Identification of Polytypes of MX_2-Type Compounds – Structures of 19 New Polytypes of Cadmium Iodide*

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Abstract

Some improvements in the method of identification of polytypes of MX_2-type crystals are presented. It was found that there is a marked reduction in the number of models of hypothetical polytypes required to be considered in unique determinations of polytype structures when these new improvements are introduced: (1) a polytypic structure MX_2 is described in the molecular-layer notations xyz and t–o–f, (2) polytypes are divided into four groups with respect to the symmetry of the intensities of $10.l$ and $10.\bar{l}$ reflexions, (3) the formulae of stacking sequences of t–o–f layers in polytype cells are classified in structural series, (4) the diagrams with the intensities of the $10.l$ and $10.\bar{l}$ reflexions are plotted together. The crystal structures of 19 new polytypes of CdI_2 have been established: $14H_6$ $tf1(o)_4f2$; $22H_4$ $(t)_4(f1f2)_2tf1f2$; $22H_5$ $(t)_9f1f2$; $24H_9$ $tf1(o)_6f2tf1f2$; $26H_4$ $(t)_4f1(o)_2f2(t)_2f1of2$; $38H_1$ $(t)_4(f1f2)_2((t)_2f1f2)_2tf1f2$; $42H_1$ $(t)_2(f1f2)_2-(tf1f2)_5$; $50H_1(t)_{23}f1f2$; $58H_1$ $(t)_7f1f2((t)_3f1f2)_4$; $12H_7$ $tf1of1tf5$; $24H_7$ $(t)_7f4(t)_3f5$; $24H_8$ $(t)_4(tf4tf5)_2$; $32H_2$ $(t)_{11}f4(t)_3f5$; $34H_4$ $(t)_3f1f1tf5$-$((t)_3f1f2)_2$; $48R_1$ $f1f1f2f1(t)_3f5$; $54R_1$ $(t)_6$-$f1f1f5$; $54R_2$ $(t)_6f2f2f4$; $60R_2$ $f1(o)_7f1f5$; $72R_2$ $(t)_6f4(t)_4f5$. The existence of 13 polytypes of CdI_2 already known has been confirmed: $12H_4$ $(t)_2(f1f2)_2$; $16H_7$ $((t)_2f1f2)_2$; $6H_1$ $tf1f2$; $8H_1$ $tf1of2$; $10H_1$ $(t)_3f1f2$; $18H_6$ $(t)_3f1f2tf1of2$; $28H_1$ $(t)_{11}f1of2$; $8H_3$ $tf4tf5$; $12R$ $f4f5$; $18R_1$ $f1f1f5$; $24R_1$ $(t)_2-f4f5$; $30R_1$ $(t)_2f1f1f5$; $42R_1$ $(t)_4f1f1f5$.

Introduction

Since polytypism was discovered in SiC 70 years ago a significant increase of interest in the phenomenon has been observed in last two decades. This followed from the discovery of the dependence of physical properties of some polytypic materials on their structure and also directly as a natural extension of the analysis of the structure of solids. Progress in investigations of polytypism of inorganic crystals, and in application of the phenomenon, depends mainly on the ease of obtaining crystals of a desired polytypic modification. The identification of polytypic structures occurring in crystals is one of the basic problems in the search for reasons for polytypism. By discovering the rules governing the organization of layer sequences of polytypic structures one may construct increasingly precise models of the structure of real crystals.

Polytypic structures are usually classified into two main structural groups: polytypes, ordered-periodic modifications, and disordered non-periodic structures. This classification, however, is not always unique. It is, in fact, an experimentally based classification. The X-ray and electron diffraction methods of structural analysis usually used for polytypic crystals make possible the identification of layer sequences consisting of a few tens or, at most, a few hundreds of layers. If the lattice period is too high the reflexions appearing on the interference pattern overlap. In this case 'diffuse streaks' and not individual reflexions will appear in the pattern. Thus, it should be taken into account that in some cases polytypes may be classified as 'disordered structures'. On the other hand the broadened maxima appearing in the interference patterns are often regarded as reflexions from a polytype.

The identification of a polytype depends on the determination of the atomic coordinates in the cell. Basically, it is the determination of the stacking of layers in the period. Note that the solution of this problem is always unique. The identification of a disordered structure depends on finding 'an average' polytypic structure. In this case the structure is described by a set of parameters characterizing the structure only approximately, *e.g.* by determining the basic structure, types of faults, density of faults, their distribution in the structure, *etc.*

The main problem in the identification procedure of polytypes is the choice of the smallest possible number of hypothetical structures which are to be considered for a unique determination of the actual structure of the polytype cell. This problem differs, in general, for structures that occur in different substances. It was found that specific regularities in the stacking of layers

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in polytype cells are observed for the specific type of crystal structure, MX, MX_2 etc., as well as for specific chemical composition (e.g. Srinivasan & Parthasarathi, 1973; Dubey, 1975). Use of the rules found for a given substance enables us to complete the set of the most probable models of packing of unit layers in the cell. Progress in identification of polytypes depends on finding the rules which reduce the initial set of hypothetical polytypes.

Notation of MX_2 polytypic structures

The structure of polytypic crystals may be described with a number of symbolic notations: notations based on the description of the stacking of monoatomic layers, namely X layers for MX and MX_2 crystals (Hägg, 1943; Zhdanov, 1945; Verma & Krishna, 1966) and special forms of notation, e.g. the xyz and t-o-f notations of molecular X-M-X layers (Pałosz, 1980a; Pałosz & Przedmojski, 1980). Among these, the Zhdanov notation is the most frequently used for the description of the structures of all polytypic crystals. Consequently this notation is usually used to identify the polytypes, and the rules of construction of MX_2 polytypic structure found earlier were also described in the Zhdanov notation (Prasad & Srivastava, 1972; Jain & Trigunayat, 1977, 1978a; Agraval, 1981). It was found recently by Pałosz & Przedmojski (1980) and by Pałosz (1980a) that by using slightly more complex forms of notation (the molecular-layer notations xyz and t-o-f) the rules for constructing the polytype cells

in crystals of MX_2 compounds may be described in a far simpler form than in the Zhdanov notation. The use of the xyz and t-o-f notations also enables one to establish some new relations in the stacking of X-M-X layers, which are regarded, in these notations, as unit elements of polytypic crystals MX_2.

xyz and t-o-f notations

In the molecular-layer xyz and t-o-f notations six symbols of molecular layers x, y, z, $\bar{x}$, $\bar{y}$, $\bar{z}$ and ten symbols t, o, $f1$, $f2$, ..., $f8$, respectively, replace the symbols of monoatomic layers A, B, C, α, β, γ used in classical notations. The definition of the xyz and t-o-f notations is presented in Table 1. The arrangements of the molecules X-M-X in the [11.0] plane corresponding to the symbols used in these notations are presented in Fig. 1.* The molecular-layer notations are relatively more troublesome to use than the simple ABC, hc or Zhdanov notations:

(i) The sequences ABC possible in the close-packed structures are those combinations of the letters ABC in which each two subsequent symbols are different. This notation may be easily transcribed into the hc and Zhdanov notations. Similarly, the sequence ABC may

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* The t-o-f notation for molecular layers is analogous to hc notation used for monoatomic and MX lattices, when the symbols of the layers h and c are established with respect to the layers neighbouring to the given one.

t - o - f notation

xyz notation

Fig. 1. xyz and t-o-f arrangements of X-M-X molecules in the [11.0] plane.

Table 1. *The diagram of 96 possible arrangements of three successive molecular layers xyz; symbols of layers used in the t-o-f notation*

	$A\gamma B$	$C\alpha B$	$B\alpha C$	$A\beta C$	$C\beta A$	$B\gamma A$
	x	$\bar{x}$	y	$\bar{y}$	z	$\bar{z}$
xx	o	$f1$	–	$f2$	$f6$	–
$\bar{x}\bar{x}$	$f1$	o	–	$f6$	$f2$	–
yy	$f6$	–	o	$f1$	–	$f2$
$\bar{y}\bar{y}$	$f2$	–	$f1$	o	–	$f6$
zz	–	$f2$	$f6$	–	o	$f1$
$\bar{z}\bar{z}$	–	$f6$	$f2$	–	$f1$	o
$x\bar{x}$	t	$f2$	–	$f3$	$f5$	–
$\bar{x}x$	$f2$	t	–	$f5$	$f3$	–
$y\bar{y}$	$f5$	–	t	$f2$	–	$f3$
$\bar{y}y$	$f3$	–	$f2$	t	–	$f5$
$z\bar{z}$	–	$f3$	$f5$	–	t	$f2$
$\bar{z}z$	–	$f5$	$f3$	–	$f2$	t
xy	t		$f4$	$f1$		$f7$
$\bar{x}z$	–	t	$f7$	–	$f1$	$f4$
$y\bar{z}$	–	$f7$	t	–	$f4$	$f1$
$\bar{y}x$	$f1$	$f4$	–	t	$f7$	–
$z\bar{x}$	$f4$	$f1$	–	$f7$	t	–
zy	$f7$	–	$f1$	$f4$	–	t
xz	–	$f3$	$f8$	–	$f6$	$f7$
$\bar{x}y$	$f3$	–	$f7$	$f6$	–	$f8$
yx	$f6$	$f7$	–	$f3$	$f8$	–
$\bar{y}z$	–	$f8$	$f3$	–	$f7$	$f6$
zy	$f8$	–	$f6$	$f7$	–	$f3$
$\bar{z}x$	$f7$	$f6$	–	$f8$	$f3$	–

be easily obtained from a given *hc* or Zhdanov sequence (Verma & Krishna, 1966).

(ii) The molecular layers *xyz* are arranged in close packing in such a way that the adjacent anion layers *X* of two subsequent molecular sandwiches are different. It should be stressed that in this notation two identical symbols may occur one after another, *e.g.* $x\bar{x}\bar{x}\bar{x}\bar{x}zz$ ... and this is different from the *ABC* sequence.

(iii) For the MX_2 structure the possible sequences *t–o–f* may be constructed only with the use of the diagram presented in Table 1.

Having to use Table 1 is certainly inconvenient but the use of molecular-layer notations for MX_2 structures leads to a marked simplification of the analysis of various problems of polytypism, in particular in the identification of polytypes. It should be stressed that in the *t–o–f* notation all crystallographically equivalent structures are described by a single, uniquely defined sequence. Such a sequence may be written beginning with any of the symbols in the obverse and reverse order, *e.g.* $tf1of1tttf5 \equiv f5tttf1of1t \equiv f1of1tttf5t$ *etc.* In contrast to the *t–o–f* notation, in the *ABC*, *hc*, Zhdanov and *xyz* notations a single structure may be presented in several equivalent forms with the use of different symbols, *e.g.* $xx\bar{x}xx \equiv xx\bar{y}xx \equiv \bar{x}\bar{x}z\bar{x}\bar{x} \equiv \bar{x}\bar{x}x\bar{x}\bar{x}$ *etc.*, or in some cases, several crystallographically differing structures may be described by a similar symbol, *e.g.* $1322 \neq 3221$ *etc.* (Pałosz, 1980*a*).

Classification of polytypes: construction of polytype cells

By using the *xyz* and *t–o–f* notations the polytypes occurring in real crystals of CdI_2, PbI_2 and $Ti_{1.2}S_2$ may be divided into four structural groups I–IV. It was established that this division corresponds to the division of polytypes on the basis of the symmetry of the 10.*l*

and 10.$\bar{l}$ reflexions observed on the *a*-axis oscillation photographs. This means that for structures giving an interference pattern of the specific symmetry of the 10.*l* and 10.$\bar{l}$ reflexions, the specific rules of construction of the structure may be uniquely defined.

The symmetry elements of the *a*-axis oscillation photographs for four structural groups I–IV of MX_2 polytypes are presented in Table 2. Classifications of polytypes and of faults formed in MX_2 crystals are described in detail in two papers: Pałosz (1982*a,b*).

Below are presented the basic rules of constructing polytype cells of groups I–IV described in the *xyz* notation:

Group I

The polytype cells are formed of molecular layers of two types, *e.g.* x and $\bar{x}$. The number of x layers is equal to the number of $\bar{x}$ layers, *e.g.* $12H_4$: $x\bar{x}xxx\bar{x}$; $16H_8$: $\bar{x}\bar{x}x\bar{x}xx\bar{x}x$ *etc.*

Group II

The polytype cells are formed of molecular layers of two types, *e.g.* x and $\bar{x}$. The number of x layers is different from the number of $\bar{x}$ layers. The ratio of the reflexion intensities for $l/N = 2\cdot5$ and $-2\cdot5$ is proportional to the ratio of the numbers of layers x and $\bar{x}$ in the cell (N is the number of layers X in a period), *e.g.* $6H_1$: $xx\bar{x}$; $12H_3$: $x\bar{x}x\bar{x}\bar{x}\bar{x}$ *etc.*

Group III

The layer sequences of the polytype cells are formed by layers of three types, *e.g.* x, $\bar{x}$ and $\bar{y}$. In most of the polytypes, apart from the layers x and $\bar{x}$, there exists one $\bar{y}$ layer, *e.g.* $8H_3$: $x\bar{y}x\bar{x}$; $16H_3$: $\bar{x}x\bar{x}x\bar{y}xxx\bar{x}$ *etc.*

Group IV

It is well known that a rhombohedral cell may be divided into three equivalent parts, differing by a

Table 2. *Symmetry of a-axis oscillation photographs of polytypes of groups* I–IV

Formulae of basic arrangements of the *t–o–f* layers in polytype unit cells are given.

Group of polytypes	Symmetry of 10.*l* and 10.$\bar{l}$ reflexions (*a*-axis oscillation photograph)	Formulae of unit cells– *t–o–f* notation	Symbol of series
I	The 10.*l* reflexion intensities are equal to the 10.$\bar{l}$ intensities for all values of index *l*.	$(t)_{2N}f1(o)_nf2(t)_{2N'}f1(o)_{n'}f2$	SI-1
II	The 10.*l* reflexion intensities are equal to the 10.$\bar{l}$ intensities for *l* values different from those for which $|l/N| = 2\cdot5$ and $3\cdot5$.	$(t)_{2N+1}f1(o)_nf2$	SII-1
III	The reflexion intensities fulfill the following relation: $\mathrm{Int}(l/N = 3\cdot0 + \Delta l/N)A \sim$ $\mathrm{Int}(l/N = 3\cdot0 + \Delta l/N)$, for $A < 1$.	$(t)_{2N+1}f4(t)_{2N'+1}f5$ $(t)_{2N+1}f1(o)_nf1(t)_{2N'+1}f2(o)_nf2$ $(t)_{2N+1}f4(t)_{2N'+1}f2(o)_nf2$ $(t)_{2N+1}f5(t)_{2N'+1}f1(o)_nf1$	SIII-1 SIII-2 SIII-3 SIII-4
IV	The distribution of the reflexion intensities is similar to that of group III, but in this case every third reflexion has an intensity different from zero.	$(t)_{2N}f4(t)_{2N'}f5$ $(t)_{2N}f1(o)_nf1(t)_{2N'}f2(o)_{n'}f2$ $(t)_{2N}f4(t)_{2N'}f2(o)_nf2$ $(t)_{2N}f5(t)_{2N'}f1(o)_nf1$	SIV-1 SIV-2 SIV-3 SIV-4

Table 3. *The diagram of complex polytype cells:* $SX = SA + SB$

SA →	SI	SII	SIII	SIV
SB ↓ SX ↘				
SI	SI	SII	SIII	SIV
SII	SII	SII (SI)	SIII	SIV
SIII	SIII	SIII	SIII (SIV)	SIV
SIV	SIV	SIV	SIV	SIV (SIII)

rotation of a $\pi/3$ angle around the c axis (Verma & Krishna, 1966). Thus, to identify a rhombohedral polytype, the structure of one part only may be considered. The stacking of the molecular layers xyz in each part is similar to a polytype cell of groups I–III, *e.g.* $18R$: $\bar{x}\bar{x}x\ \bar{y}\bar{y}y\ \bar{z}\bar{z}z$; $36R_4$: $x\bar{y}x\bar{x}x\bar{x}\ z\bar{x}z\bar{z}z\bar{z}\ y\bar{z}y\bar{y}y\bar{y}$ *etc.*

The t–o–f notation allows one to present the preceding rules in a far simpler form, namely by determining the general formulae of polytype cells. It was found that the t–o–f sequences of all known MX_2 polytypes may be classified into a certain number of structural series. Specific series are characteristic for a specific group. The typical formulae for groups I–IV are presented in Table 2.

It should be noted that besides those polytypes which have simple cells (Table 2) a large number of polytypes have complex cells: these complex cells are always composed of two (or more) simple cells. It can be shown that the polytype with a cell composed of several simple cells (each of them belonging to a different group) should be classified as belonging to the group denoted by the highest number, namely to the group with the lowest symmetry in the distribution of the 10.l and 10.$\bar{l}$ reflexions, *e.g.*

$$(t)_2(f1f2)_2 tf1f2 = (t)_2(f1f2)_2 + tf1f2$$
$$18H_7 = 12H_4 + 6H_1$$
$$SII = SI\text{-}1 + SII\text{-}1$$

The diagram for the classification of polytypes having cells consisting of two simple cells of the SI–SIV series is presented in Table 3.

Diagrams of the 10.l *and* 10.$\bar{l}$ *reflexions*

The use of intensity diagrams is most convenient for the identification of polytypes (Pałosz & Przedmojski, 1980): the intensities of the 10.l and 10.$\bar{l}$ reflexions for $2\cdot5 \le |l/N| \le 3\cdot5$ are plotted in the diagrams on two opposite sides of the $|l/N|$ axis (Figs. 2–20); N in $|l/N|$ corresponds to the number of individual layers X in the cell of the polytype (Pałosz & Przedmojski, 1980). On

these diagrams one may easily observe the symmetry of the distribution of the 10.l and 10.$\bar{l}$ reflexions: on this basis a given polytype may be classified as belonging to one of the groups I–IV. This form of presentation of the reflexion intensities is very convenient for comparison of the interference patterns of different polytypes. This is very important for several reasons: (1) The distributions of reflexion intensities of the polytypes belonging to one series are similar, *e.g.* the diagrams of $24H_7$, $24H_8$ and $32H_2$ (Figs. 12–14) which belong to the series $SIII$-1, as well as the diagrams of $22H_5$ and $50H_1$ (Figs. 4 and 9) which belong to the series SII-1, *etc.* Thus, on the basis of the diagrams corresponding to a number of known polytypes, the general formula for the cell content of the polytype under study may be easily established. (2) Complex polytype sequences are usually composed of simple sequences. These simple sequences may be easily found by analysing the distribution of the reflexion intensities on the diagrams: *e.g.* the intensity distributions on the diagrams of polytypes $22H_4$, $24H_9$, $38H_1$ and $42H_1$ are similar (Figs. 3, 5, 7, 8): intensity maxima occur for $|l/N| = 2\cdot5$, $2\cdot67$, $2\cdot83$, $3\cdot0$, $3\cdot17$, $3\cdot33$ and $3\cdot5$, *i.e.* in the positions of the 10.l reflexions of $6H_1$. In the cells of these four complex polytypes one may discern the sequences which correspond to the cell of $6H_1$.

Experimental data and results

The polytypes identified were all found in crystals of CdI_2 obtained by evaporation from solutions. The conditions of growth are summarized in Table 4 and have been detailed elsewhere: crystals grown in usual conditions in air (Pałosz, 1981), in an external magnetic field H (Pałosz & Przedmojski, 1982a), in an external electric field E (Pałosz & Przedmojski, 1982b).

The crystals were examined by X-rays. A cylindrical camera of radius 43 mm and with a collimator of aperture 0·5 mm were used. The crystals were oscillated in the range 19–34°; *i.e.* the angle between the incident beam and the c axis varied between
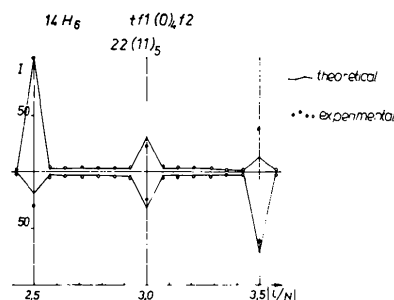

Fig. 2. Diagram of intensities of reflexions 10.l and 10.$\bar{l}$ measured experimentally and calculated theoretically for polytype $14H_6$ (group II). The remaining figures (3–20) show similar diagrams for other polytypes of group II (3–10), for polytypes of group III (11–15) and for polytypes of group IV (16–20).

Table 4. *Growth conditions of polytypes of* CdI$_2$

(*a*) New polytypes of CdI$_2$

Polytype	Solvent H$_2$O:C$_2$H$_5$OH	Temperature (K)	External field
Group II			
14H$_6$	1:0	298	E
22H$_4$	3:1	298	–
22H$_5$	1:0	298	H
24H$_9$	1:1	298	H
26H$_4$	1:1	298	–
38H$_1$	3:1	298	–
42H$_1$	1:1	323	–
50H$_1$	0:1	298	E
58H$_1$	1:0	323	–
Group III			
12H$_7$	3:1	278	–
24H$_7$	1:1	323	E
24H$_8$	0:1	323	–
32H$_2$	0:1	323	–
34H$_4$	1:0	278	H
Group IV			
48R$_1$	3:1	298	H
54R$_1$	1:0	278	H
54R$_2$	1:1	298	H
60R$_2$	1:1	298	H
72R$_2$	1:1	278	H

(*b*) Re-identified polytypes of CdI$_2$

Polytype	Solvent H$_2$O:C$_2$H$_5$OH	Temperature (K)	External field	*t–o–f* notation
Group I				
12H$_4$	3:1	298	H	$(t)_2(f1f2)_2$
16H$_7$	1:0	298	E	$((t)_2f1f2)_2$
Group II				
6H$_1$	1:0/3:1	278/298	H/–	$tf1f2$
8H$_1$	1:0	298	E	$tf1of2$
10H$_1$	1:0/1:1/1:1	298/298/298	E/H/H	$(t)_3f1f2$
18H$_6$	1:1	298	E	$(t)_3f1f2tf1of2$
28H$_1$	3:1	298	H	$(t)_{11}f1of2$
Group III				
8H$_1$	1:1/0:1/1:0	323/278/298	–/H/E	$tf4tf5$
Group IV				
12R	1:1	298	E	$f4f5$
18R	1:1	298	H	$f1f1f5$
24R$_1$	1:0	278	H	$(t)_2f4f5$
24R$_2$	1:1	278	H	$f1of1f5$
30R$_1$	1:0	298	–	$(t)_2f1f1f5$
42R$_1$	3:1	298	H	$(t)_4f1f1f5$

19–34°. The intensities of the 10.*l* reflexions were measured on the *a*-axis oscillation photographs by photometry and were then plotted on the diagrams which compare the measured with the calculated intensities in the range $2·5 \leq |l/N| \leq 3·5$ (Figs. 2–20).

Some examples of the application of the rules of constructing polytype cells, discussed in the preceding paragraph, now follow.

Polytype 14H$_6$ (*Fig. 2, group* II)

The unit cell of this polytype belongs to group II and is composed of x and $\bar{x}$ layers: a total of seven molecular layers. By calculating the ratio of the reflexion intensities $I(10.l)/I(10.\bar{l})$ (here equal to about 0·25) it may be established that the percentage of x layers in the cell is about 80%. Thus, two $x/\bar{x}$ layer compositions of the cell should be considered for this polytype: $x/\bar{x} = 5/2$ and $x/\bar{x} = 6/1$.
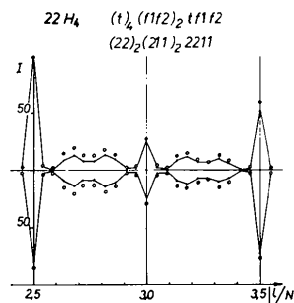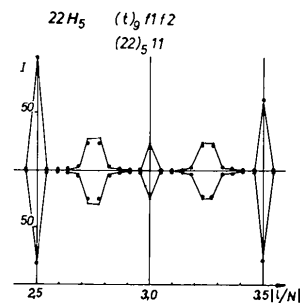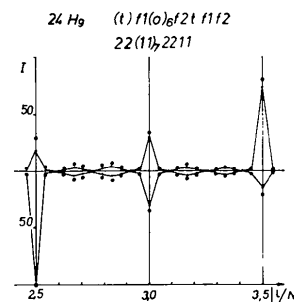
22H$_4$ $(t)_4 (f1f2)_2 tf1f2$
          $(22)_2(211)_2 2211$

Fig. 3

22H$_5$ $(t)_9 f1f2$
          $(22)_5 11$

Fig. 4

24H$_9$ $(t) f1(o)_6 f2t f1f2$
          $22(11)_7 2211$

Fig. 5

26H$_4$ $(t)_4 f1(o)_2 f2 (t)_2 f1 of2$
          $(22)_2 2(m)_3 222(m)_2$

Fig. 6

38H$_1$ $(t)_4 (f1f2)_2((t)_2 f1f2)_2 t f1f2$
          $(22)_2(211)_2(22211)_2 2211$

Fig. 7

42H$_1$ $(t)_2(f1f2)_2 t(f1f2)_5$
          $22(211)_2 (2211)_5$

Fig. 8

50H$_1$ $(t)_{23} f1f2$
          $(22)_{12} 11$

Fig. 9

58H$_1$ $(t)_7 f1f2((t)_3 f1f2)_4$
          $(22)_4 11((22)_2 11)_4$

Fig. 10

12H$_7$ $t f5 t f1of1$
          22122111

Fig. 11
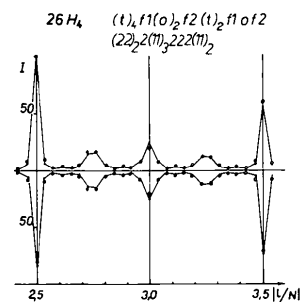
24H$_7$ $(t)_7 f4 (t)_3 f5$
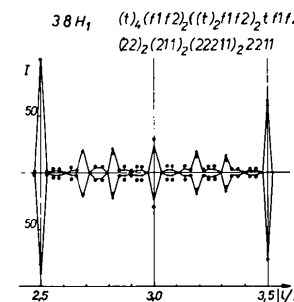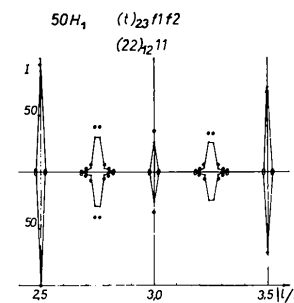 $(22)_3 212223$
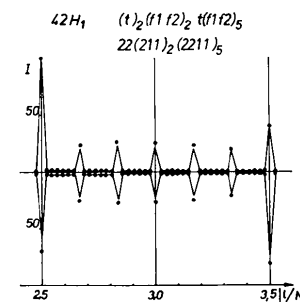
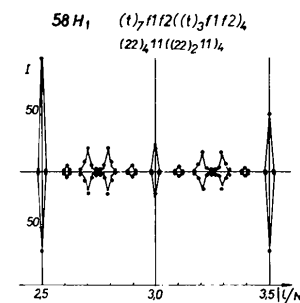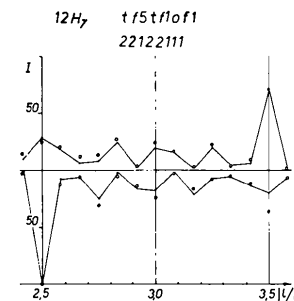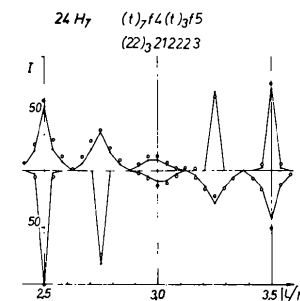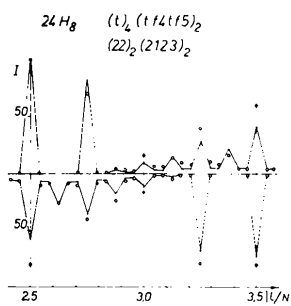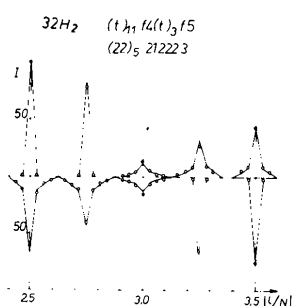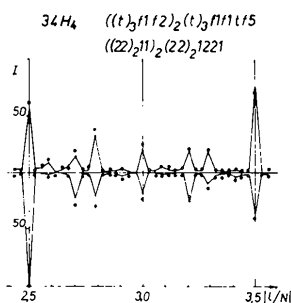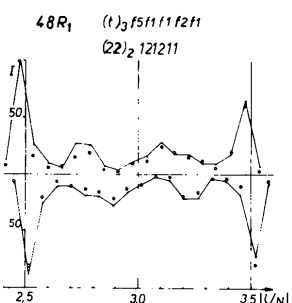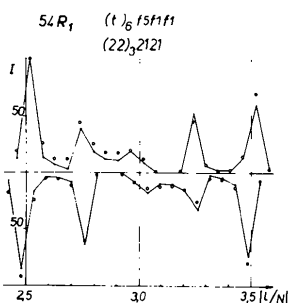Fig. 12

Fig. 13

Fig. 14

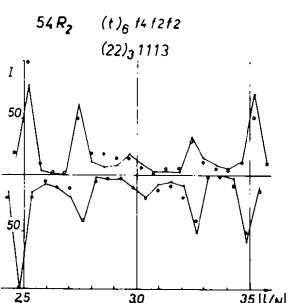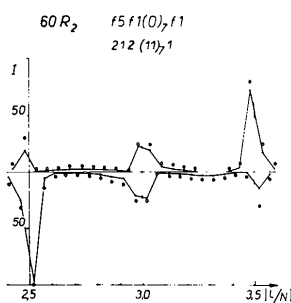
Fig. 15

Fig. 16

Fig. 17
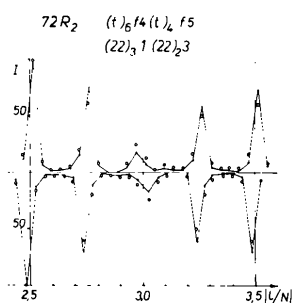

Fig. 18

Fig. 19

Fig. 20

(1) $x/\bar{x} = 5/2$. The possible arrangements of these layers are as follows:

   (i) $xxxxxx\bar{x}\bar{x}$: $(o)_3(f1f2)_2$
   (ii) $xxxx\bar{x}x\bar{x}$: $(t)_3f1(o)_2f2$
   (iii) $xxx\bar{x}xx\bar{x}$: $tf1of2tf1f2$.

(2) $x/\bar{x} = 6/1$. The x and $\bar{x}$ layers may be arranged in only one sequence:

   (iv) $xxxxxx\bar{x}$: $tf1(o)_4f2$.

From the above, the sequences (i), (ii) and (iii) correspond to the already known polytypes $14H_5$, $14H_4$ and $14H_2$, respectively. By comparing the theoretically calculated and experimentally found diagrams (Fig. 2) the structure of the investigated polytype $14H$ was uniquely established to be $tf1(o)_4f2$.

It should be noted that the four hypothetical sequences presented above may be directly found from the general formula of the polytype cell of group II (Table 2). In general, however, the sequences composed of four, five and six x layers and three, two and one $\bar{x}$ layers, respectively, should be considered. These sequences in which the layers x and $\bar{x}$ occur in the ratio $4/3$ were here excluded on the basis of the ratio $I(10.l)/I(10.\bar{l})$.

Polytype $24H_7$ (Fig. 12, group III)

By comparing the intensity diagram obtained experimentally with the diagrams of the earlier identified polytypes of CdI_2, the general formula of the cell content was established to be $(t)_{2N+1} f4(t)_{2N+1}f5$, series $SIII$-1. In this series only three polytypes composed of 12 molecular layers are possible:

   (i) $tf4(t)_9f5$: $(x\bar{x})_5x\bar{y}$
   (ii) $(t)_3f4(t)_7f5$: $(x\bar{x})_4(x\bar{y})_2$
   (iii) $(t)_5f4(t)_5f5$: $(x\bar{x})_3(x\bar{y})_3$.

Among these hypothetical sequences (ii) corresponds to that found in the investigated polytype.

Polytype $60R_2$ (Fig. 19, group IV)

The distribution of the reflexion intensities on the diagram presented in Fig. 19 indicates that the structure of this polytype is based on the structure $2H$: this means that the majority of molecular layers which form the $60R$ polytype cell are arranged in the sequences o. As is seen from Table 2 layers o may occur in polytype cells of three series: SIV-2, 3 and 4. Taking this into account, only 11 hypothetical cells were constructed to identify this polytype:

  SIV-2: (i) $f1(o)_6f1f2f2$
        (ii) $f1f1f2(o)_6f2$
        (iii) $f1of1f2(o)_5f2$
        (iv) $f1(o)_5f1f2of2$
        (v) $f1(o)_2f1f2(o)_4f2$
        (vi) $f1(o)_4f1f2(o)_2f2$
        (vii) $f1(o)_3f1f2(o)_3f2$
  SIV-3:(viii) $f4f2(o)_7f2$
        (ix) $(t)_2f4f2(o)_5f2$
  SIV-4: (x) $f5f1(o)_7f1$
        (xi) $(t)_2f5f1(o)_5f1$.

The sequence (x) corresponds to the polytype $60R$ of Fig. 19.

From the preceding examples it appears that the number of hypothetical sequences taken into con-

sideration to uniquely determine the structure of polytypes is dependent on the complexity of the polytype cells. The sequences $t-o-f$ which were considered necessary for identification of the 19 new polytypes of CdI_2 are listed below (correct models are indicated by an asterisk):

Polytypes of group II

$14H_6$ $tf1(o)_4f2^*$

$22H_4$ $(t)_4(f1f2)_2tf1f2^*, (t)_2(f1of2)_2tf1f2,$
         $(t)_5f1of2tf1f2, (t)_7f1(o)_2f2$

$22H_5$ $(t)_9f1f2^*, (t)_7f1(o)_2f2$

$24H_9$ $tf1(o)_6f2tf1f2^*, tf1(o)_2f2tf1(o)_4f2$
         $(t)_3f1f2tf1(o)_4f2, (t)_2f1f2(t)_2f1(o)_4f2$
         $(t)_3f1(o)_2f2(t)_3f1f2$

$26H_4$ $(t)_4f1(o)_2f2(t)_2f1of2^*, (t)_3f1of2(t)_3f1(o)_2f2$
         $(t)_2f1(o)_4f2(t)_2f1of2, (t)_7f1(o)_4f2,$
         $(t)_9f1(o)_2f2$

$38H_1$ $(t)_4(f1f2)_2((t)_2f1f2)_2tf1f2^*,$
         $(t)_4f1f2(t)_3f1of2tf1f2tf1of2,$
         $(t)_4f1f2tf1f2(t)_3f1of2(t)_2f1f2,$
         $(t)_4f1f2(t)_2(f1f2)_2(t)_2f1f2f1of2,$
         $(t)_4(f1f2)_2(t)_2f1f2tf1f2(t)_2f1f2$
         $(t)_3(f1f2)_2tf1of2(t)_2f1of2tf1f2$

$42H_1$ $(tf1f2)_5(t)_2(f1f2)_2^*,$
         $(t)_2f1of2(f1f2)_2(t)_3(f1of2)_2,$
         $(t)_2f1of2(f1of2)_2(t)_2f1f2(t)_3f1of2,$
         $(tf1f2)_2(t)_2f1f2(tf1f2)_2t(f1f2)_2,$
         $(tf1f2)_3(t)_2f1f2tf1f2t(f1f2)_2$

$50H_1$ $(t)_{23}f1f2^*$

$58H_1$ $((t)_3f1f2)_4(t)_7f1f2^*,$
         $((t)_3f1f2)_4(t)_5f1(o)_2f2,$
         $((t)_3f1f2)_5tf1of2,$
         $((t)_3f1f2)_2(t)_4f1f2(t)_5f1f2(t)_4f1f2.$

Polytypes of group III

$12H_7$ $tf5tf1of1^*, tf5f1f2f1f1, tf4tf2of2,$
         $tf4f2f1f2f2$

$24H_7$ $(t)_7f4(t)_3f5^*, (t)_5f4(t)_5f5, (t)_9f4tf5$

$24H_8$ $(t)_4(tf4 tf5)_2^*, (t)_3f4tf5tf4(t)_3f5$

$32H_2$ $(t)_{11}f4(t)_3f5^*, (t)_9f4(t)_5f5, (t)_{13}f4 tf5,$
         $(t)_7f4(t)_7f5$

$34H_4$ $(t)_3f1f1tf5((t)_3f1f2)_2^*,$
         $(t)_3f1(o)_3f1tf5(t)_2f1(o)_2f2,$
         $tf1(o)_3f1(t)_3f5(t)_2f1(o)_2f2,$
         $(t)_3f1of1tf5(t)_2f1(o)_4f2,$
         $tf1of1(t)_3f5(t)_2f1(o)_4f2,$
         $(t)_3f1(o)_4f1tf5(t)_2f1of2,$
         $(t)_3f1f1tf5(t)_2(f1(o)_2f2)_2.$

Polytypes of group IV

$48R_1$ $f1f1f2f1(t)_3f5^*, f1of1(t)_4f5, f2of2(t)_4f4,$
         $f1of1(t)_2f5(t)_2, f2of2(t)_2f4(t)_2,$
         $f1f1tf2f1(t)_2f5, f1f1tf2f1f5(t)_2$

$54R_1$ and $54R_2$ $(t)_6f1f1f5^*, (t)_6f2f2f4^*,$
         $(t)_4f1f1(t)_2f5, (t)_4f2f2(t)_2f4$

$60R_2$ $f5f1(o)_7f1^*, (t)_2f5f1(o)_5f1, f4f2(o)_7f2,$
         $(t)_2f2(o)_5f2, f1(o)_6f1f2f2, f1f1f2(o)_6f2,$
         $f1of1f2(o)_5f2, f1(o)_5f1f2of2,$
         $f1(o)_2f1f2(o)_4f2, f1(o)_4f1f2(o)_2f2,$
         $f1(o)_3f1f2(o)_3f2$

$72R_2$ $(t)_6f4(t)_4f5^*, (t)_{10}f4f5.$

Theoretical intensities for hypothetical polytypes were computed from the formula commonly used for CdI_2 crystals (e.g. Jain & Trigunayat, 1978a). The intensities measured experimentally were compared with those calculated theoretically: in the comparison the following features were assumed as relevant:

(i) Symmetry of distribution of $10.l/10.\bar{l}$ reflexions, characteristic for the given group.

(ii) The specific shape of the distribution of the reflexion intensities, characteristic for structural series.

(iii) Agreement between relative intensities measured experimentally and calculated theoretically for specific reflexions.

The discrepancies between the experimental and theoretical values of the observed intensities in some of the 2–20 diagrams seem to be negligible from the point of view of the criteria listed above.

Table 4(a) presents the 19 new polytypes and the conditions for their formation, while Table 4(b) presents 14 polytypes already known, re-identified in this work. The 19 new polytypes of CdI_2 are presented again in Table 5. The structure is described in the Zhdanov notation and in the $t-o-f$ notation; it should be stressed that the $t-o-f$ sequence describes the structure uniquely, while the Zhdanov sequences listed in Table 5 represent those chosen among several equivalent forms of this notation (Pałosz, 1980a).

From the $t-o-f$ sequences the positions of individual atoms in the unit cells may be easily obtained: the simplest way for this depends on (1) reconstruction of the sequence of the layers $ABC\alpha\beta\gamma$ in the cell and (2) establishing the xyz spatial coordinates of individual atoms: the scheme for obtaining the xyz coordinates of the atoms belonging to the layers $ABC\alpha\beta\gamma$ in the cell is presented in Table 6.

Final remarks

The complete information about the organization of stacking sequences of polytypic structures MX_2 presented earlier may be collected in a set of rules for the construction of Zhdanov sequences for these structures (e.g. Jain & Trigunayat, 1978a; Agraval, 1981). These rules, however, appeared inconvenient in their application because of the non-uniqueness of the Zhdanov notation and are now replaced by simple rules describing the organization of $t-o-f$ and xyz sequences in polytypic structures MX_2. These forms of notation appeared especially useful in the procedure for identi-

Table 5. *List of 19 new polytypes of* CdI_2

No.	Ramsdell symbol*	Zhdanov notation – sequence of layers of iodine	t–o–f notation	Complexity of cell
Group II				
1	$14H_6$	$22(11)_5$	$tf1(o)_4f2$	SII-1
2	$22H_4$	$(22)_2(221)_22211$	$(t)_4(f1f2)_2tf1f2$	SI-1 + SII-1
3	$22H_5$	$(22)_511$	$(t)_9f1f2$	SII-1
4	$24H_9$	$22(11)_72211$	$tf1(o)_6f2tf1f2$	$(SII-1)_2$
5	$26H_4$	$(22)_22(11)_3222(11)_2$	$(t)_4f1(o)_2f2(t)_2f1of2$	$(SI-1)_2$
6	$38H_1$	$(22)_2(211)_2(22211)_22211$	$(t)_4(f1f2)_2((t)_2f1f2)_2tf1f2$	$(SI-1)_3$ + SII-1
7	$42H_1$	$22211211(2211)_5$	$(t)_2(f1f2)_2(tf1f2)_5$	SI-1 + $(SII-1)_5$
8	$50H_1$	$(22)_{12}11$	$(t)_{23}f1f2$	SII-1
9	$58H_1$	$(22)_411((22)_211)_4$	$(t)_7f1f2((t)_3f1f2)_4$	$(SII-1)_5$
Group III				
10	$12H_7$	22122111	$tf1of1tf5$	SIII-4
11	$24H_7$	$(22)_3212223$	$(t)_7f4(t)_3f5$	SIII-1
12	$24H_8$	$(22)_2(2123)_2$	$(t)_4(tf4tf5)_2$	$(SIII-1)_2$
13	$32H_2$	$(22)_5212223$	$(t)_{11}f4(t)_3f5$	SIII-1
14	$34H_4$	$(22)_21221((22)_211)_2$	$(t)_3f1f1tf5((t)_3f1f2)_2$	SIII-4 + $(SII-1)_2$
Group IV				
15	$48R_1$	$(22)_2121211$	$f1f1f2f1(t)_3f5$	SIV-4 + SII-1
16	$54R_1$	$(22)_31212$	$(t)_6f1f1f5$	SIV-4
17	$54R_2$	$(22)_31113$	$(t)_6f2f2f4$	SIV-3
18	$60R_2$	$212(11)_71$	$f1(o)_7f1f5$	SIV-4
19	$72R_2$	$(22)_31(22)_23$	$(t)_6f4(t)_4f5$	SIV-1

* The indices of Ramsdell symbols are after Pałosz (1980a).

Table 6. *Diagram of xyz coordinates of individual ions of* Cd *and* I *in polytype cells*

Layer	Spatial coordinates		
	z	y	z
A	$(n-1)c_0$	0	0
α	$(m-\frac{1}{2})c_0$	0	0
B	$(n-1)c_0$	$\frac{1}{3}b_0$	$\frac{2}{3}a_0$
β	$(m-\frac{1}{2})c_0$	$\frac{1}{3}b_0$	$\frac{2}{3}a_0$
C	$(n-1)c_0$	$\frac{2}{3}b_0$	$\frac{1}{3}a_0$
γ	$(m-\frac{1}{2})c_0$	$\frac{2}{3}b_0$	$\frac{1}{3}a_0$

$a_0 = b_0 = 4\cdot24$ Å, $c_0 = 3\cdot417$ Å. n: position of the X layer in the cell. m: position of the molecular layer in the cell.

$$n = \begin{array}{cccccc} 1 & 2 & 3 & 4 & 5 & 6 \\ \underbrace{A\,\gamma B} & & \underbrace{C\,\alpha B} & & \underbrace{A\,\gamma B}\ldots & \end{array}$$
$$m = \quad 1 \qquad\quad 2 \qquad\quad 3$$

fication of polytypes of CdI_2, *i.e.* in selecting the most probable of the hypothetical structural models. The number of models of hypothetical polytypes considered earlier for the identification of a polytype frequently contained several tens of models (*e.g.* Jain & Trigunayat, 1978a,b), while the number of t–o–f sequences considered in this work was always less than ten: in some cases only one model was constructed. Such an elimination of less probable, or simply 'forbidden', structures from the geometrically possible models was made possible by the use of the following improvements:

(1) Polytypes were classified into groups I–IV with respect to the symmetry of distribution of the $10.l/10.\bar{l}$ reflexions.

(2) The number of models of the basic set of structures was reduced when the t–o–f notation was used: there are no equivalent notations for a single structure.

(3) Simple rules for the periodic ordering of xyz and t–o–f layers were established: layer formulae of polytype cells for some basic structural series were elaborated for polytypes of groups I–IV.

(4) Special diagrams for plotting the intensities of the $10.l$ and $10.\bar{l}$ reflexions were used; these enable one to observe regularities in the distribution of the reflexion intensities, characteristic for specific layer compositions of polytype cells: the layers t–o–f which form the polytype cell may be easily established.

As indicated above, the intensity distributions observed on the diagrams of the $10.l/10.\bar{l}$ intensities for polytypes of one structural series are very similar. It can be shown that this relation is valid not only for polytypes but also for disordered structures. As discussed elsewhere (Pałosz, 1982a,b), by considering various t–o–f sequences, called t–o–f layers, as structures composed of basic layers o and t (here, layers o represent the polytype $2H$, layers t, $4H$) and of faults $f1$, $f2$, $f3$, ..., $f8$, each polytypic modification may be presented as a basic structure, or a mixture of two basic structures, with specific types of faults, one fault being represented by one of the f layers. It was found that the specific distribution of the reflexion

intensities for polytypes and specific shape of the diffuse streaks (broadened $10.l$ reflexions) for disordered structures are closely connected with the type of faulting occurring in the crystals (Pałosz, 1980b). Based on this it seems possible to determine directly the type and degree of faulting for disordered structures: in this case the experimentally observed intensity curves should be compared with the $10.l/10.\bar{l}$ reflexion intensities calculated for structural models. A similar procedure was earlier applied to identify disordered structures of ZnS (Pałosz, 1977), and is now being extensively investigated for its possible use with disordered MX_2 structures.

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Atomic Positions of Three New Polytypes of CdI₂

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Abstract

The crystal structures of three new polytypes $16H_9$, $24H_8$ and $44H_1$ of cadmium iodide have been determined. The structures are $22(11)_6$, $2222(211211)_2$ and $(22211211)(121121)_4$ in Zhdanov notation, each with space group $P\bar{3}m1$. All three polytypes have been found syntactically coalesced with other polytypes in three different crystals. Polytype $44H_1$ is the largest hexagonal polytype of cadmium iodide whose structure has been reported so far.

Introduction

Extensive work during the last two decades has resulted in the discovery not only of many new polytypes of known substances but also of many new polytypic substances. Not only do these discoveries help in understanding the phenomenon of polytypism more clearly but many new fields, like interpolytypic, intrapolytypic, phase transformation (Tewari &

Srivastava, 1974), dielectric behaviour of polytypes (Fernandez & Srivastava, 1975) and polytypes as a new class of variable band-gap materials (Rao & Srivastava, 1980), also develop side by side. Of late, many new techniques have been employed for investigating various aspects of polytypism (Trigunayat, 1981). Although much work has been done on polytypism the total number of CdI_2 polytypes with known structure is less than a hundred (Wahab & Trigunayat, 1980). Recently the structure-factor calculations of MX_2-type compounds have been simplified (Chadha, 1980) and, using this simplified structure-factor formula, the largest hexagonal structure of CdI_2 ($44H$) to be determined so far is presented here. Besides this, two other structures, $16H$ and $24H$, have also been determined.

Experimental methods and structure determination

Good hexagonal platy crystals, measuring 1–2 mm across and having a thickness of about 100 μm grown