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Refinements in the Method for the Structure Determination of Polytypes: Crystal Structure Analysis of 11 New Cadmium Iodide Polytypes

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A brief collective account of the various refinements in the method for the structure determination of polytypes, introduced recently by the authors, is presented. The refinements are: (1) application of a Lorentz–polarization factor correction for the correct range of reflexions, (2) application of a suitable absorption correction for plate-shaped crystals, (3) the use of an analytic function in place of the cumbersome graphical method for the determination of atomic scattering factors, (4) the derivation of the correct condition on the Zhdanov notation for an MX_2-type polytype to be centrosymmetric, (5) the resolution of existing ambiguities in the Zhdanov notation of polytypic structures and (6) the demonstration of the existence of homometric structures in MX_2- and MX-type polytypic crystals. With the above refinements taken into account, the crystal structures of the following 11 new cadmium iodide polytypes have been determined: $14H_5$ $[2112(11)_4]$, $16H_8$ $[(22211)_2]$, $20H_7$ $[(221111)_21111]$, $20H_8$ $[(22)_3112211]$, $24H_3$ $[(22)_4112211]$, $24H_4$ $[(2211)_21122(11)_3]$ or $[(11)_32211(1122)_2]$, $24H_5$ $[(22)_21122(11)_22211]$, $24H_6$ $[(211)_3112221111]$, $18R_1$ $[(2121)_3]$, $24R_2$ $[(212111)_3]$, $30R_2$ $[(21211111)_3]$.

Introduction

Extensive investigations during the last two decades have resulted not only in the discovery of many new polytypic substances but also in the discovery of an increasingly large number of different polytypes of various substances, with completely or partially known crystal structures. In particular, zinc sulphide, silicon carbide and cadmium iodide have emerged as three richly polytypic substances. The crystal structure analysis of the polytypes of these and other substances has helped in more than one way in the understanding of the growth of polytypes. Recently, we have made certain improvements in the method for the structure determination of polytypes. The improvements essentially pertain to (i) the removal of the existing shortcomings in the method and (ii) pointing out the existence of hitherto unknown shortcomings and removing them. Though the rudiments of these refinements are already available in a scattered form in various journals, for the sake of providing a coherent picture we shall give a brief collective account of these in this paper and subsequently use them in determining the crystal structures of 11 new polytypes of cadmium iodide.

Experimental methods and structure determination

Hexagonal (also triangular) plate-shaped crystals of cadmium iodide were grown by the evaporation of an aqueous solution of reagent-grade salt (Mitchell, 1956). The usual methods were employed for examining these crystals by optical and X-ray diffraction techniques (*e.g.* Chadha & Trigunayat, 1967*a*). The new polytypes were subjected to a detailed structure determination.

The $10.l$ reflexions are sufficient for a complete structure analysis of CdI_2 crystals (Verma & Krishna, 1966). The intensities for these reflexions are calculated using the expression

$$\begin{aligned} I \propto |F_{hkl}|^2 = \Bigg\{ \Bigg[& \sum_{z_{A,\alpha}}{}' f_{\mathrm{I,Cd}} \cos 2\pi lz \\ & + \sum_{z_{B,\beta}}{}' f_{\mathrm{I,Cd}} \cos 2\pi(lz - \tfrac{1}{3}) \\ & + \sum_{z_{C,\nu}}{}' f_{\mathrm{I,Cd}} \cos 2\pi(lz + \tfrac{1}{3}) \Bigg]^2 \\ & + \Bigg[\sum_{z_{A,\alpha}}{}' f_{\mathrm{I,Cd}} \sin 2\pi lz \\ & + \sum_{z_{B,\beta}}{}' f_{\mathrm{I,Cd}} \sin 2\pi(lz - \tfrac{1}{3}) \\ & + \sum_{z_{C,\nu}}{}' f_{\mathrm{I,Cd}} \sin 2\pi(lz + \tfrac{1}{3}) \Bigg]^2 \Bigg\}, \qquad (1) \end{aligned}$$

where $z_{A,\alpha}$, $z_{B,\beta}$ and $z_{C,\nu}$ denote the z coordinate of the iodine (italic letters) and cadmium (Greek letters) atoms along the vertical A, B and C axes, respectively. After taking into account the necessary corrections, the expression for $10.l$ reflexions is

$$I \propto (\mathrm{Lp}\rho|F|^2) A_s T,$$

where Lp is the Lorentz–polarization factor, ρ the rho factor, A_s the absorption factor for a single crystal, F the structure amplitude and T the temperature factor.

Since the 10.l spots are all recorded on the zero layer, the rho factor is the same for all of them and is thus eliminated from the calculation of relative intensities. Since no temperature factor is available for cadmium iodide, we have chosen to follow the usual practice of ignoring this factor.

Refinements in the method of structure determination

(i) *Lorentz–polarization factor*

Recently Jain & Trigunayat (1975*a*) have shown that in the case of cadmium iodide polytypes the usual practice of recording the reflexions in the range 10.2n to 10.4n and calculating the X-ray intensities in the range 10.0 to 10.2n is erroneous, as the variation of the Lorentz–polarization factor $[=(1+\cos^2 2\theta)/\sin 2\theta]$ is different in the two ranges. This can appreciably affect the results in some cases, particularly for long-period polytypes. The following examples illustrate this.

Consider two hypothetical hexagonal CdI_2 structures, $(22)_3(11)_4$ and $(22)_2(11)_6$, both having 20 iodine layers in their unit cells. Their calculated intensities are the same except for the reflexions given in Table 1.

Table 1. *Calculated relative intensities for* 10.l *reflexions for the polytypes* $(22)_3(11)_4$ *and* $(22)_2(11)_6$

l	I_{calc} $(22)_3(11)_4$	I_{calc} $(22)_2(11)_6$
40	0·6	0·8
45	39·6	17·6
50	432·1	326·4
55	251·6	111·8
60	402·6	565·7
65	259·6	115·7
70	1366·7	1675·6
75	61·4	27·3
80	2·9	4·0

Table 2. *Calculated relative intensities for* 10.l *reflexions for the polytypes* $(22)_5(11)_8$ *and* $(22)_4(11_{10})$

l	I_{calc} $(22)_5(11)_8$	I_{calc} $(22)_4(11)_{10}$
72	0·2	0·2
81	11·0	7·1
90	131·5	112·5
99	69·9	44·7
108	140·3	169·7
117	72·1	46·2
126	464·0	519·6
135	17·1	10·0
144	1·0	1·2

Similarly, 28-layered hexagonal structures $(22)_4(11)_6$ and $(22)_3(11)_8$ yield the same calculated intensities except for the reflexions $l=[2N+(N/4)n]$, with $N=28$ and n taking values from 0 to 8. The difference in intensities becomes subtler as the periodicity of the polytype increases; this can be seen for the case of the 36H structures $(22)_5(11)_8$ and $(22)_4(11)_{10}$ in Table 2, where the calculated intensities for the two structures are given for only those reflexions which have different intensities.

It is clear from the above that there exist structures for which the calculated intensities differ only for a few spots. The application of the Lorentz–polarization factor correction for the wrong range of reflexions often causes a qualitative reversal of the calculated intensities for some separated spots and can therefore lead to a wrong structure determination. It is thus essential that the calculated and observed reflexions pertain to the same range. The same mistake should be avoided in other crystals like $CdBr_2$ and SnS_2, where, as in CdI_2, the distance between the successive anion layers is constant, making the intensity expression (1) periodic after every 2n reflexions. However, for crystals like PbI_2, where the successive anion layers are not equidistant, the error no longer needs to be taken into consideration as expression (1) itself is different in the two ranges and therefore the observed and calculated intensities essentially have to be compared for the same range.

(ii) *Absorption factor*

The polytypic crystals of CdI_2, PbI_2, SnS_2, AgI, *etc.*, show high absorption of X-ray intensities. Since they usually grow as hexagonal platelets, the absorption varies considerably in different directions. Until recently, for the want of a convenient expression for absorption in such crystals, the practice had been to ignore the absorption correction altogether. However, a suitable expression is now available (Jain & Trigunayat, 1975*b*). For crystals which are big enough not to be completely bathed by X-rays, the necessary correction is given by

$$A_s=\frac{1}{1-\cos\varphi.\sec(2\theta+\varphi)}$$

where θ is the Bragg angle and φ is the angle made by the X-ray beam with the perpendicular to the crystal plate. For crystals completely bathed by X-rays, the expression is

$$A_s=\frac{1}{\sec\varphi-\sec(2\theta+\varphi)}\,.$$

The calculated values of A_s for the polytype 4H of SnS_2 are presented in Table 3. It is clear that the correction factor varies considerably for different values of l. Still larger variations exist for polytypes of CdI_2 (Jain & Trigunayat, 1975*b*), PbI_2 and $CdBr_2$.

Table 3. *Values of* θ, φ *and the absorption factor for back reflexion for the* SnS_2 *polytype* 4*H*, *for* 10.*l spots* ($l = 8$ *to* 14)

The spots $l = 15$ and 16 are not obtained because they do not satisfy the Bragg conditions for any θ.

l	θ (°)	φ (°)	$\frac{1}{1-\cos\varphi.\sec(2\theta+\varphi)}$	$\frac{1}{\sec\varphi-\sec(2\theta+\varphi)}$
8	35·18	29·80	0·169	0·147
9	39·49	27·98	0·248	0·219
10	44·16	25·37	0·308	0·278
11	49·30	21·95	0·354	0·328
12	55·10	17·61	0·392	0·373
13	61·97	12·00	0·442	0·414
14	71·02	4·05	0·454	0·453

(iii) *Use of the analytic function in determining the values of the atomic scattering factors*

As seen in expression (1) (for calculating the diffracted intensities from a crystal) the f values (the atomic scattering factors for the constituent atoms) are required. The theoretically calculated f values for a large number of atomic species have been tabulated by Lonsdale (1962). For the structure analysis of polytypes, the usual practice has been to plot a graph of f *vs* $(\sin\theta)/\lambda$ for each constituent atom and to use it to obtain the f values for the required θ's and λ's. However, this graphical method is unnecessarily time-consuming and cumbersome. For work carried out by computers, it is easier to present the values of the scattering factors in the form of an analytic function which the computer can use for directly evaluating the required f values. Vand, Eiland & Pepinsky (1957) have shown that the atomic scattering factors may be expressed as a function of the form

$$f = A\exp(-ax^2) + B\exp(-bx^2) + C, \qquad (2)$$

where $x = \sin\theta/\lambda$. Forsyth & Wells (1959) have given a table of the values of the five constants (A, a, B, b and C); this reproduces the accepted scattering-factor curves of all the atoms and some ions, ranging from H to U. Recently, Lee & Pakes (1969) have published a revised list of the constants using the more recent f values of Hanson, Herman, Lea & Skillman (1964). These values for the constants have been used in the present work.

(iv) *Centrosymmetry in* MX_2*-type polytypes*

A close-packed MX_2-type structure can have one of the following five space groups (Verma & Krishna, 1966): $P3m1$, $P\bar{3}m1$, $R3m$, $R\bar{3}m$, $P6_3mc$. The centrosymmetric space group $P\bar{3}m1$ and the noncentrosymmetric $P3m1$ cannot be differentiated with the help of X-rays (if Friedel's law is assumed to hold); similarly for the space groups $R\bar{3}m$ and $R3m$. The correct space group is known only after the complete crystal structure of the polytype has been determined. The Zhdanov symbol is found to be particularly suited for revealing the space-group symmetry of a polytype. The conditions imposed on the Zhdanov symbol of a CdI_2 crystal by the presence of centrosymmetry or the 6_3 axis were derived earlier (Srivastava, 1964). However, the conditions due to the presence of centrosymmetry have been found to be misleading by Jain & Trigunayat (1977*a*), who have shown that the necessary and sufficient condition for a close-packed MX_2-type structure to be centrosymmetric is that its Zhdanov symbol should have a symmetric arrangement of digits around an odd digit. Accordingly, the space groups of six CdI_2 and two PbI_2 polytypes, found to be wrongly reported earlier, have now been rectified.

(v) *Resolution of ambiguities in the Zhdanov notation*

Sometimes ambiguities exist in the Zhdanov notation of a polytype so that it becomes difficult to decide whether or not two similar-looking Zhdanov sequences represent the same crystal structure. Thus the postulation of distinct structures for the polytype becomes troublesome. However, of late, simple practical criteria have been developed to resolve such ambiguities in close-packed MX_2- and MX-type structures (Jain & Trigunayat, 1977*b*). To determine whether two given Zhdanov sequences represent the same structure, one has simply to examine if they are translationally congruent (TC) or reversibly congruent (RC), by applying the following criteria.

For close-packed MX_2-type structures two Zhdanov symbols are TC if one is obtainable from the other by an 'even shift' of the starting point, *i.e.* a shift through Zhdanov digits whose sum is even. For MX-type structures, two Zhdanov symbols are TC if one is obtainable from the other by any shift of the starting point.

For MX_2-type structures two Zhdanov symbols are RC if one is obtainable from the other by literally reversing the sequence plus rewriting it after an 'odd shift' of the starting point. For MX-type structures no two Zhdanov symbols are RC.

(vi) *Existence of homometric structures in polytypes*

Dornberger-Schiff & Farkas-Jahnke (1970) have shown the existence of homometric structures in MX-type polytypes. Jain & Trigunayat (1977*a*,*b*) have independently discovered the existence of homometric structures and have given a detailed analysis of them in the case of close-packed MX_2- and MX-type polytypes. We have developed the following semi-empirical practical criteria which enable an easy identification of such structures to be made. In an MX_2-type polytype a Zhdanov symbol consisting of only even digits, and that obtained from it by a translation of the starting point by an odd number of layers, would be either RC (which occurs when the arrangement of Zhdanov numbers is symmetric about one of the two numbers or about the space between two successive numbers) or homometric. Secondly, if the Zhdanov symbol of a structure consists of only 2's and pairs of 1's, then this structure and that obtained by an 'odd shift' are either RC (which again occurs when the Zhdanov numbers are symmetric, as before) or homometric. In *MX*-type compounds, however, a pair of direct and reverse Zhdanov sequences, in a case where the Zhdanov symbol is not symmetric (*e.g.* 2233), represents two homometric structures.

Crystal structures of new polytypes

With the incorporation of the above refinements, complete crystal structures of 11 new CdI_2 polytypes (eight hexagonal and three rhombohedral) have been determined. The polytypes, along with their structural details, are listed in Table 4. (The detailed atomic coordinates of the atoms have not been given as these can be easily derived from the respective *ABC* sequences of the polytypes.)

The oscillation photographs of the polytypes are reproduced in Fig. 1 and the calculated and observed values of their $10.l$ reflexions are given in Tables 6 to 13. Some details regarding the growth and dimensions of the crystals containing the respective polytypes are summarized in Table 5.

In the structure determination of polytypes, an enormous number of structures are usually possible for a given polytype, running into several thousands and more for large unit cells. However, experimental clues are often available, which initially reduce the number of possibilities drastically. A brief description of the structure determination of the polytypes follows. The polytype symbolism follows the pattern suggested in an earlier review (Trigunayat & Chadha, 1971). The

Table 4. *Detailed crystal structures of the new* CdI_2 *polytypes* ($a = b = 4{\cdot}24$ Å *for all polytypes*)

No.	Polytype	Zhdanov symbol	*ABC* sequence	Space group	c (Å)
1	$14H_5$	$2112(11)_4$	$(A\gamma B)(C\alpha B)_2(A\gamma B)_4$	$P3m1$	47·85
2	$16H_8$	$(22211)_2$	$[(A\gamma B)(C\alpha B)]_2[(C\alpha B)(A\gamma B)]_2$	$P6_3mc$	54·68
3	$20H_7$	$(221111)_21111$	$(A\gamma B)(C\alpha B)(A\gamma B)_3(C\alpha B)(A\gamma B)_4$	P_3m1	68·35
4	$20H_8$	$(22)_3112211$	$[(A\gamma B)(C\alpha B)]_3(A\gamma B)_2(C\alpha B)(A\gamma B)$	$P3m1$	68·35
5	$24H_3$	$(22)_4112211$	$[(A\gamma B)(C\alpha B)]_4(A\gamma B)_2(C\alpha B)(A\gamma B)$	$P3m1$	82·02
6	$24H_4$	$(2211)_21122(11)_3$	$(A\gamma B)(C\alpha B)(A\gamma B)_2(C\alpha B)(A\gamma B)_3(C\alpha B)(A\gamma B)_3$	$P3m1$	82·02
		or			
		$(11)_32211(1122)_2$	$(A\gamma B)_4(C\alpha B)(A\gamma B)_3(C\alpha B)(A\gamma B)_2(C\alpha B)$	$P3m1$	82·02
7	$24H_5$	$(22)_21122(11)_22211$	$[(A\gamma B)(C\alpha B)]_2(A\gamma B)_2(C\alpha B)(A\gamma B)_3(C\alpha B)(A\gamma B)$	$P3m1$	82·02
8	$24H_6$	$(211)_3112221111$	$(A\gamma B)(C\alpha B)_2(A\gamma B)_2(C\alpha B)_3(A\gamma B)(C\alpha B)(A\gamma B)_2$	$P3m1$	82·02
9	$18R_1$	$(2121)_3$	$(A\gamma B)(C\alpha B)(C\beta A)_2(B\gamma A)(B\alpha C)_2(A\beta C)(A\gamma B)$	$R\bar{3}m$	61·52*
10	$24R_2$	$(212111)_3$	$(A\gamma B)(C\alpha B)(C\beta A)_3(B\gamma A)(B\alpha C)_3(A\beta C)(A\gamma B)_2$	$R\bar{3}m$	82
11	$30R_2$	$(21211111)_3$	$(A\gamma B)(C\alpha B)(C\beta A)_4(B\gamma A)(B\alpha C)_4(A\beta C)(A\gamma B)_3$	$R\bar{3}m$	102·53*

* Hexagonal indexing.

Table 5. *Morphological, dimensional and growth details of the crystals*

Polytype	Crystal shape	Approximate diameter of the crystal (mm)	Approximate crystal thickness (μm)	Polytype on the opposite face
$14H_5$	Hexagonal	$2\frac{3}{4}$	200	$30H_3[(22)_7(11)]$ (Gyaneshwar *et al.*, 1975)
$16H_8$	Triangular	3	100	$32H$
$20H_7$	*	2	150	$4H$ + unidentified type
$20H_8$	Triangular	$2\frac{1}{2}$	180	$20H$
$24H_3$	Triangular	$1\frac{1}{2}$	150	$4H$
$24H_4$	Hexagonal	3	120	Unidentified
$24H_5$	Hexagonal	$1\frac{1}{4}$	150	$24H$
$24H_6$	Hexagonal	$2\frac{1}{2}$	220	$12H_8[2112(11)_3]$ (Jain & Trigunayat, 1975*c*)
$18R_1$	*	*	*	$6H$ + unidentified type
$24R_2$	Hexagonal	$1\frac{1}{2}$	150	Unidentified type
$30R_2$	Hexagonal	$1\frac{1}{4}$	80	Unidentified type

* Not recorded; the crystal is now lost.

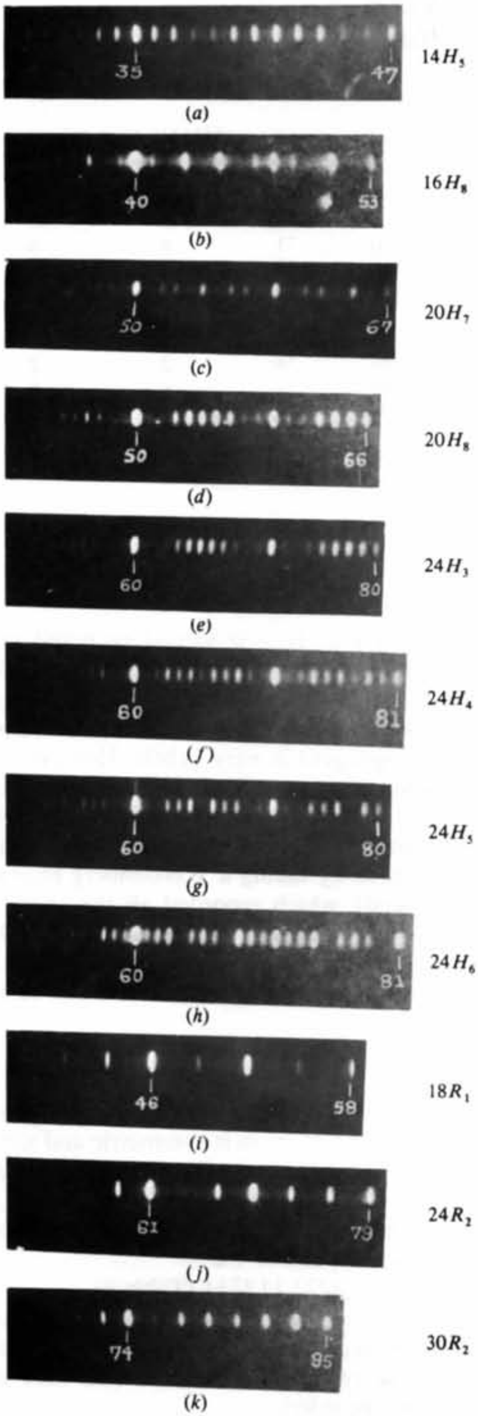

Fig. 1. 15° *a*-axis zero-layer oscillation photographs of the various polytypes, showing a succession of $10.l$ reflexions (×2·25) (3 cm camera; Cu $K\alpha$ radiation).

crystal structures finally arrived at on the basis of satisfactory agreement between observed and calculated intensities are given in Tables 6 to 13.

Table 6. *Calculated and observed relative intensities for* $10.l$ *reflexions of the polytype* $14H_5$

l	I_{calc}	I_{obs}	l	I_{calc}	I_{obs}
28	1	*vvw*	38	9	*vw*
29	2	*vvw*	39	10	*vw*
30	4	*vvw*	40	81	*ms*
31	1	*vvw*	41	175	*s*
32	2	*vvw*	42	347	*vs*
33	23	*w*	43	176	*s*
34	68	*ms*	44	82	*ms*
35	1000	*vvs*	45	10	*vw*
36	109	*s*	46	9	*vw*
37	61	*ms*	47	65	*ms*

Table 7. *Calculated and observed intensities for* $10.l$ *reflexions of the polytype* $16H_8$

l	I_{calc}	I_{obs}	l	I_{calc}	I_{obs}
32	0	*a*	43	367	*s*
33	1	*a*	44	0	*a*
34	0	*a*	45	431	*vs*
35	35	*vvw*	46	0	*a*
36	0	*a*	47	80	*w*
37	100	*w*	48	367	*s*
38	0	*a*	49	80	*w*
39	33	*vvw*	50	0	*a*
40	1000	*vvs*	51	439	*vs*
41	49	*w*	52	0	*a*
42	0	*a*	53	385	*s*

The photometric procedure adopted is the method of visual estimation, commonly employed in polytype structure work (*e.g.* Mitchell, 1956). The scale '*vvw*' to '*vvs*' is arbitrary and has been taken in the increasing order of visual intensity of the X-ray diffraction spots.

Polytype $14H_5$

Clue: The intense spots are on or around $2H(11)$ positions, suggesting the presence of several (11) units in the Zhdanov sequence of the polytype (Fig. 1*a*).

Structures postulated: (i) $2112(11)_4$, (ii) $211112(11)_3$, (iii) $211222(11)_2$ and (iv) 2111122211.

Final structure: $2112(11)_4$ (Table 6).

Polytype $16H_8$

Clue: Intense spots are around $4H$ positions, suggesting the presence of several 2's in the Zhdanov symbol; a symmetric distribution of the spots suggests the presence of 2's and pairs of 1's only in the Zhdanov symbol (Fig. 1*b*).

Structures postulated: Seven sequences containing more than one (22) unit.

Final structure: $(22211)_2$ (Table 7).

Since the Zhdanov symbol of the polytype consists of an odd set of numbers repeated twice and the number of iodine layers in the unit cell is a multiple of 4, the space group of the polytype is $P6_3mc$ (Srivastava, 1964). This is a very uncommon space

Table 8. *Calculated and observed relative intensities for* 10.*l reflexions of the structures* $(221111)_2 1111$ *and* $(221111)_2 22$ (*polytype* $20H_7$)

	I_{calc}				I_{calc}				I_{calc}		
l	$(221111)_2 1111$	$(221111)_2 22$	I_{obs}	l	$(221111)_2 1111$	$(221111)_2 22$	I_{obs}	l	$(221111)_2 1111$	$(221111)_2 22$	I_{obs}
40	1	1	*a*	54	10	10	*vw*	68	61	61	*
41	0	0	*a*	55	112	252	*s*	69	8	8	*
42	2	2	*a*	56	11	11	*vw*	70	385	506	*
43	4	4	*vvw*	57	81	81	*ms*	71	6	6	*
44	1	1	*a*	58	83	83	*ms*	72	36	36	*
45	18	40	*w*	59	12	12	*vw*	73	30	30	*
46	2	2	*vvw*	60	566	403	*vs*	74	4	4	*
47	23	23	*w*	61	12	12	*vw*	75	27	61	*
48	29	29	*w*	62	84	84	*ms*	76	2	2	*
49	5	5	*vvw*	63	82	82	*ms*	77	8	8	*
50	1450	1181	*vvs*	64	12	12	*vw*	78	4	4	*
51	7	7	*vvw*	65	115	260	*s*	79	0	0	*
52	56	56	*ms*	66	10	10	*vw*	80	4	3	*
53	63	63	*ms*	67	66	66	*ms*				

* These reflexions do not occur in the chosen range of reflexion.

Table 9. *Calculated and observed relative intensities for* 10.*l reflexions of the polytype* $20H_8$

l	I_{calc}	I_{obs}	l	I_{calc}	I_{obs}
40	0	*a*	54	313	*s*
41	0	*a*	55	196	*s*
42	0	*a*	56	355	*s*
43	8	*vvw*	57	142	*ms*
44	33	*w*	58	8	*vvw*
45	31	*w*	59	21	*vw*
46	77	*ms*	60	533	*vs*
47	40	*w*	61	21	*vw*
48	4	*vvw*	62	8	*vvw*
49	9	*vw*	63	144	*ms*
50	1000	*vvs*	64	363	*s*
51	13	*vw*	65	201	*s*
52	6	*vvw*	66	326	*ms**
53	109	*ms*			

* See text.

group in CdI_2 polytypes. Apart from the common polytype $4H$, so far only two other polytypes, $8H_2$ and $24H_1$, have been reported as belonging to this space group (Chadha & Trigunayat, 1967*b*).

Polytype $20H_7$

Clue: The distribution of spots is symmetric and akin to that of $8H$ (221111) (Mitchell, 1956), suggesting the presence of (221111) units in the Zdhanov sequence (Fig. 1*c*).

Structures postulated: Nearly 30 sequences.

A calculation of the intensities for these sequences showed that $(221111)_2 1111$ and $(221111)_2 22$ gave a close resemblance to the observed intensities, as seen in Table 8 and Fig. 1(*c*). It should be noted that the calculated intensities are exactly the same for all reflexions except for $l = 40$, 45, 50, 55, 60, 65, 70, 75 and 80. Thus the difference in the calculated intensities for the two sequences is very subtle. However, the *a*-axis oscillation photograph of the polytype (Fig. 1*c*) showed better agreement with the calculated intensities for the sequence $(221111)_2 1111$. The agreement was further confirmed by taking a Weissenberg photograph (not reproduced), which recorded all the spots in the range $l = 2n$ to $4n$. It may be mentioned here that an improper application of the Lorentz–polarization factor correction could lead to a wrong result in this case.

Polytype $20H_8$

Clue: Intense spots are on or around $4H$ positions, and the distribution of spots is symmetric and similar to that of $20H_6$ $[(22)_3(211)_2]$ (Gyaneshwar, Chadha & Trigunayat, 1975) (Fig. 1*d*).

Structures postulated: Nearly 20 structures containing several 2's and pairs of 1's.

Final structure: $(22)_3 112211$ (Table 9).

The observed intensity of the spot 10.66 is less than the calculated value because this spot happens to lie at the end of the range of oscillation and thus its full intensity is not recorded.

Polytype $24H_3$

Clue: Intense spots are on or around $4H$ positions, and the distribution of spots is symmetric (Fig. 1*e*).

Structures postulated: Nearly 40 sequences containing 2's and pairs of 1's.

Final structure: $(22)_4 112211$ (Table 10).

Table 10. *Calculated and observed relative intensities for* $10.l$ *reflexions of the polytypes* $24H_3$, $24H_4$, $24H_5$ *and* $24H_6$

	$24H_3$		$24H_4$		$24H_5$		$24H_6$	
l	I_{calc}	I_{obs}	I_{calc}	I_{obs}	I_{calc}	I_{obs}	I_{calc}	I_{obs}
48	0	*a*	0	*a*	0	*a*	0	*a*
49	0	*a*	0	*a*	0	*a*	0	*a*
50	0	*a*	0	*a*	0	*a*	2	*a*
51	2	*a*	7	*vvw*	3	*vvw*	8	*vvw*
52	9	*vvw*	10	*vvw*	5	*vvw*	0	*a*
53	27	*vw*	16	*vvw*	14	*vw*	6	*vvw*
54	46	*w*	6	*vvw*	0	*a*	16	*vw*
55	53	*w*	32	*vw*	28	*w*	12	*vvw*
56	37	*vw*	35	*vw*	20	*vw*	0	*a*
57	11	*vvw*	73	*w*	25	*w*	73	*ms*
58	0	*a*	16	*vw*	0	*a*	44	*w*
59	9	*vvw*	6	*vvw*	5	*vvw*	27	*w*
60	1000	*vvs*	787	*vs*	1000	*vvs*	1000	*vvs*
61	12	*vvw*	6	*vvw*	6	*vvw*	35	*w*
62	0	*a*	29	*vw*	0	*a*	89	*ms*
63	27	*vw*	166	*ms*	57	*ms*	170	*s*
64	115	*ms*	108	*ms*	62	*ms*	0	*a*
65	230	*s*	143	*ms*	124	*s*	50	*w*
66	293	*s*	41	*vw*	0	*a*	104	*ms*
67	254	*s*	159	*ms*	138	*s*	55	*w*
68	141	*ms*	134	*ms*	77	*ms*	0	*a*
69	37	*vw*	229	*s*	79	*ms*	235	*s*
70	0	*a*	48	*w*	0	*a*	120	*ms*
71	19	*vvw*	13	*vvw*	11	*vvw*	60	*w*
72	495	*vs*	1000	*vs*	330	*vs*	367	*vs*
73	21	*vvw*	13	*vvw*	11	*vvw*	62	*w*
74	0	*a*	48	*w*	0	*a*	121	*ms*
75	37	*vw*	233	*ms*	80	*ms*	238	*s*
76	145	*ms*	137	*ms*	78	*ms*	0	*a*
77	262	*s*	162	*ms*	142	*s*	56	*w*
78	302	*s*	41	*vw*	0	*a*	108	*ms*
79	239	*s*	150	*ms*	130	*s*	51	*w*
80	122	*ms*	115	*ms*	67	*ms*	0	*a*
81			178	*ms*			182	*vs*

Polytype $24H_4$

Clue: Strongest spots are at the $2H(11)$ positions, and the distribution of spots is symmetric (Fig. 1*f*).

Structures postulated: Nearly 100 sequences containing 2's and several (11) units.

Final structure: $(2211)_2 1122(11)_3$ (Table 10).

Another sequence, *viz* $(11)_3 2211(1122)_2$, gives the same values of the calculated intensities but it is actually homometric to the above sequence, as can be seen by applying the earlier-mentioned conditions for homometric structures in MX_2-type compounds. The two structures are, therefore, indistinguishable.

Polytype $24H_5$

Clue: The most intense spots are at $2H$ positions, and the distribution of spots is symmetric (Fig. 1*g*).

Structures postulated: Nearly 100 sequences containing 2's and several (11) units.

Final structure: $(22)_2 1122(11)_2 2211$ (Table 10).

Polytype $24H_6$

Clue: Spots at the $2H$ positions are most intense and the distribution of spots is symmetric (Fig. 1*h*).

Structures postulated: Nearly 100 sequences containing 2's and several (11) units.

Final structure: $(211)_3 112221111$ (Table 10).

Polytype $18R_1$*

This is the first 18-layered rhombohedral polytype in cadmium iodide (Fig. 1*i*). It has only six distinct possibilities: (i) $(2121)_3$, (ii) $(1311)_3$, (iii) $(3111)_3$, (iv) $(42)_3$, (v) $(51)_3$ and (vi) $(15)_3$. Only (i) gave a satisfactory agreement with the observed values (Table 11). This agreement does not exist for reflexion 10.58 for the same reason as mentioned for the polytype $20H_8$. However, the equivalent spot 01.50 on the first layer line is seen to have the same relative intensity as that calculated. The Zhdanov sequence $(2121)_3$ of the

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* This polytype, discovered earlier by Jain (1976), has also been reported by Minagawa (1976).

polytype is symmetric about the odd numbers 1. Therefore, according to the condition mentioned earlier, the space group of the polytype is $R\bar{3}m$.

Polytype $24R_2$ (*Fig.* 1*j*)

Structures postulated: All the distinct possibilities (numbering 14 in all).

Final structure: $(2\underline{1}21\underline{1}1)_3$ (Table 12).

As for the polytype $18R_1$, the Zhdanov symbol is symmetric about the underlined odd numbers 1. Accordingly, the space group of the polytype is $R\bar{3}m$.

Polytype $30R_2$ (*Fig.* 1*k*)

Clue: Zhdanov symbols of most of the cadmium iodide structures consist of only 2's and 1's.

Structures postulated: (i) $(222121)_3$, (ii) $(21211111)_3$, (iii) $(21112111)_3$, (iv) $(21111121)_3$.

Final structure: $(2\underline{1}211\underline{1}11)_3$ (Table 13).

Here, again, the Zhdanov symbol is symmetric around the underlined odd numbers 1, and hence the space group is $R\bar{3}m$.

Conclusion

The introduction of various refinements has resulted in the evolution of a correct, more accurate and efficient method for the structure determination of polytypes. By helping to avoid possible mistakes in the structure work and allowing greater precision, it should generate greater confidence in future workers. Besides, it has helped to remove the misgivings about the application of the Lorentz–polarization factor correction and about the space-group determination of close-packed MX_2-type structures and has filled a gap in the existing knowledge by attaining resolution of ambiguities in the Zhdanov notation. Further, the discovery of actual examples of homometric structures has presumably added a new dimension to the field of crystal structure determination and is likely to stimulate more research in this direction. Some of the polytypic structures earlier reported as having been uniquely determined have now been found to have alternative structures; this point should be taken note of in future investigations. Finally, the crystal structure analysis of 11 new CdI_2 polytypes has substantially added to the existing wealth of structural data on cadmium iodide polytypes; this is likely to be found useful in future theoretical work on polytypism.

Table 11. *Calculated and observed relative intensities for* 10.*l reflexions of the polytype* $18R_1$

l	I_{calc}	I_{obs}	l	I_{calc}	I_{obs}
37	13	*vvw*	49	42	*w*
40	8	*vw*	52	715	*vvs*
43	146	*s*	55	18	*vw*
46	1000	*vvs*	58	263	*ms*

Table 12. *Calculated and observed relative intensities for* 10.*l reflexions of the polytype* $24R_2$

l	I_{calc}	I_{obs}	l	I_{calc}	I_{obs}
49	5	*vvw*	67	104	*ms*
52	9	*w*	70	541	*vs*
55	0	*a*	73	87	*ms*
58	187	*s*	76	105	*ms*
61	1000	*vvs*	79	137	*ms*
64	0	*a*			

Table 13. *Calculated and observed relative intensities for* 10.*l reflexions of the polytype* $30R_2$

l	I_{calc}	I_{obs}	l	I_{calc}	I_{obs}
62	8	*vw*	80	160	*ms*
65	0	*a*	83	211	*ms*
68	23	*vw*	86	99	*ms*
71	112	*ms*	89	332	*s*
74	695	*vs*	92	1000	*vs*
77	38	*vw*	95	259	*s*

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