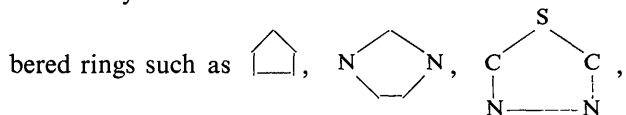



Fig. 6. The probable configuration along the twin boundary.

In many derivatives in which saturated five-mem-



for example, occur, the five-membered rings have four coplanar atoms and one about 0.6 Å out of the plane.

In the  ring in D, L-6-thioctic acid, however, no four atoms form a plane. The -CSSC- atoms attempt to arrange themselves in the hydrogen peroxide configuration but are constrained by the ring closure. The dihedral angle in the -CSSC- group is near 96° in

tetraethylthiuram disulfide (Karle, Estlin & Britts, 1967) and t-butyl-N,N-dimethyltrithioper-carbamate (Mitchell, 1966) whereas in D, L-6-thioctic acid the dihedral angle is only 35°.

The S-S bond length, 2.01 Å, and the C-S bond lengths, 1.81 and 1.85 Å, are near those found in tetraethylthiuram disulfide, t-butyl-N,N-dimethyltrithioper-carbamate and *trans*-2,5-dibromo-1,4-dithiane for example. The large difference between the two C-C bond lengths in the ring, 1.46 and 1.58 Å, is unexplained.

We are grateful to Dr Jerome Karle for his continuing interest and we wish to express our appreciation to Mr Stephen Brenner and Dr Donald Mitchell, who performed all the calculations.

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First-Found Rhombohedral Polytypes of Cadmium Iodide Two Unique Cases of Structure-Transformation during Growth

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Although a large number (over 80) of hexagonal polytypes of cadmium iodide have been reported earlier, two rhombohedral polytypes of this substance have been discovered for the first time during an investigation of a batch of crystals grown from the vapour phase. These are 30*R* and 42*R*, respectively. Their complete structures have also been worked out and are found to be (221212)₃ and (2221212)₃ respectively. A unique characteristic is that each of these polytypes occurs in syntactic coalescence with a hexagonal polytype having the same cell dimensions as the rhombohedral one, showing that the lattice was transformed from hexagonal to rhombohedral, or *vice versa*, during crystal growth. The results are discussed.

Introduction

There seems to be no upper limit to the number of polytypic modifications of cadmium iodide. Experience

shows that investigation of a group of cadmium iodide crystals chosen at random is certain to yield one or more new polytypes. A total of over 80 modifications has so far been discovered by different workers (Mitchell, 1956; Trigunayat & Verma, 1962; Srivastava & Verma, 1965; Chadha & Trigunayat, 1966), with

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cell heights ranging from 6.84 to 218.88 Å. However, all these modifications possess a hexagonal structure. One rhombohedral modification, *viz.* 24*R*, was reported by Mitchell (1956) but later he expressed doubts about its existence (private communication; Srivastava & Verma, 1962). During an investigation of cadmium iodide crystals grown from the vapour phase (Trigunayat & Chadha, 1964) we have come across two rhombohedral structures of this substance. As their identity has been definitely established, they may be regarded as the first-ever discovered rhombohedral modifications of cadmium iodide. These are 30*R* and 42*R*, respectively. Their complete structures have also been worked out and are found to bear a remarkable resemblance to each other. The structures are (221212)₃ and (22221212)₃, respectively. The two structures involve a special crystallographic interest for another reason, too. Each of the two modifications is found to occur in syntactic coalescence with a hexagonal modification having the same cell dimensions as the rhombohedral one, showing that the lattice was transformed from hexagonal to rhombohedral, or *vice versa*, during crystal growth. We shall first describe the details of structure determination and then proceed to discuss implications of the various findings.

Experimental techniques

The *c*-axis oscillation photographs of cadmium iodide crystals are not suited for the identification of polytypes as they generally show streaking and smearing of diffraction spots (Trigunayat & Verma, 1962). However, the *c* dimension can also be evaluated from *a*-axis oscillation photographs (Trigunayat, 1959), which are relatively free from these unwanted features. Therefore *a*-axis oscillation photographs were used for the identification of polytypes. The oscillation range chosen was from 25° to 40°, *i.e.* so that the *c* axis makes an angle of 25–40° with the incident X-ray beam. The range is found to be most convenient for identification purposes as it records a large number of 10.*l* spots on the zero layer. Besides, as each of the two crystals in our case consisted of two parts (30*H*+30*R* and 42*H*+42*R* respectively; to be referred to as crystals no.1 and 2, respectively, in the following), this range was also most suited to record the spots of one part alone at a time, because the orientation of the crystal flake is such that what we get on one side of the photograph is just the surface reflexion, with neither the incident X-ray beam nor the diffracted beams needing to penetrate any appreciable thickness of the crystal (Buerger, 1960). For the determination of structure, too, the intensities were compared in reflexion, because in transmission there is the possibility of mixing of the spots from the two sides of the crystal, as the crystals were not thick enough to absorb the diffracted beams from one side. The thickness of the crystals was only a few microns. As already shown by Ramsdell (1944) and Mitchell (1955), it is sufficient to compare the

observed and calculated intensities for 10.*l* or 01.*l* reflexions alone for computing the crystal structure. Therefore, only the normal beam Weissenberg photographs were taken for structure determinations.

The crystals were grown from the vapour phase. The method of growing them has been described elsewhere (Trigunayat & Chadha, 1964).

Structure of 30*R*

This new polytype was discovered in a small hexagonal crystal (no.1) with a hexagonal growth spiral on it. Fig.1 is the micrograph of the crystal, prominently showing the spiral on its (0001) basal plane. As the photograph has been taken in monochromatic Hg-green light, contouring two-beam internal interference fringes are also seen along with the spiral steps. The fringes are used for the measurement of step height (Trigunayat & Verma, 1962). In this crystal there has been a change from rhombohedral to hexagonal symmetry, or *vice versa*, during growth, without any change in the dimensions of the unit cell. The crystal consists of two types, 30*H* and 30*R*, occurring in syntactic coalescence with each other. Fig.3, which is an *a*-axis oscillation photograph of the crystal, shows the sequence of 10.*l* diffraction spots on the zero layer line for type 30*H*. This sequence is particularly suited for the identification of a crystal type by the well-known methods (Mitchell, 1956). As stated earlier, the orientation of the crystal was so chosen that the 10.*l* spots in Fig.3 were obtained by surface reflexion from one side of the crystal. On rotating the crystal through 180°, the surface reflexion occurred from the other side of the crystal, giving rise to a different sequence of 10.*l* spots shown in Fig.4, which is also an *a*-axis oscillation photograph. By a consideration of their spacings alone these spots could represent either a 10-layered hexagonal cell or a 30-layered rhombohedral cell, *i.e.* either a type 10*H* or a type 30*R*. Since an *a*-axis oscillation photograph cannot easily distinguish between a hexagonal and a rhombohedral type, the usual tests (Srivastava, 1964) were applied for identifying the character of the lattice. As the first check, a zero layer *a*-axis normal-beam Weissenberg photograph was taken. It is shown in Fig.7. It can be seen that the 10.*l* spots are non-symmetrical about the central Laue streak (*h*00) in Fig.7, which is possible only if the lattice be rhombohedral. Had the lattice been hexagonal, the 10.*l* and 10.*l* spots should have occurred symmetrically about the central streak. As a second check this photograph was superimposed on an identical Weissenberg photograph of the basic 4*H* type. For the hexagonal lattice every fifth spot of the polytype in question should have coincided with every second spot of 4*H*, because for hexagonal polytypes the range 10.0 to 10.8 of 4*H* should exactly fit the range 10.0 to 10.2*n* of a polytype *nH*. But it was not found to be the case; on the +*l* side the spots occurred a little above and on the -*l* side a little below the 4*H* spots. Thus, it

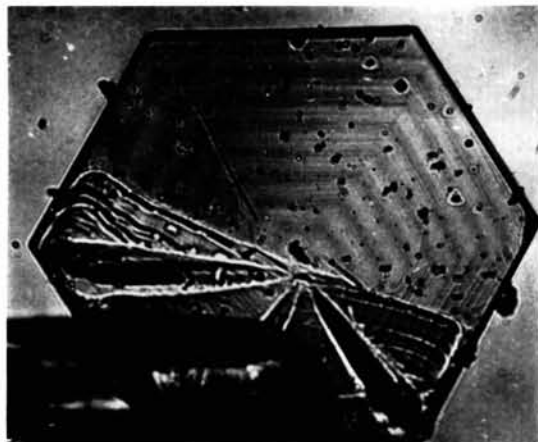


Fig. 1. Combined micrograph and interferogram of crystal no. 1; (0001) face; Hg-green light ($\times 162$). The horizontal thick 'rod' seen on the lower left hand side is the glass fibre on which the crystal was mounted for taking X-ray photographs.



Fig. 2. Combined micrograph interferogram of crystal no. 2; (0001) face; Hg-green light ($\times 205$).

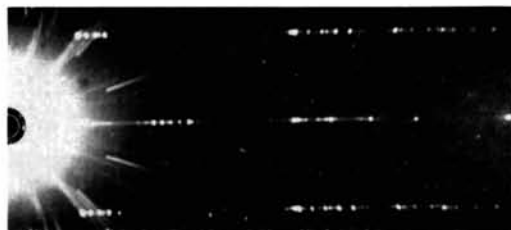


Fig. 3. A 15° *a*-axis oscillation photograph of polytype 30H (crystal no. 1); 3 cm camera; Cu *K α* radiation.

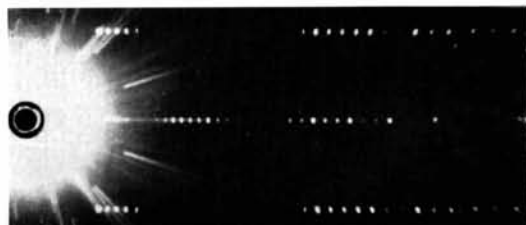


Fig. 4. A 15° *a*-axis oscillation photograph of polytype 30R (crystal no. 1); 3 cm camera; Cu *K α* radiation.

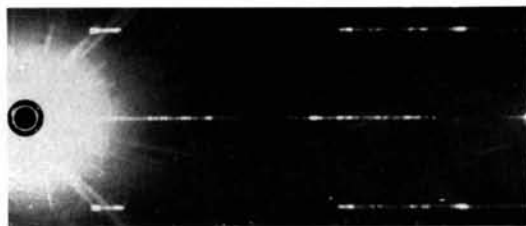


Fig. 5. A 15° *a*-axis oscillation photograph of polytype 42H (crystal no. 2); 3 cm camera; Cu *K α* radiation.

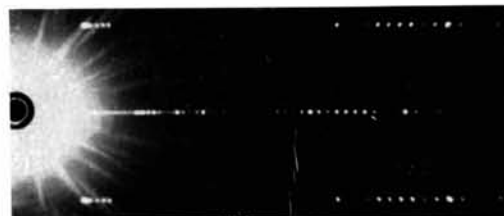


Fig. 6. A 15° *a*-axis oscillation photograph of polytype 42R (crystal no. 2); 3 cm camera; Cu *K α* radiation.

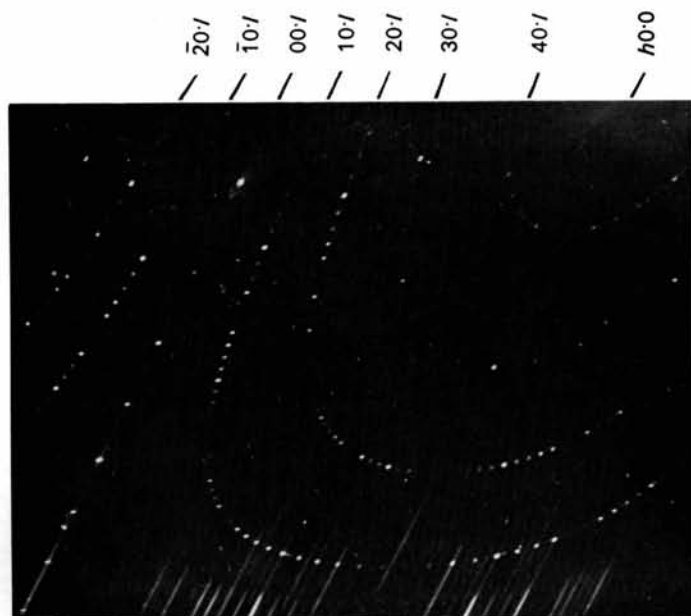


Fig. 7. Zero layer a -axis Weissenberg photograph of polytype 30R; Cu $K\alpha$ radiation; camera diameter 5.73 cm; the four consecutive faint spots near the minimum of the $10.l$ festoon are, from left to right, 10.4 , 10.1 , 10.2 and 10.5 .



Fig. 9. Zero layer a -axis Weissenberg photograph of polytype 42R; Cu $K\alpha$ radiation; camera diameter 5.73 cm; the festoons corresponding to $10.l$ and $\bar{1}0.l$ rows of spots are recorded on the right and left side, respectively, of the straight row of $00.l$ spots; The first intense spot from the top corresponds to $l=146$ in the $10.l$ festoon and to $l=148$ in the $\bar{1}0.l$ festoon.

was unequivocally confirmed that this side of the crystal was $30R$ and not $10H$. Since for a rhombohedral lattice indexed on a hexagonal cell the $10.l$ reflexions are missing when $l-1 \neq 3n$, the first spot on the $+l$ side in Fig. 7 has the index 10.1 , while on the $-l$ side it has the value $10\bar{2}$. The c dimension of this type $30R$ taking account of the missing spots, has been found to be 102.52_5 \AA .

Because of the interesting structure-transformation displayed by crystal no. 1 and because of the fact that $30R$ happened to be the first-found rhombohedral polytype of cadmium iodide, attempts were made to work out the complete crystal structure of the latter. The task appeared to be difficult as the large c dimension enormously increases the number of possible arrangements of atoms in the unit cell. Without any assumptions, there are 2^9 possible ways in which the various atoms can be arranged in the unit cell of $30R$. But many of the structures reported by Mitchell (1956) and Srivastava (1965) have only Zhdanov numbers 1 and 2 in the zigzag sequence representing the sequence of iodine atoms in the $11\cdot0$ cross-section. Using this fact and starting with Δ and always ending with ∇ reduces the possible number of ways to six only. They are:

- (a) [11121211]₃
- (b) [122212]₃
- (c) [12111112]₃
- (d) [121222]₃
- (e) [221212]₃
- (f) [11111212]₃.

But, if examined carefully, ways (a), (c) and (f) are essentially the same, differing only in the starting point, and the same is true of (b), (d) and (e). So, using the Zhdanov nos. 1 and 2, only two structures are possible for the polytype $30R$.

Intensities for $10.l$ reflexions were computed for both the structures using the formula,

$$I \propto A^2 + B^2 \quad (1)$$

where

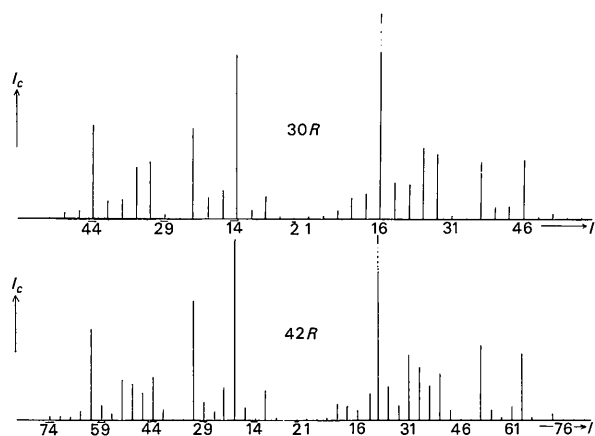


Fig. 8. Calculated intensities of $10.l$ spots for polytypes $30R$ and $42R$.

$$A = \sum_{z_{A,\alpha}} f_{I, \text{cd}} \cos 2\pi lz + \sum_{z_{B,\beta}} f_{I, \text{cd}} \cos 2\pi(lz - \frac{1}{3}) + \sum_{z_{C,\gamma}} f_{I, \text{cd}} \cos 2\pi(lz + \frac{1}{3}),$$

and

$$B = \sum_{z_{A,\alpha}} f_{I, \text{cd}} \sin 2\pi lz + \sum_{z_{B,\beta}} f_{I, \text{cd}} \sin 2\pi(lz - \frac{1}{3}) + \sum_{z_{C,\gamma}} f_{I, \text{cd}} \sin 2\pi(lz + \frac{1}{3}).$$

$z_{A,\alpha}, z_{B,\beta}, z_{C,\gamma}$ denote the respective z coordinates of the iodine (roman letters) and cadmium (Greek letters) atoms, on the vertical A, B, C axes, respectively, passing through $(0, 0, 0), (\frac{2}{3}, \frac{1}{3}, 0), (\frac{1}{3}, \frac{2}{3}, 0)$, respectively. $\sum_{A,\alpha}$ represents summation over iodine atoms at A -sites and cadmium atoms at α -sites. Similarly the other two summations. The intensities obtained by employing expression (1) are multiplied by the Lorentz-polarization factor $(1 + \cos^2 2\theta) / \sin 2\theta$ where θ is the Bragg angle.

The calculated and observed intensities of $10.l$ spots are given in Table 1. These results have been plotted and are shown in Fig. 8. The intensities were compared from 10.60 to 10.120 and $10.6\bar{0}$ to $10.1\bar{20}$ (Fig. 7) as the spots in the $10.6\bar{0}$ to 10.60 range are not purely due to one type. It was not practicable to apply an absorption correction for the hexagonally shaped crystal. However, taking into account the shape and orientation of the crystal, it can be generally said that the change in the intensities due to absorption should be slight and gradual. It should be maximum for $l=60$ and should go on decreasing with increasing values of l . Therefore, as compared with the observed intensities, the intensities of reflexions with larger l values should be relatively greater than those with smaller l values. This situation exists exactly in the present case. Hence, it can be safely concluded that there is almost complete agreement between the observed and calculated intensities.

The detailed structure of $30R$ is therefore as follows:
Space group $R3m1$
Zhdanov symbol [221212]₃
 ABC sequence: $(A\gamma B) (C\alpha B) (A\gamma B) (A\beta C) (A\beta C),$
 $(B\alpha C) (A\beta C) (B\alpha C) (B\gamma A) (B\gamma A),$
 $(C\beta A) (B\gamma A) (C\beta A) (C\alpha B) (C\alpha B).$

$a = b = 4.24 \text{ \AA}$ $c = 102.52_5 \text{ \AA}$ (hexagonal indexing).
Atomic coordinates:
10 iodine atoms at $0, 0, z_1$
 $z_1 = 0, 8z, 12z, 16z, 24z, 34z, 38z, 42z, 46z, 50z$
10 iodine atoms at $\frac{2}{3}, \frac{1}{3}, z_2$
 $z_2 = 2z, 6z, 10z, 20z, 28z, 32z, 36z, 44z, 54z, 58z$
10 iodine atoms at $\frac{1}{3}, \frac{2}{3}, z_3$
 $z_3 = 4z, 14z, 18z, 22z, 26z, 30z, 40z, 48z, 52z, 56z$
5 cadmium atoms at $0, 0, z_4$
 $z_4 = 5z, 21z, 29z, 53z, 57z$
5 cadmium atoms at $\frac{2}{3}, \frac{1}{3}, z_5$
 $z_5 = 13z, 17z, 25z, 41z, 49z$
5 cadmium atoms at $\frac{1}{3}, \frac{2}{3}, z_6$
 $z_6 = 1z, 9z, 33z, 37z, 45z$
where $z = 1/60$.

Structure of 42R

This new modification was found to exist in a well-developed hexagonal crystal (no.2), displaying a hexagonal spiral on its (0001) basal plane (Fig.2). Like crystal no.1, this crystal was also found to consist of two parts in syntactic coalescence with each other, having the same cell dimensions but different lattices. The two parts have been identified as types 42H and 42R respectively. Figs.5 and 6 depict the respective a -axis oscillation photographs of the two polytypes, obtained in the same way as for the two parts of crystal no.1. To confirm the rhombohedral character of the lattice of crystal no.2, the same tests were employed as for the earlier type 30R. However, the zero layer a -axis Weissenberg photograph of the polytype in question failed to reveal the non-symmetrical distribution of diffraction spots around the central Laue streak, as these spots were obscured on account of absorption. But on superimposing upon this photograph an identical photograph of the basic type 4H, it was clearly seen that the 4H spots did not coincide with those of the polytype. Had the polytype possessed a hexagonal lattice, its every seventh spot should have coincided with every second spot of 4H. But in this case the spots occurred a little above the 4H spots on the $+l$ side and a little below on the $-l$ side, thus confirming that the polytype was 42R and not 14H.

On account of the similar interest involved in this case as for crystal No.1, it was proposed to work out the complete atomic structure of type 42R. Starting from first principles and using all the Zhdanov numbers, *prima facie* it appears almost impossible to achieve this end. Even upon assuming that only Zhdanov numbers 1 and 2 are likely to appear in the structure, the number of possible structures is very large in this case. How-

ever, upon examining the intensity sequence of 10. l spots, it was found to be exactly similar to that of the earlier investigated type 30R. Using the structure of 30R and adding one more (22) unit, which is the structure of the basic 4H type, one gets the arrangement [22221212]₃. The 10. l intensities for this have been computed by means of formula (1). These found to agree very well with the observed ones. To confirm the structure, the intensities of 10. l reflexions have been computed and are also found to match the observed values well. The observed and calculated intensities are listed in Table 2. The intensities have been compared for the spots 10.84 to 10.168 and 10.84 to 10.168 (Fig.9). These spots are recorded on the reflexion part of the photograph and hence as such they are purely due to type 42R. Fig.8, showing the relative intensities for types 30R and 42R, clearly brings out the similarity of structure of these two polytypes.

The detailed structure of 42R is as follows:

Space group $R3m1$

Zhdanov symbol [22221212]₃

ABC sequence:

(A γ B) (C α B) (A γ B)(C α B) (A γ B) (A β C) (A β C),
 (B α C) (A β C) (B α C) (A β C) (B α C) (B γ A) (B γ A),
 (C β A) (B γ A) (C β A) (B γ A) (C β A) (C α B) (C α B).
 $a=b=4.24 \text{ \AA}$ $c=143.53_5 \text{ \AA}$ (hexagonal indexing)

Atomic coordinates:

14 iodine atoms at 0, 0, z_1

$z_1=0, 8z, 16z, 20z, 24z, 32z, 40z, 50z, 54z, 58z, 62z, 66z, 70z, 74z$

14 iodine atoms at $\frac{2}{3}, \frac{1}{3}, z_2$

$z_2=2z, 6z, 10z, 14z, 18z, 28z, 36z, 44z, 48z, 52z, 60z, 68z, 78z, 82z$

14 iodine atoms at $\frac{1}{3}, \frac{2}{3}, z_3$

Table 1. Calculated and observed relative intensities for the structure 30R

l	Calculated intensity	Observed* intensity	l	Calculated intensity	Observed* intensity
1	9.4	<i>a</i>	2	3.2	<i>a</i>
4	15.8	<i>a</i>	5	11.1	<i>vvw</i>
7	40.1	<i>w</i>	8	97.7	<i>ms</i>
10	95.0	<i>ms</i>	11	43.2	<i>w</i>
13	117.9	<i>ms</i>	14	719.7	<i>vvs</i>
16	1000	<i>vvs</i>	17	127.8	<i>ms</i>
19	164.6	<i>ms</i>	20	97.5	<i>ms</i>
22	155.1	<i>ms</i>	23	401.7	<i>vs</i>
25	317.7	<i>s</i>	26	11.6	<i>vvw</i>
28	290.7	<i>s</i>	29	23.2	<i>vw</i>
31	21.7	<i>vvw</i>	32	253.7	<i>s</i>
34	8.9	<i>a</i>	35	229.2	<i>s</i>
37	254.1	<i>s</i>	38	91.8	<i>ms</i>
40	50.8	<i>vw</i>	41	80.7	<i>ms</i>
43	55.0	<i>vw</i>	44	410.2	<i>vs</i>
46	264.4	<i>s</i>	47	40.1	<i>w</i>
49	13.5	<i>vw</i>	50	27.5	<i>w</i>
52	25.7	<i>vw</i>	53	10.3	<i>vw</i>
55	2.7	<i>vvw</i>	56	3.4	<i>vvw</i>
58	0.7	<i>a</i>	59	1.8	<i>a</i>

* As mentioned in the text, the observed intensities were actually taken from the series 10.60 to 10.120. This series has the same intensity sequence as 10.0 to 10.60.

$z_3 = 4z, 12z, 22z, 26z, 30z, 34z, 38z, 42z, 46z, 50z, 64z,$
 $72z, 76z, 80z$
 7 cadmium atoms at $0, 0, z_4$
 $z_4 = 5z, 13z, 29z, 37z, 45z, 77z, 81z$
 7 cadmium atoms at $\frac{2}{3}, \frac{1}{3}, z_5$
 $z_5 = 21z, 25z, 33z, 41z, 57z, 61z, 73z$
 7 cadmium atoms at $\frac{1}{3}, \frac{2}{3}, z_6$
 $z_6 = z, 9z, 17z, 49z, 53z, 61z, 69z$
 where $z = \frac{1}{84}$.

Discussion

As pointed out earlier, $30R$ and $42R$ are the first-discovered rhombohedral polytypes of cadmium iodide whose identities have been definitely established. The large number (over 80) of cadmium iodide polytypes so far reported by various workers have all been hexagonal types. Indeed this 'monopoly' of hexagonal types led Srivastava & Verma (1962) to predict that the existence of rhombohedral types is prohibited on theoretical grounds. According to them, if the generation of polytypes be governed by the dislocation mechanism of crystal growth, a rhombohedral modification will grow when the ledge exposed by the dislocation has the first and the last layer in the same position (A , B , or C). It is necessary to invoke a horizontal slip of the stack in this case (Frank, 1951), after one turn of the spiral has been completed. Three such slips in the same direction bring the stack back to an identical position, so that the X-ray unit cell is

completed. It implies that a rhombohedral structure created in this way will have its X-ray unit cell thrice as high as the exposed ledge. All cadmium iodide structures are essentially made up of an integral number of close-packed minimal sandwiches. One sandwich consists of two layers of hexagonally close-packed iodine ions with small cadmium ions nested in between. It can be represented by either of the arrangements ($A\gamma B$), ($B\alpha C$), or ($C\beta A$). It is obvious that whatever be the type of cadmium iodide crystal in which the ledge is exposed, the first and the last layer are necessarily in a different position. Hence, it cannot lead to the formation of a rhombohedral polytype. However, this suggestion suffers from the basic drawback of assuming the validity of the dislocation theory of polytypism. It is now well-established that the above theory fails to explain the creation of all the known polytypes of cadmium iodide (Trigunayat & Verma, 1962; Srivastava & Verma, 1965; Chadha & Trigunayat, 1966). Hence Srivastava & Verma's prediction of the non-existence of rhombohedral types of this substance loses its meaning. In fact, the present discovery of the two rhombohedral modifications by us provides added and very definite evidence of the inadequacy of dislocation theory of polytypism in the case of cadmium iodide.

This conclusion is further supported by the observed non-correlation between the X-ray c dimension and the spiral step-height for each of the two crystals, as seen from the following data:

Table 2. Calculated and observed relative intensities for the structure $42R$

l	Calculated intensity	Observed* intensity	l	Calculated intensity	Observed* intensity
1	5.1	<i>a</i>	2	2.6	<i>a</i>
4	8.4	<i>a</i>	5	1.9	<i>a</i>
7	8.3	<i>a</i>	8	13.3	<i>a</i>
10	72.8	<i>w</i>	11	130.2	<i>ms</i>
13	66.2	<i>w</i>	14	11.5	<i>vw</i>
16	48.3	<i>w</i>	17	56.8	<i>w</i>
19	119.9	<i>ms</i>	20	794.1	<i>vvs</i>
22	1000	<i>vvs</i>	23	144.2	<i>ms</i>
25	146.6	<i>ms</i>	26	40.7	<i>vw</i>
28	63.3	<i>w</i>	29	83.97	<i>w</i>
31	290.4	<i>vs</i>	32	527.2	<i>vvs</i>
34	231.96	<i>vs</i>	35	5.2	<i>a</i>
37	153.1	<i>ms</i>	38	6.8	<i>a</i>
40	208.3	<i>s</i>	41	48.6	<i>vw</i>
43	46.3	<i>w</i>	44	188.7	<i>ms</i>
46	5.6	<i>a</i>	47	119.8	<i>ms</i>
49	3.7	<i>a</i>	50	158.98	<i>ms</i>
52	330.8	<i>vs</i>	53	173.76	<i>ms</i>
55	45.8	<i>w</i>	56	33.0	<i>vw</i>
58	19.4	<i>vw</i>	59	67.0	<i>w</i>
61	60.3	<i>w</i>	62	402.9	<i>vvs</i>
64	295.4	<i>vs</i>	65	42.3	<i>vw</i>
67	18.8	<i>vw</i>	68	15.0	<i>vw</i>
70	3.4	<i>a</i>	71	18.5	<i>vw</i>
73	33.9	<i>vw</i>	74	18.7	<i>vw</i>
76	3.3	<i>a</i>	77	1.9	<i>a</i>
79	0.4	<i>a</i>	80	1.8	<i>a</i>
82	0.6	<i>a</i>	83	1.0	<i>a</i>

* As mentioned in the text, the observed intensities were actually taken from the series 10.84 to 10.168. This series has the same intensity sequence as 10.0 to 10.84.

Crystal no.	Type	c	h
1	30R+30H	102.52 ₅ Å	281.8 ± 3.0 Å
2	42R+42H	143.53 ₅	176.8 ± 1.0

The step-heights (h) were measured by the two-beam internal interference method (Chadha & Trigunayat, 1966). If the dislocation theory of polytypism were valid, the step-height should have been either equal to or an integral multiple of $c/3$. However, we shall not discuss this aspect in greater detail as it forms the subject matter of another publication (Chadha & Trigunayat, 1966). There a large number of such cases observed in vapour-grown crystals have been presented.

A very remarkable feature of the two rhombohedral types, 30R and 42R, is that each of these occurs in syntactic coalescence with a hexagonal modification having the same cell dimensions as the rhombohedral one. Although the occurrence of syntactic coalescence is not uncommon in cadmium iodide (Srivastava & Verma, 1965; Chadha & Trigunayat, 1966), these are two unique cases in which (i) the cell dimensions of the two syntactically coalesced parts remain the same, and (ii) the two parts have different lattices. Somewhat similar cases of structure-transition have been observed by Edwards & Lipson (1942) in hexagonal cobalt and by Krishna & Verma (1963) in silicon carbide. The former observed a remarkable mixture of sharp and diffuse lines on the X-ray powder photographs of hexagonal cobalt; this has been explained by Wilson (1942), who states that 'the structure possesses a lattice in which the unit cells are all of the same size and shape, but that the distribution of atoms within the unit cell varies throughout the crystal; neighbouring cells tend to be like each other, but at each layer there is a chance of a fault'. Krishna & Verma have observed the coalescence of two types, 36H_a and 36H_b, in a single-crystal piece of silicon carbide, showing that the distribution of atoms in their case changed more or less abruptly across a certain (0001) plane in such a way that the periodicity and the nature of the lattice remained unaffected. A somewhat similar situation exists for cadmium iodide types 30R and 42R, but because the nature of the lattice has also changed from hexagonal to rhombohedral, or *vice versa*, the structure-transition has in these cases been far more drastic.

We have already ruled out the possibility of obtaining a rhombohedral modification of cadmium iodide by the origination of a screw dislocation in some basic hexagonal type. The same will be true for the reverse procedure, *i.e.* all hexagonal modifications cannot similarly be generated by creating a screw dislocation in some basic rhombohedral type. The argument can be extended to show that even a cooperation of two or more sufficiently close dislocations cannot easily bring about any of the above situations. Thus in crystal no. 1 the type 30R could not have been obtained from the type 30H in this way, or *vice versa*. Similar considerations apply to crystal no. 2, which consists of types 42R and 42H. It seems that the only way in which one can explain such structure-transformations

is by the layer-transposition mechanism of Jagodzinski (1954*a, b*). It has been proposed that since the work done to create an edge dislocation in the (0001) plane of the crystal is essentially much smaller than that required to form a screw dislocation, the former can be generated far more easily, producing a displacement of the close-packed layers of the crystal into another possible position (*A, B, or C*). This results in stacking faults in the crystal. If the crystal has to grow further by the well-known nucleation mechanism, a two-dimensional critical size nucleus needs to be formed on the surface. The 'guiding' forces for such nucleus formation should naturally be provided by the structure below. But as the latter has developed faults, the nucleus will also have stacking faults and consequently it will require higher energy for its formation. For a higher probability of nucleus formation it is necessary that this energy be lowered, and this is possible only if a number of stacking faults 'cooperate' together to produce an ordering of stacking faults, finally leading to the generation of 'super-periods'. According to Jagodzinski, the ordering effect of faults is provided by vibration entropy. If the ordering of the faults is complete, the 'super-period' will completely succeed, *i.e.* the X-ray photograph of the crystal will show clear single diffraction spots without any 'smearing' or 'streaking'. These features on one-dimensional disorder will otherwise be present, implying that the vibration entropy has failed to produce a complete ordering of the faults so that the structure does have some residual faults. Thus, according to Jagodzinski, the observed polytypes of a substance should be regarded as ordered states favoured by crystal growth, rather than structures of genuine thermodynamic stability. These conclusions are well-substantiated for cadmium iodide crystals, the X-ray photographs of which very frequently display the above predicted features of one-dimensional disorder (Trigunayat, 1960). It should be noted in Fig. 3, which is the X-ray oscillation photograph of type 30H, that streaking is present on all the layer lines, indicating that the structure involves faults at various places. Then we can explain the growth of crystal no. 1 as follows. In the initial stages of growth, 30R was formed from the basic 4H structure by layer displacements and a subsequent complete ordering of stacking faults by vibration entropy. After the crystal had grown to an appreciable thickness, more layer displacements took place but the statistical fluctuations were such that this time the vibration entropy could cause only a partial ordering of the faults, thus leaving behind some residual faults. This gave rise to type 30H, with stacking faults at various places. The same reasoning applies to crystal no. 2 since, as seen in Fig. 5, which is the X-ray photograph of type 42H, streaking is present on all layer lines.

As mentioned earlier, Wilson (1942) has also proposed the creation of similar faults as an explanation of the observed disorder in hexagonal cobalt (Edwards & Lipson, 1942).

It is interesting to note that the structural sequences, viz. (221212)₃ and (2221212)₃, of types 30R and 42R respectively, closely resemble each other. In fact, as indicated earlier, the structure of type 42R could be calculated relatively easily by anticipating that it could be similar to that of type 30R. Whether this resemblance is purely a matter of chance or is indicative of the existence of a structural series of the form [(22)_n(12)₂]₃ for rhombohedral polytypes of cadmium iodide is difficult to say at present. The issue can be decided only after more rhombohedral modifications of cadmium iodide are discovered and their structures worked out. Nevertheless, this point may be of great help in the determination of the structures of any future rhombohedral types.

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The Crystal Structure of Gd₁₃Zn₅₈

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By single-crystal X-ray diffraction methods, a compound, Gd₁₃Zn₅₈, has been identified in the Gd-Zn system and its crystal structure determined. Gd₁₃Zn₅₈ is a complex structure with 142 atoms (two units of Gd₁₃Zn₅₈) in a unit cell of space group *P6₃mc* with dimensions $a = 14.35$, $c = 14.21$ Å.

Introduction

A₆B₂₃ (Th₆Mn₂₃-type; Florio, Rundle & Snow, 1952) compounds have been found to exist both in the R (rare earths)–Mn (Wang, Gilfrich, Ernst & Hubbard, 1964; Wang & Holden, 1965) and R–Fe (Kripyakevich & Frankevich, 1965) systems. The basic atomic arrangement in these compounds is the octahedrally clustered group of six rare earth atoms. The limitation to the formation of A₆B₂₃ compounds of such a geometrical arrangement has been discussed (Wang & Holden, 1965). Because the atomic radii of Mn and Zn are nearly equal (Mn 1.36 Å, Zn 1.33 Å)*, based on the 'size factor' consideration alone, the existence of A₆B₂₃ compounds in the R–Zn systems would be expected. This paper is a partial report on the efforts

which have been made to find A₆B₂₃-type compounds or compounds with similar atomic arrangements such as SrMg₄ (Wang, Kanda, Miskell & King, 1965) in the R–Zn systems.

The complexities of R–Zn systems are exemplified by the works of Rolla & Iandelli (1941) on the La–Zn system, Chiotti, Mason & Gill (1963) on the Y–Zn system and Chiotti & Mason (1965) on the Ce–Zn system. While the numbers of intermediate phases reported to exist in these three systems differ, there is a profound similarity in the general features of the three reported phase diagrams. Therefore, it is likely that the three systems have the same number of intermediate phases and that these phases have the same crystal structures. Extension of this reasoning suggests that the same crystal structures will be found for the intermediate phases between all the rare earths (except perhaps Eu and Yb) and zinc.

* The atomic radii used throughout this paper are from *Tables of Interatomic Distances* (1958).