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Interferometric and X-ray Investigation of Polytypism in Cadmium Iodide Crystals in Relation to Crystal Growth

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A combined optical and X-ray diffraction study has been undertaken of the phenomenon of polytypism in cadmium iodide crystals, which grow by a dislocation mechanism. 88 CdI_2 crystals have been investigated to study Frank's ideas of a 'buckle followed by slip' mechanism in the creation of dislocations and subsequently of polytypes. A correlation between the spiral step height and X-ray unit cell is found for a few 2H and 4H structure types. However, for polytypes with larger unit cells no such correlation was observed. This is at variance with previous observations and with Frank's theory and cannot yet be fully explained. Some X-ray diffraction photographs show 'diffuse background' and 'smearing of diffraction spots', with spots elongated along streaks, similar to Jagodzinski's observations on silicon carbide crystals. 13 (possibly 18) new polytypes of CdI_2 are described. In addition, several crystals resembling 2H and 4H types, but having either intensity differences or conspicuous absences of certain reflections, have been found.

1. Introduction

It is now well established that polytypism is a widely occurring phenomenon in crystals. Silicon carbide (Verma, 1953), cadmium iodide (Mitchell, 1955), cadmium bromide (Mitchell, 1958), zinc sulphide (Buck & Strock, 1955; Strock & Brophy, 1955), etc., are known to be polytypic. These polytypic crystals, especially SiC and CdI_2, often exhibit growth spirals on their faces. This observation led Frank (1951) to explain polytypism in terms of dislocations. However, Jagodzinski (1954) has advanced an alternative theory of polytypism based on the vibration entropy of crystals. Mitchell (1956), by combining his X-ray diffraction results on CdI_2 crystals with the measurements of step heights of growth spirals previously published by Forty (1952), has supported Frank's 'buckle followed by slip' mechanism for the creation of dislocations. However, for an unequivocal verification of Frank's theory it is essential to perform the interferometric and X-ray diffraction studies upon the same crystals, as was done by Verma (1957) for silicon carbide. In the present investigation we have carried out this combined optical and X-ray study on cadmium iodide to study its polytypism. For measurement of step height, we need crystals with well-developed growth spirals, and a simple method of growing such crystals was followed. These crystals were isolated for X-ray diffraction work. A preliminary study on a few crystals has been reported earlier (Trigunayat, 1959). A detailed study on 88 crystals has now been completed. These results are reported in the present paper and are discussed in relation to the ideas of Frank & Jagodzinski. This investigation has further resulted in the discovery of 13 (possibly 18) new polytypes in addition to those already found by Mitchell (1956).

2. Experimental methods

Details of the various experimental techniques employed in this investigation have been described earlier (Trigunayat, 1959). Briefly they consist of the following:

(i) *Crystal growth*

A drop of aqueous solution of CdI_2 saturated at about 90 °C. was placed on a cooled glass slide. Nucleation of several small crystal platelets took place immediately due to the sudden change of temperature and consequent high supersaturation. The drop was then suitably enclosed and crystals allowed to grow at reduced temperature till they dried out in about 10–12 hr. Crystals exceeding 0·1 mm. across and a few microns thick were formed. The few crystals showing well-developed growth spirals on their (0001) faces were selected for investigation.

(ii) *Microscopic examination*

The crystals were studied both by transmitted and reflected light employing bright field illumination using a narrow pencil, a procedure which considerably improves the visibility of growth steps as demonstrated by Griffin (1951).

(iii) *Interferometric measurement of step height*

For step height measurement, the fringe methods used by Forty (1952) and by Verma & Reynolds

(1953), which involve the interference of light between the two basal surfaces of the crystal platelet, were utilized. These fringes contour the growth steps and can be observed simultaneously with them in the field of view of the microscope when using a monochromatic light source. In order to distinguish between two successive polytypes it is necessary to measure the step height, h, to within $\frac{1}{2}M$, where $M=6{\cdot}84$ Å is the thickness of the basic layer or 'minimal sandwich' as referred to by Forty (1952). Since these two-beam fringes are much broader than the multiple-beam fringes, Forty's microphotometric method of 'successive differences of photographic density', which leads to considerable accuracy, was employed. To be conservative the errors in step height measurements, quoted in Table 1, have been taken to be four times as much as calculated mathematically by Forty, in order to take account of the presence of dust particles and other impurities on the surface which might cause irregularities in the microphotometric records.

(iv) *X-ray diffraction methods*

Taking advantage of the findings of Mitchell (1956) that practically all CdI_2 polytypes are hexagonal with polytypes differing only in c-spacing, a simplified diffraction method was evolved. This enabled identification of the crystal type, unique indexing of most of the diffraction spots, and evaluation of the unit-cell dimensions from one 15°-oscillation, a-axis photograph by preselecting the range. In fact by a suitable choice of the range of oscillation, a series of ten consecutive $(10\bar{1}l)$ spots, which were taken by Mitchell for the determination of the stacking sequence of various polytypes, could be obtained on the zero layer-line for a type 4H crystal ($c=13{\cdot}67$ Å, see Fig. 9). All the X-ray photographs reproduced are 15°-oscillation, a-axis photographs using Cu $K\alpha$ radiation.

3. Experimental results

Upon (0001) a wide range of growth patterns of familiar shapes was observed. Thus single spirals with hexagonal, trigonal or circular symmetry, spirals due to cooperating dislocations, cross-laced spirals, closed loops due to dislocations of opposite hands, etc., have all been photographed. These patterns are familiar and will not be discussed here. Only certain representative examples relevant to polytypism will be described, along with their corresponding X-ray diffraction patterns.

Fig. 1 shows a single hexagonal spiral on the surface of a crystal (Table 1, No. 47) with clear internal interference fringes contouring the step structure. Fig. 2 is the corresponding 15°-oscillation photograph, in which the diffraction spots resemble those of type 2H but are not identical with them. In this and other similar cases there are either conspicuous absences of certain reflections or there exist intensity differences. This crystal has therefore been classified as 'resembling 2H'.

Fig. 3 shows a typical case (Table 1, No. 46) of one crystal lying over the other, each with its own growth spiral. Both series of growth steps, which are not visible in the figure, are of similar magnitude in height, and only their fringes can be observed. The corresponding X-ray photograph (Fig. 4) shows diffraction spots due only to one type, namely $10H_{(a)}$ (see Section 5), and thus both crystallites have the same structure.

Fig. 5 exhibits as many as eight rounded growth spirals with at least three different step heights (Table 1, No. 26). The corresponding X-ray photograph (Fig. 6) shows spots similar to those of 4H and has been classified as 'resembling 4H'. Thus it is a case of interacting spirals having different step heights but with the crystal structures being the same.

Fig. 8 illustrates the spiral steps and the contouring fringes due to a number of cooperating dislocations upon crystal No. 51. The central part is shown enlarged in Fig. 7. The 15°-oscillation photograph corresponding to this is given in Fig. 9, which shows it to be clearly of type 4H without any deviation. This is to be expected, since a number of dislocations lying close to, and cooperating with, one another will naturally be elementary dislocations.

Two separate crystal platelets lying adjacent to each other are shown in Fig. 10. The crystal on the left (Table 1, No. 55) has a thickness of nearly 15 microns and exhibits a hexagonal spiral which acquires increasing circular symmetry on going away from the centre. The crystal on the right (Table 1, No. 56) has a thickness of nearly 20 microns and shows a spiral with trigonal symmetry upon its surface. As seen in Table 1 and indeed revealed by the contouring fringes the step heights for the two crystals are widely different. The corresponding X-ray photographs (Figs. 11 and 12) show the crystals to be of type $38H_{(b)}$ and 16H, respectively.

Fig. 13 is the X-ray photograph of a crystal (Table 1, No. 59) which had a growth pattern of closed hexagonal loops due to dislocations of opposite hand on its surface. It shows a confused series of diffraction spots due perhaps to a coalescence of crystals which cannot be identified.

The growth sequence of crystal No. 85 was watched throughout its growth. Its 15°-oscillation photograph, shown in Fig. 14 consists of two series of diffraction spots, one due to 4H and the other to 6H. This case may therefore be classified as coalescence of two identified types.

Fig. 15 shows the micrograph of crystal No. 43 whose steps, on going away from the centre, begin to dissociate and interlace with one another in certain orientations. Its X-ray photograph (Fig. 16) shows it to be of type 4H but the spots are elongated along powder pattern arcs.

A close examination of the X-ray diffraction photo-

Fig. 1. Micrograph of (0001) with the interference fringes contouring the step-structure of crystal No. 47. Mag. × 320.

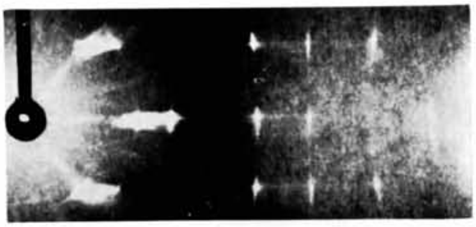

Fig. 2. 15° X-ray oscillation photograph abou ta axis, showing the zero layer-line with $10\bar{1}l$ diffraction spots, along with the first layer lines (3 cm. camera, Cu $K\alpha$). Crystal No. 47. Mag. × 1.

Fig. 3. Micrograph of (0001) with contouring fringes of crystal No. 46. Mag. × 110.

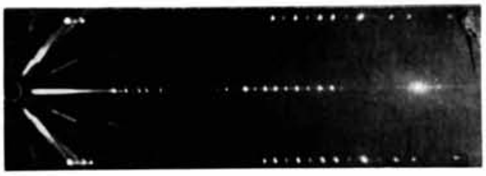

Fig. 4. 15°-oscillation photograph about a axis of crystal No. 46 (Cu $K\alpha$, 3 cm. camera). Mag. × 1.

Fig. 5. Micrograph of (0001) with interference fringes on crystal No. 26. Mag. × 320.

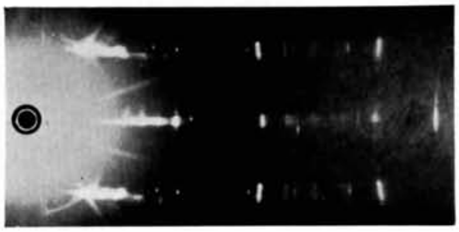

Fig. 6. 15°-oscillation photograph about a axis of crystal No. 26 (Cu $K\alpha$, 3 cm. camera). Mag. × 1.

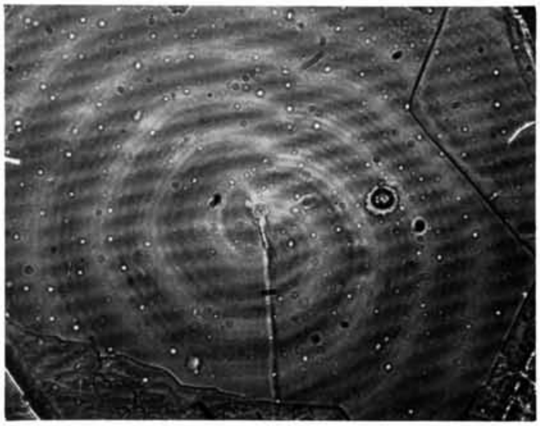

Fig. 7. Micrograph of (0001) with interference fringes of crystal No. 51. Mag. × 320.

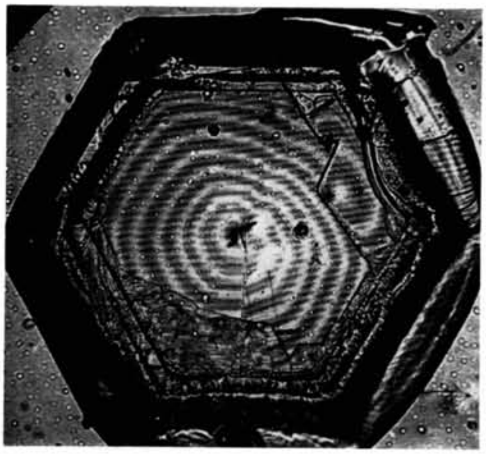

Fig. 8. Micrograph of the entire crystal No. 51. Mag. × 162.

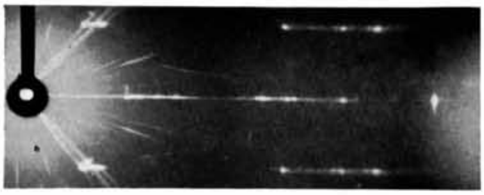

Fig. 12. 15°-oscillation photo about *a* axis of crystal No. 56 (Cu $K\alpha$, 3 cm. camera). Mag. × 1.

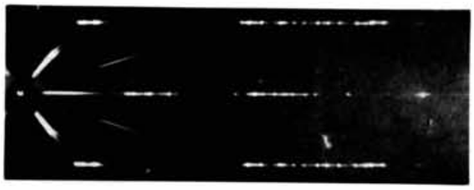

Fig. 13. 15°-oscillation photo about *a* axis of crystal No. 59 (Cu $K\alpha$, 3 cm. camera). Mag. × 1.

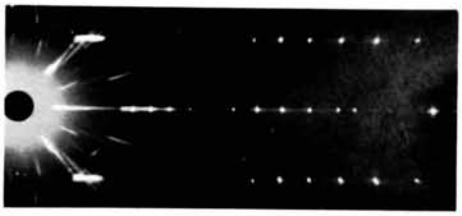

Fig. 9. 15°-oscillation photo about *a* axis of crystal No. 51 (Cu $K\alpha$, 3 cm. camera). Mag. × 1.

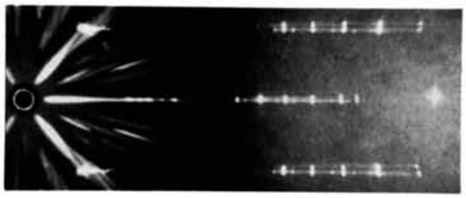

Fig. 14. 15°-oscillation photo about *a* axis of crystal No. 85 (Cu $K\alpha$, 3 cm. camera). Mag. × 1.

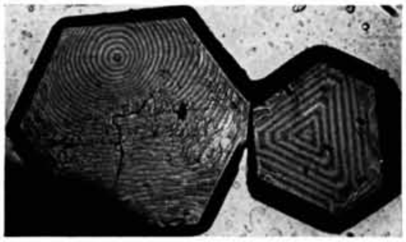

Fig. 10. Combined micrographs of crystals No. 55 and 56 with the contouring interference fringes visible on (0001). Mag. × 90.

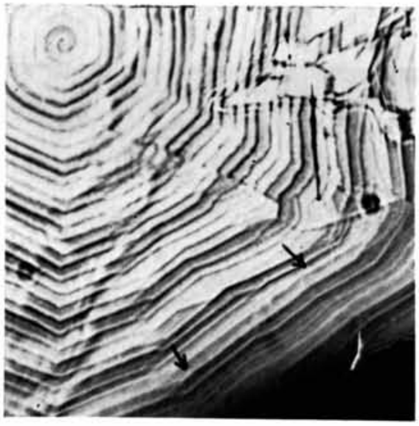

Fig. 15. Micrograph of crystal No. 43. Mag. × 400.

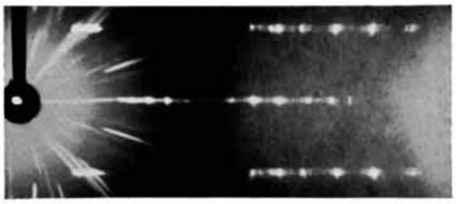

Fig. 11. 15°-oscillation photo about *a* axis of crystal No. 55 (Cu $K\alpha$, 3 cm. camera). Mag. × 1.

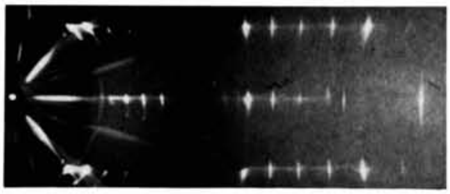

Fig. 16. 15°-oscillation photo about *a* axis of crystal No. 43 (Cu $K\alpha$, 3 cm. camera). Mag. × 1.

graphs reveals that, besides showing the various polytypes through appropriate spacing of spots, these photographs also differ in their fine details and characteristics and may be classified in the following categories:

(i) The diffraction photographs show clear X-ray reflections, so that the corresponding polytypes can be identified without ambiguity, e.g., Figs. 4 and 9.

(ii) The distribution of diffraction spots is similar to that of a particular type, e.g., 2H, 4H or 8H, but there exist either conspicuous absences of certain reflections or intensity differences. These have been classified as 'resembling 2H, 4H or 8H'; an example is Fig. 2.

(iii) The diffraction spots can be resolved into series of spots, each of which can be identified separately with a particular polytype. Such have been designated as 'coalescence identified', an illustration of which is given in Fig. 14.

(iv) The photographs show a confused series of diffraction spots, in which separate constituent types are indistinguishable, and have been classified as 'coalescence unidentified'. An example of this is shown in Fig. 13.

(v) A random distribution of diffraction spots appears. These have been classified as 'unidentified'.

(vi) Lastly, on many oscillation photographs diffraction spots on the zero and other layer-lines are connected by horizontal streaks (e.g., Figs. 2 and 14). These are not Laue streaks and are similar to the 'diffuse background' observed by Jagodzinski in silicon carbide along row lines for oscillation about the *c* axis. The 'smearing' of diffraction spots described by Jagodzinski (1954) has also been observed here and is illustrated by Figs. 2, 6, and 12. Apart from these two effects an unusual phenomenon has been found to occur on a large number of photographs in which the X-ray reflections are drawn into small arcs of a circle which do not lie along lines of constant ξ-value in the Bernal chart, but along powder lines of the substance, e.g., Figs. 2, 6, and 16. This would indicate that successive layers of the crystal plate are randomly oriented about the *c* axis through a certain range. Sometimes the arcs are clearly split into a string of two or more spots (e.g., Fig. 14), showing that the crystal is made up of two or more groups of layers rotated slightly with respect to each other about the *c* axis. The 'powder effect' might be due partly to strain, but in several cases it was certainly not so; some of the crystal plates appeared perfect under polarized light. Thus it is significant to note that during growth, successive layers of the crystal plate could be rotated through a small range with respect to one another, and there must be several stable positions of the stacking of the thin layers on each other. The elongation of the spots, however, did not present any difficulty in the identification of the crystal.

The X-ray and optical measurements are collected in Table 1. Step height measurements have been expressed in Ångström units and also as multiples of $M = 6{\cdot}84$ Å; fractional parts of M are indicated only where it has been possible to measure the height to within $\frac{1}{2}M$, i.e., nearly 3 Å. The *c* dimension, as found by X-ray diffraction has been shown as the nearest integral multiple of $M = 6{\cdot}84$ Å, the observed differences being very small. The symbols used for denoting the various polytypes are in accordance with the general scheme introduced by Ramsdell (1947) and Ramsdell & Kohn (1952). The polytypes having the same number of layers but differing in their arrangement have been distinguished by a subscript, e.g., $H_{(a)}$, $H_{(b)}$. Whether or not the step height, *h*, has a direct correlation with the X-ray unit cell height (the *c* dimension), i.e., *h* is either equal to or an integral multiple of *c*, has been indicated in Table 1 under 'remarks'. The proportional numbers of the various categories of crystals mentioned above are listed in Table 2.

4. Discussion

From the examples given in Table 1, it is evident that in CdI_2 crystals it is not always possible to find a correlation between the step height of the growth spiral and the X-ray unit cell. This is at variance with the observations of Verma (1957) on silicon carbide and with the ideas of Frank (1951). According to the latter, a dislocation would be created in the silicon carbide crystal plate, which may have initially grown by a nucleation mechanism, when it becomes self stressed, through non-uniform distribution of impurities or thermal stresses, up to its theoretical yield stress; it will then buckle and shear, exposing a ledge. The dislocations created in this process will be of different strengths, and since the crystal subsequently growing on these dislocations will necessarily have the structure of the ledge, it will lead to the formation of different polytypes. Forty (1952) extended these ideas to CdI_2 crystals by taking the basic structure to be 4H, which has a structural sequence of layers (22) in Ramsdell's notation or $[(A\gamma B)(C\alpha B)]$ in the classical *ABC* notation, where the Roman letters represent iodine ions and the Greek letters represent cadmium ions. The creation of an 'even' dislocation of any strength in the 'ideal' structure during the early stages of growth leaves the layers in perfect fit with each other, i.e., in a stable configuration, so that the same 4H structure is retained throughout the subsequent growth. This explains the growth steps observed on crystals of type 4H being an integral multiple of its *c* parameter. However 'odd' dislocations of various strengths leave a misfit in the structure at the initial step, so that the subsequent growth leads to formation of various polytypes of the $(22)_n11$ series. A method for the creation of polytypes with a stacking sequence of layers differing from $(22)_n11$ has been suggested by Mitchell (1956), who postulated a combination of dislocations close enough to cooperate.

Table 1. *X-ray and optical data*

Crystal no.	Step height (*h*) in Å	*h* expressed in multiples of *M*	Crystal type determined by X-rays	Remarks
1.	500 or greater	—	18H$_{(a)}$	Step height estimated from visibility of steps
2.			4H	
3.			4H	
4.			2H	
5.			4H	
6.	235·2 ± 1·6	34·38 ± 0·23	resembles 4H	
7.	221·2 ± 1·4	32·32 ± 0·20	2H	
8.	205·0 ± 6·0	∼ 30	4H	
9.	189·7 ± 1·0	27·75 ± 0·15	4H	correlation exists
10.	134·3 ± 3·7	∼ 20	4H	
11.	295·4 ± 9·0	∼ 43	coalescence (identified 2H + 10H)	
12.	303·1 ± 2·4	44·36 ± 0·34	resembles 4H	
13.	324·2 ± 4·0	∼ 47	resembles 4H	
14.	270·0 ± 25·0	∼ 40	2H	
15.	184·7 ± 5·8	∼ 27	unidentified	
16.	170·2 ± 3·0	24·88 ± 0·45	34H$_{(a)}$	*c* = 116·3 Å; no correlation
17.	123·2 ± 3·4	17·20 ± 0·49	resembles 4H	
18.	357·9 ± 2·8	52·33 ± 0·40	resembles 4H	
19.	246·3 ± 5·9	∼ 36	coalescence (unidentified)	
20.	164·6 ± 9·2	∼ 24	resembles 4H	
21.	190·8 ± 6·2	∼ 28	resembles 4H	
22.	124·1 ± 4·3	∼ 18	resembles 4H	
23.	82·3 ± 4·6	∼ 12	18H	*c* = 61·5 Å; no correlation
24.	132·2 ± 1·8	19·33 ± 0·26	4H	*c* = 13·7 Å; no correlation
25.	260·9 ± 7·8	∼ 38	2H	
26.	h_1 = 296·1 ± 14·8	∼ 43	resembles 4H	Fig. 5
	h_2 = 176·9 ± 0·9	25·86 ± 0·13		
	h_3 = nearly 210	∼ 30		
27.	234·3 ± 11·9	∼ 34	resembles 4H	
28.	155·5 ± 2·7	22·73 ± 0·39	unidentified	
29.	175·8 ± 1·6	25·69 ± 0·23	22H$_{(a)}$	*c* = 75·2 Å; no correlation
30.	429·2 ± 4·8	∼ 63	resembles 4H	
31.	261·6 ± 15·4	∼ 38	unidentified	
32.	214·3 ± 2·4	31·33 ± 0·35	resembles 4H	
33.	h_1 = 228·1 ± 2·7	33·34 ± 0·38	resembles 2H	
	h_2 = 151·8 ± 3·4	22·19 ± 0·49		
34.	164·3 ± 1·4	24·02 ± 0·20	resembles 4H	
35.	82·1 ± 1·5	12·00 ± 0·22	unidentified	
36.	92·4 ± 2·9	13·51 ± 0·42	resembles 4H	
37.	89·6 ± 1·8	13·09 ± 0·26	unidentified	
38.	184·8 ± 5·8	∼ 27	10H$_{(b)}$	*c* = 34·2 Å; no correlation
39.	405·0 ± 3·3	59·21 ± 0·48	resembles 2H	
40.	246·6 ± 10·3	∼ 36	resembles 2H	
41.	410·1 ± 1·1	59·94 ± 0·16	resembles 4H	
42.	93·8 ± 1·5	13·71 ± 0·22	resembles 4H	
43.	358·7 ± 1·7	52·43 ± 0·25	4H	correlation exists; Fig. 15
44.	266·3 ± 0·9	38·92 ± 0·14	resembles 4H	
45.	369·3 ± 7·7	∼ 54	6H$_{(c)}$	
46.	247·9 ± 20·7	∼ 36	10H$_{(a)}$	Fig. 3
47.	116·3 ± 0·4	17·01 ± 0·05	resembles 2H	Fig. 1
48.	163·6 ± 1·4	23·92 ± 0·20	36H	*c* = 123·1 Å; no correlation
49.	205·2 ± 0·8	30·02 ± 0·11	resembles 2H	
50.	198·8 ± 1·1	29·06 ± 0·16	38H$_{(a)}$	*c* = 129·9 Å; no correlation
51.	246·3 ± 6·9	∼ 36	4H	Fig. 8
52.	263·7 ± 3·6	∼ 39	coalescence (unidentified)	
53.	h_1 = 169·7 ± 4·2	∼ 25	unidentified	
	h_2 = ∼ 500	—		
54.	160·0 ± 1·3	23·38 ± 0·19	34H$_{(b)}$	*c* = 116·2 Å; no correlation
55.	245·6 ± 3·1	35·90 ± 0·46	38H$_{(b)}$	*c* = 129·9 Å; no correlation; Fig. 10
56.	70·4 ± 1·7	10·29 ± 0·25	16H	*c* = 54·7 Å; no correlation; Fig. 10
57.	164·6 ± 3·8	∼ 24	4H	
58.	371·1 ± 2·0	54·23 ± 0·28	38H$_{(c)}$	*c* = 129·9 Å no correlation
59.	184·7 ± 2·9	27·01 ± 0·42	coalescence (unidentified)	
60.	323·8 ± 3·0	47·34 ± 0·43	resembles 2H	
61.	333·3 ± 2·0	48·27 ± 0·30	resembles 2H	
62.	124·4 ± 0·8	18·19 ± 0·12	coalescence (identified 2H + 14H)	

Table 1 (*cont.*)

Crystal no.	Step height (h) in Å	h expressed in multiples of M	Crystal type determined by X-rays	Remarks
63.	156·0 ± 2·7	22·82 ± 0·39	4H	$c = 13·7$ Å; no correlation
64.	393·9 ± 6·5	~ 58	resembles 4H	
65.	129·6 ± 2·2	18·94 ± 0·32	resembles 8H	
66.	107·1 ± 1·6	15·66 ± 0·23	$22H_{(b)}$	$c = 75·2$ Å; no correlation
67.	278·0 ± 17·3	~ 41	4H	
68.	$h_1 = 123·2 ± 2·6$	18·00 ± 0·37	resembles 4H	
	$h_2 = 111·5 ± 2·1$	16·30 ± 0·31		
69.	nearly 140 Å	—	unidentified	
70.	nearly 240 Å	—	resembles 4H	
71.	252·2 ± 1·6	36·85 ± 0·23	2H	
72.	288·9 ± 0·8	42·24 ± 0·12	52H	$c = 177·8$ Å; no correlation
73.	202·8 ± 4·0	~ 30	resembles 2H	
74.	184·9 ± 7·7	~ 27	unidentified	
75.	296·1 ± 14·8	~ 43	coalescence (unidentified)	
76.	$h_1 = 369·8 ± 15·4$	~ 54	20H	$c = 68·4$ Å; no correlation
	$h_2 = 87·2 ± 5·1$	~ 13		
77.	260·9 ± 7·8	~ 38	$12H_{(d)}$	$c = 41·0$ Å; no correlation
78.	246·9 ± 13·8	~ 36	32H	$c = 109·4$ Å; no correlation
79.	231·8 ± 1·3	38·89 ± 0·15	50H	$c = 171·0$ Å; no correlation
80.	~500 Å or greater	—	4H	Step heights estimated from visibility of steps
81.			coalescence (identified 2H + 4H)	
82.			4H	
83.			4H	
84.			4H	
85.			coalescence (identified 6H + 4H)	
86.			4H	
87.			undecided	
88.			4H	

From energy considerations 'even' dislocations are more likely, which explains the abundant occurrence of type 4H.

According to the above one should therefore expect a direct correlation between the spiral step height and the unit cell height. However, from the examples in Table 1 it is seen that such a correlation exists only for all the cases of 2H and two cases of 4H types (Nos. 9 and 43). This relationship could be tested in 18 more cases with larger unit cells (Nos. 16, 23, 24, 29, 38, 48, 50, 54, 55, 56, 58, 63, 66, 72, 76, 77, 78, and 79); in the rest of the cases either the polytype is not exactly identified or the error in the measurement is too large. It is observed that in all these 18 cases no such correlation has been found to exist. It is easy to explain the correlation for the 2H and 4H types. Every step height should be a multiple of the 2H unit cell, since type 2H corresponds to the 'minimal sandwich' of cadmium iodide; correlation in this case is thus natural and expected. In the case of type 4H it can be understood on the grounds that type 4H happens to be a very common polytype of CdI_2. However, to account for the non-correlation, it may be thought, as was done by Forty to explain the formation of polytypes deviating from a $(22)_n11$ structure, that a crystal plate already containing a polytypic variant in its structure may later acquire a slip. If this slip happened to take place in the concluding stages of growth, a non-correlation between the step-height and the c dimension will be explicable because, then, the measured height of the growth steps upon the end surface will not be a true representative of the structure of the main bulk of the crystal. The last dislocation will have helped the crystal to grow in thickness inappreciably, so that it will be the structure of the main body of the crystal alone that will dominate the X-ray photograph.

It was therefore decided to study the growth sequence of crystals by observing them continuously during growth. Nine crystals (Table 1, Nos. 80 to 88) were subjected to this examination. The step heights given in Table 1 for these crystals are those corresponding to the first of the several spirals originating upon their surface and were estimated from visibility. Consider the example of crystal No. 85. It started growing in thickness by the operation of a growth spiral with a step height greater than 500 Å. Within a few minutes the crystal had grown to a thickness of nearly 15 microns; then two more growth spirals appeared with step heights ~ 500 and 100 Å, respectively, which completely overshadowed the previous one and thickened the crystal to about 25 microns in about an hour. At this stage, growth started by the advancement of certain long 'steps' and 'blocks' of trigonal and hexagonal shapes, which appeared on the crystal surface such that the existing growth spirals, although visible till the end, were rendered absolutely inactive. This mode of growth is very much similar to the one described by Williams (1957) on lead nitrate crystals and by Reynolds & Greene (1958) on cadmium sulphide, and most likely the occasional mode of growth observed by Tolansky & Emara (1955) is also similar. The crystal went on to grow to a thickness of nearly 50 microns till it dried out, when its X-ray examination showed it to be a combination of types 4H and 6H. At no stage in the growth were the elementary growth spirals of step heights 13·7 and 18·5 Å, corresponding to types 4H and 6H, observed. These small steps would not be visible under the microscope but would have been noted by their contouring fringes. Only multiple steps were observed. Now multiple steps corresponding to the 4H structure are easily explained on the basis of Frank's ideas. An 'odd' dislocation and then a further slip in this polytype would be needed to explain the observation for type 6H. It is likely that the non-correlation between the step height and X-ray unit cell height in CdI_2 crystals in contrast to silicon carbide may be due to the non-stability of the dislocation group, which then easily breaks up and recombines to bring about a change in the polytype during growth. However, this observation of non-correlation is not fully explained as yet.

Table 2.

4H	18
2H	5
Rare types (other polytypes)	19
Resembling 4H	20
Resembling 2H	8
Resembling 8H	1
Coalescence, identified	4
Coalescence, unidentified	4
Unidentified	8
Undecided	1
Total	88

Jagodzinski (1954), who has examined fault-order phenomena in 150 silicon carbide crystals, has advanced another theory of polytypism based on vibration entropy of crystals. The 'diffuse background' and the 'smearing' of diffraction spots, which are the essentials of Jagodzinski's theory, have been observed on several X-ray photographs in the present work (examples have already been given). Moreover, the observation of eight 'unidentified' types (see Tables 1 and 2), which had a random distribution of spots due most likely to high disorder (the crystals were perfect optically), shows that fault-order of high degree postulated by Jagodzinski does occur in CdI_2 crystals. Thus, it appears highly desirable to extend the experimental verification of his theory to the case of CdI_2 crystals by evaluating the fault-order degree of every crystal by his method and then analyzing the statistics.

5. New polytypes

This study has resulted in the finding of 13 new polytypes. All the polytypes of CdI_2 are composed of identical layers but differ only in their arrangement and in the number composing the unit cell. Using Ramsdell's notation, the new polytypes found in addition to the 29 reported by Mitchell (1956) and one reported by Pinsker (1941) are $6H_{(c)}$, $10H_{(b)}$, $12H_{(d)}$, $18H_{(a)}$, $22H_{(a)}$, $22H_{(b)}$, $34H_{(a)}$, $34H_{(b)}$, 36H, $38H_{(a)}$, $38H_{(b)}$, $38H_{(c)}$, and 52H, after excluding types 2H and 4H. As noted earlier, when several varieties of a particular type are found in which there is the same number of layers in the unit cell but a difference in their arrangement, we have differentiated them by attaching a small letter as subscript, e.g., $38H_{(a)}$, $38H_{(b)}$ and $38H_{(c)}$. We have found five polytypes with the same number of layers in the unit cell as found by Mitchell, but these have not been differentiated by a subscript letter though they may differ by virtue of their arrangement. However, two polytypes of 18H were encountered as against one by Mitchell, and the new one has been labelled $18H_{(a)}$. Similarly, two type 10H crystals were encountered, one of which had the same stacking sequence as found by Mitchell; accordingly this has been designated $10H_{(a)}$ and the other $10H_{(b}$;. The polytypes 16H, 18H, 20H, 32H, and 50H have ambiguous identity.

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References

Buck, D. C. & Strock, L. W. (1954). *Amer. Min.* **39**, 318.

Forty, A. J. (1952). *Phil. Mag.* **43**, 377.

Frank, F. C. (1951). *Phil. Mag.* **42**, 1014.

Griffin, L. J. (1951). *Phil. Mag.* **42**, 775.

Jagodzinski, H. (1954). *Neues Jb. Miner. Mh.* **3**, 49.

Mitchell, R. S. (1955). *Phil. Mag.* **46**, 1141.

Mitchell, R. S. (1956). *Z. Kristallogr.* **108**, 296.

Mitchell, R. S. (1957). *Z. Kristallogr.* **108**, 341.

Mitchell, R. S. (1958). *Nature, Lond.* **182**, 337.

Pinsker, Z. G. (1941). *Acta Physicochim. USSR*, **14**, 5, 503.

Ramsdell, L. S. (1947). *Amer. Min.* **32**, 64.

Ramsdell, L. S. & Kohn, J. A. (1952). *Acta Cryst.* **5**, 215.

Reynolds, D. C. & Greene, L. C. (1958). *J. Appl. Phys.* **29**, 559.

Strock, L. W. & Brophy, V. A. (1955). *Amer. Min.* **40**, 96.

Tolansky, S. & Emara, S. H. (1955). *Proc. Phys. Soc.* B, **68**, 559.

Trigunayat, G. C. (1959). *Bull. on Crystal Physics Symposium Nat. Inst. Sci. India*, **14**, 109.

Verma, A. R. (1953). *Crystal Growth and Dislocations.* London: Butterworths Publications.

Verma, A. R. (1957). *Proc. Roy. Soc.* A, **240**, 462.

Verma, A. R. & Reynolds, P. M. (1953). *Proc. Phys. Soc.* B, **66**, 414.

Williams, Anne P. (1957). *Phil. Mag. Series*, 8, **2**, 317.