide; he obtained 88 well-ordered specimens out of a total number of 150 crystals. Indeed, it seems that a disorder of  $\alpha \approx 0.06$  should normally be present in a cadmium iodide crystal.

As also found by earlier workers, (Mitchell, 1956; Trigunayat & Verma, 1962; Srivastava & Verma, 1962; Kleber & Fricke, 1963) type 4*H* is the most abundant of all polytypes in cadmium iodide. Hence it is commonly regarded as the basic cadmium iodide structure. The 2*H* type, although occurring far less frequently, than the 4*H* type but more frequently than any other CdI<sub>2</sub> polytype, may be regarded as another basic cadmium iodide structure, as it can be simply built up by laying down the minimal sandwiches one over the other in identical positions. All other polytypes may be generated from these two basic types by introduction of faults, which subsequently become ordered by vibration entropy. If the ordering succeeds, *i.e.* a higher polytype is formed, the degree of disorder will be necessarily small. Otherwise the basic structure will generally have a higher degree of disorder. It is seen in Table 1 that in the cases of all disordered specimens ( $\alpha \neq 0$ ) the value of  $\alpha$  is generally less for all higher polytypes (6*H* onwards; 8*H* and 28*H* excepted) whereas for the basic types 2*H* and 4*H* it is generally on the higher side. This is in harmony with Jagodzinski's (1954*a*) result for silicon carbide that the crystals with high degrees of disorder invariably have a tendency to the formation of mixed superperiods and that if a single superperiod can succeed the degree of disorder is essentially less. The tendency to the formation of mixed superperiods has also been observed in the present investigation in practically all the cases of the crystals showing heavy streaking on their X-ray photographs, *e.g.* Fig. 10.

A very common and striking feature observed has been that one side of almost every crystal is relatively more disordered than the other. In some cases, while the one side is completely ordered, the other is quite disordered. This common feature is in complete accordance with the Jagodzinski's theory which predicts the coexistence of order and disorder in the same crystal piece.

Several rhombohedral polytypes have been observed in the present investigation. The existence of these polytypes is prohibited on the dislocation theory but it is comprehensible on the disorder theory (Chadha & Trigunayat, 1967*b*).

According to Jagodzinski's theory a long period polytype should generally be accompanied by some degree of disorder. In the present investigation all higher polytypes except the 16*H*, have been found to be disordered. However, in an investigation of cadmium iodide crystals grown from vapour phase Chadha (1967*c*) has obtained some well-ordered long period



polytypes. Krishna & Verma (1963) have also reported well-ordered long period polytypes,  $90R$ ,  $36H$ ,  $111R$ , in silicon carbide. The formation of such polytypes, although not totally improbable, is difficult to understand on Jagodzinski's theory.

An argument often advanced against the disorder theory has been its inability to explain the existence of structural series in silicon carbide and cadmium iodide. The following series have been established so far.

SiC			
	Series	Members of the series	Polytype
1	$[(33)_n32]_3$	(i) $[(33)32]_3$	$33R$
		(ii) $[(33)_232]_3$	$51R_a$
		(iii) $[(33)_432]_3$	$87R$
		(iv) $[(33)_532]_3$	$105R$
		(v) $[(33)_732]_3$	$141R$
		(vi) $[(33)_{21}32]_3$	$393R$
2	$[(33)_n34]_3$	(i) $[(34)]_3$	$21R$
		(ii) $[(33)34]_3$	$39R$
		(iii) $[(33)_234]_3$	$57R$
		(iv) $[(33)_534]_3$	$111R$
CdI <sub>2</sub>			
	Series	Members of the series	Polytype
1	$(22)_n11$	(i) 11	$2H$
		(ii) $(22)11$	$6H$
		(iii) $(22)_211$	$10H$
		(iv) $(22)_311$	$14H$
		(v) $(22)_411$	$18H_b$
		(vi) $(22)_611$	$26H_a$
2	$(22)_n1111$	(i) $(22)1111$	$8H$
		(ii) $(22)_21111$	$12H_c$
		(iii) $(22)_61111$	$28H_c$

The existence of these series indicates that the polytypes have a regular pattern of growth and thus, *prima facie*, it points to the possibility of the existence of a well-defined mechanism for the generation of polytypes. A careful examination, however, reveals that it may not necessarily be so. It is seen in the above list that all the members of the two series in silicon carbide have a tendency to include (33) units in their structures. The higher the polytype, the more is the number of such units. Now, (33) is the structure of the type  $6H$ , which is the most stable polytype of silicon carbide. So the SiC polytypes have a normal tendency to stabilize their structures by including more and more of the (33) units amongst them. This is substantiated by the observation that of the nearly 35 SiC polytypes whose structures have been determined (Verma & Krishna, 1966; Yuasa & Tomita, 1966, 1967; Gomes de Mesquita, 1968), 18 have been found to be based on the (33) phase. According to the disorder theory, formation of polytypes is governed by statistical fluctuations, which implies that all polytypes can form during crystal growth. Nevertheless, it is naturally expected that those with a greater stability will have greater probability of formation. Hence the existence of structure series. The same situation exists in cadmium iodide in which the members of the series have

a tendency to include (22) units in their structures. As (22) is the structure of type  $4H$ , the most stable of all cadmium iodide polytypes, such a tendency is once again naturally explained.

Another possible reason for the discovery of the above series may be that it has been easier to determine the crystal structures of the members of the series. A SiC polytype with an intensity distribution of diffraction spots approaching that of the common type  $6H$  indicates the existence of several (33) units in its unit cell. Hence a large part of its crystal structure becomes known in the very beginning, making the task of determining its complete structure relatively far easier. Therefore the investigator who sets upon the task of working out the crystal structures of SiC polytypes finds it convenient to pick up those having an intensity distribution resembling that of the type  $6H$ . The same applies to the CdI<sub>2</sub> polytypes. Thus, it is very probable that the members of the above series have been discovered more by choice than by chance.

### Conclusion

Of the various theories put forward to account for the phenomenon of polytypism, Frank's (1951) dislocation theory and Jagodzinski's (1954*a*) disorder theory appear to have a promising approach to the problem. Although the dislocation theory is fascinatingly simple and is based on definite principles of crystal growth, the observations of the different workers (Trigunayat & Verma, 1962; Srivastava & Verma, 1962, 1964, 1965; Chadha & Trigunayat, 1967*a,b*) and the findings of the present investigation indicate that it does not provide a plausible explanation for the said phenomenon in the case of cadmium iodide crystals. Instead, the experimental results of Trigunayat & Verma (1962), Chadha & Trigunayat (1967*b*) and the present study, find agreement with Jagodzinski's disorder theory based on the vibration entropy of crystals. The later theory is less direct in its approach and is consequently, less appealing. Nevertheless, its predictions have been well-upheld for the case of SiC crystals, in the experimental investigation carried out by Jagodzinski himself, and now for the CdI<sub>2</sub> crystals.

The observations of Verma (1957), who in a combined optical and X-ray study on silicon carbide crystals has been able to establish a definite correlation between the step heights of surface growth spirals and the unit cell heights, support the Frank theory of polytypism. Although the number of such cases, 9 in all, reported by him is small, the results indicate that the dislocation mechanism may be operative in the generation of at least some percentage of polytypes during crystal growth.

The other theories of polytypism (Ramsdell & Kohn, 1952; Schneer, 1955; Peibst, 1963) must, as yet, be regarded as speculative since the assumptions on which they are based have not been experimentally verified. At present, the most promising single theory

of polytypism appears to be the Jagodzinski's disorder theory.

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## The Geometry of Lattice Planes

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The advantages are discussed of using a ball model to determine the arrangement of lattice points in a given lattice plane and for determining the stacking properties of such planes. It is shown that the ball model can be considered as a simple analogue computer for solving the Diophantine equations involved. To date, such ball models have been used only for cubic and hexagonal crystals, but they can be constructed for many other structures.

In papers with the above title, Jaswon & Dove (1955) and Bevis (1969) have presented systematic methods for mapping the projection of a lattice on to a plane of given Miller indices ( $hkl$ ). The aim of this paper is to draw attention to another method, that of constructing a ball model of a crystal divided parallel to ( $hkl$ ), and to note an error in the earlier papers.

The essential problem is that of finding lattice vectors  $\mathbf{u}, \mathbf{v}, \mathbf{w}$  such that  $\mathbf{u}, \mathbf{v}$  define a primitive mesh in an ( $hkl$ ) plane and  $\mathbf{u}, \mathbf{v}, \mathbf{w}$  define a primitive unit cell in the lattice. It is usually advantageous if the vectors are as small as possible, *i.e.* if the angles between them approach  $90^\circ$ .

Jaswon & Dove (1955) solve the problem by using

$$\begin{aligned} \mathbf{a}' &= l, 0, \bar{h} \\ \mathbf{b}' &= 0, l, \bar{k} \end{aligned} \quad (1)$$

to define a unit mesh in ( $hkl$ ) and then searching out all extra lattice points within this mesh in order to determine a primitive mesh. They then look for a suitable  $\mathbf{w} = w_1, w_2, w_3$  by solving

$$hw_1 + kw_2 + lw_3 = 1. \quad (2)$$

On the other hand, Bevis (1969) chooses

$$\mathbf{u} = \frac{k}{d}, \frac{\bar{h}}{d}, 0, \quad (3)$$

where  $d$  is the highest common factor of  $h$  and  $k$ , looks for an integral solution  $m_1, m_2$  of

$$m_1k - m_2h = d, \quad (4)$$

and can then write down

$$\mathbf{v} = k(1 + m_3) - lm_2, -h(1 + m_3) + lm_1, -d, \quad (5)$$

where  $m_3$  (or, more simply,  $1 + m_3$ ) is an arbitrary integer. Equation (2) is then solved to give  $\mathbf{w}$ .

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