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Identification of Polytypes of MX_2 -Type Compounds. II. Structures of 20 New Polytypes of Cadmium Iodide*

BY BOGDAN PAŁOSZ

Institute of Physics, Warsaw Technical University, 00 662 Warszawa, ul. Koszykowa 75, Poland

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Abstract. The identification of polytypes of crystals of MX_2 type using the intensity diagrams of the $10.l$ and $10.l$ reflexions is discussed. It is shown that these diagrams enable some standardization of the structures of simple polytypes, classifying them into structural series. The structures of 20 new polytypes of CdI_2 obtained from solutions have been determined: $16H_8$: $(t)_3f1o_1tf5$; $20H_{12}$: $(t)_5f4(t)_3f5$; $22H_6$: $(t)_7f1f1tf5$; $22H_7$: $(t)_5f2(o)_2f2tf4$; $22H_8$: $tf2(o)_2f2f1f2(t)_2f1f1$; $26H_5$: $(t)_7f2(o)_2f2tf4$; $28H_5$: $(t)_9f4(t)_3f5$; $38H_2$: $(t)_{17}f1f2$; $40H_2$: $(t)_{13}f4(t)_5f5$; $40H_3$: $tf1(o)_2f1(t)_{13}f2f2$; $24R_3$: $f1f1f2f2$; $48R_2$: $f1f1tf2f1(t)_2f5$; $48R_3$: $(t)_4f4(t)_2f5$; $54R_3$: $f1f1f2(o)_3f1tf5$; $66R_1$: $f1f1(t)_5f2f1f2f2$; $66R_2$: $f1f1(t)_5f2of1f5$; $84R_3$: $f1f1(tf2f1)_2(t)_4f2f2$; $84R_4$: $f1(o)_6f1(t)_4f2f2$; $96R_1$: $(t)_8f4(t)_6f5$; $120R_1$: $(t)_{10}f4(t)_8f5$; 18 already known polytypes have also been recognized. The uniqueness of the structures of polytypes determined by the standard a -axis oscillation method is discussed.

Introduction. The main source of information on the organization of polytypic crystals is the knowledge of the structures of the periodic modifications. In real polytypic crystals, the number of geometrically possible different modifications for a given material is unlimited; however, only some specific structures do occur.

Recently, we discussed the problem of the identification of MX_2 polytypes, presenting some simple rules of construction for the polytype cells (Pałosz & Przedmojski, 1980; Pałosz, 1980, 1982). The basis for the determination of these rules was the analysis of the stacking of the molecular layers in the identified polytypes of CdI_2 , PbI_2 and $Ti_{1.2}S_2$ (Pałosz, 1983). In this work we present the results of the analysis of the structures of about 300 polytypes of CdI_2 . We identified the stacking of layers in the cells of 20 new polytypes, recognizing also the structures of 18 already known polytypes and determining the period and type of cell (hexagonal or rhombohedral) for 250 polytypes. By means of these data we established some new construction rules for polytype cells of CdI_2 , which enable some standardization in the identification of a number of simple multilayer polytypes. The uniqueness of the structures determined for polytypes by standard X-ray analysis is also discussed.

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Table 1. Structure and growth conditions of 20 new polytypes of CdI₂

Ramsdell symbol*	<i>t-o-f</i> sequence	Solvent H ₂ O:C ₂ H ₅ OH (K)	Temp-erature (K)	External field (E: electric; H: magnetic)
Hexagonal polytypes				
16H ₈	(i) ₃ f1 ₀ f1 _t f5	1:0	298	E
20H ₁₂	(i) ₅ f4(i) ₃ f5	1:1	323	E
22H ₆	(i) ₇ f1f1 _t f5	1:0	323	—
22H ₇	(i) ₅ f2(o) ₂ f2 _t f4	1:1	308	E
22H ₈	(i) ₂ f1f1 _t f2(o) ₂ f2f1f2	1:1	308	E
26H ₅	(i) ₇ f2(o) ₂ f2 _t f4	1:0	323	—
28H ₅	(i) ₉ f4(i) ₃ f5	1:1	308	E
38H ₂	(i) ₁₇ f1f2	1:1	308	E
40H ₂	(i) ₁₃ f4(i) ₅ f5	3:1	298	H
40H ₃	<i>t</i> f1(o) ₂ f1(i) ₁₃ f2f2	1:1	298	H
Rhombohedral polytypes				
24R ₃	f1f1f2f2	1:0	323	E
48R ₂	f1f1f2f1(i) ₂ f5	1:0	298	H
48R ₃	(i) ₄ f4(i) ₂ f5	1:1	298	E
54R ₃	f1f1f2(o) ₃ f1 _t f5	1:0	278	H
66R ₁	f1f1(i) ₅ f2f1f2f2	1:0	278	H
66R ₂	f1f1(i) ₅ f2of1f5	1:1	308	E
84R ₃	f1f1(<i>t</i> f2f1) ₂ (i) ₄ f2f2	1:1	298	H
84R ₄	f1(o) ₅ f1(i) ₄ f2f2	0:1	298	E
96R ₁	(i) ₈ f4(i) ₆ f5	1:1	323	E
120R ₁	(i) ₁₀ f4(i) ₈ f5	1:1	323	E

* The indices of the Ramsdell symbols are after Pałosz (1980, 1982).

Table 2. Structure and growth conditions of 18 re-identified polytypes of CdI₂

Ramsdell symbol	<i>t-o-f</i> sequence	Solvent H ₂ O:C ₂ H ₅ OH (K)	Temp-erature (K)	External field (E: electric; H: magnetic)
Hexagonal polytypes				
6H ₁	<i>t</i> f1f2	1:0/3:1/	323/278	E/H/
		1:1/0:1	298/298	E/H
8H ₃	<i>t</i> f4 _t f5	1:0/1:0/	323/278	-H/
		1:1/0:1	298/323	H/-
10H ₁	(i) ₃ f1f2	3:1	323	E
10H ₂	<i>t</i> f1f1f5	1:1	323	E
12H ₂	<i>t</i> f1f1f2f1f5	1:1	323	E
12H ₃	(i) ₃ f1of2	3:1	278	H
14H ₁	(i) ₅ f1f2	1:0	308	E
18H ₅	(i) ₅ f1f1 _t f5	1:1	323	E
28H ₅	(i) ₉ f4(i) ₃ f5	1:0	308	E
30H ₂	(i) ₄ (f1f2) ₂ (i) ₅ f1f2	1:0	298	—
30H ₃	(i) ₁₃ f1f2	1:0	298	H
Rhombohedral polytypes				
12R	f4f5	1:1/1:1	298/308	H/E
18R ₁	f1f1f5	1:1	298	H
24R ₁	(i) ₂ f4f5	1:1	298	H
24R ₂	f1of1f5	1:1	298	—
30R ₁	(i) ₂ f1f1f5	1:0	323	E
36R ₄	(i) ₂ f4(i) ₂ f5	1:1	298	E
60R ₁	(i) ₆ f4(i) ₂ f5	1:1	298	E

crystals were examined by X-rays using a cylindrical camera of radius 43 mm and a collimator of aperture 0.5 mm. The oscillation method was used with the angle between the incident beam and the *c* axis varying between 19 and 34°. For this range of oscillation the values of $|l/N|$, calculated for the 10.*l* and 10. \bar{l} reflexions of the *NH* and *NR* polytypes, lie between 2.5 and 3.5 (Pałosz & Przedmojski, 1980). The intensities of these reflexions were plotted (Pałosz, 1982) above and below the $|l/N|$ axis for *l* and \bar{l} , respectively (see 10.*l*/10. \bar{l} diagrams, Figs. 1–20). The identification of the polytypes was based on a comparison of the intensities of these reflexions, measured photometrically, with the calculated values for a number of models of polytype cells. The theoretical intensity was calculated using the standard formula for *MX*₂ crystals, e.g. Jain & Trigunayat (1978).

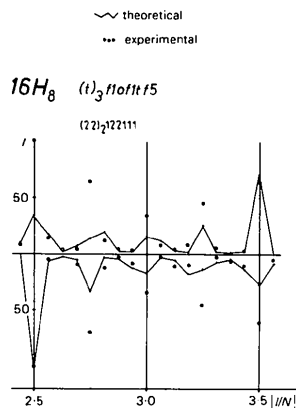


Fig. 1. Diagram of intensities of 10.*l* and 10. \bar{l} reflexions measured experimentally and calculated theoretically for the 16H₈ CdI₂ polytype. Figs. 2–20 show similar diagrams for other polytypes of CdI₂.

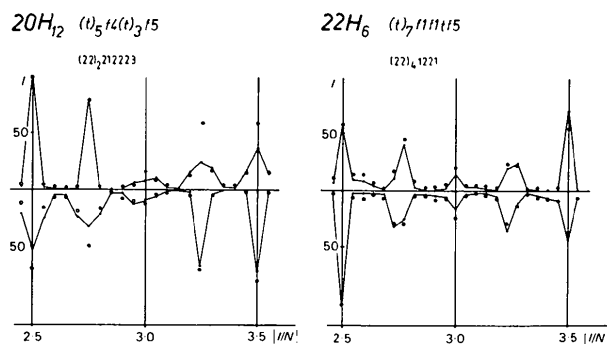


Fig. 2.

Fig. 3.

Experimental. The crystals of CdI₂ were grown from solutions by evaporation in air both in the absence of external fields (Pałosz, 1981), and in the presence of external electric and magnetic fields (Pałosz & Przedmojski, 1982*a,b*). The growth conditions for the identified polytypes are specified in Tables 1 and 2. The

22H₇ (l)₅f₂(o)₂f₂l₁l₄
(22)₂2¹1₃2³

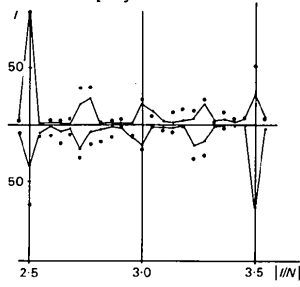


Fig. 4.

22H₈ l₂(o)₂f₂l₁f₂(l)₂l₁l₁
22(11)₃2¹1222¹

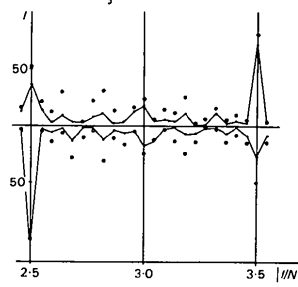


Fig. 5.

48R₂ l₁l₁f₂l₁(l)₂f₅
222¹2¹1122¹1

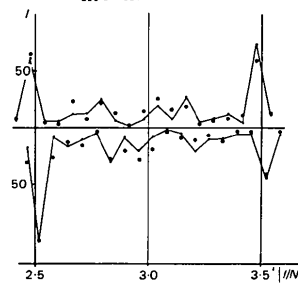


Fig. 12.

48R₃ (l)₄l₄(l)₂f₅
22¹(22)₃

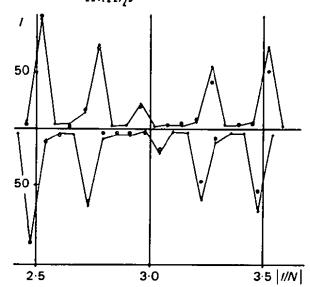


Fig. 13.

26H₅ (l)₇f₂(o)₂f₂l₁l₄
(22)₃2¹1₃2³

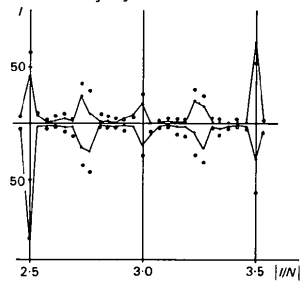


Fig. 6.

28H₅ (l)₉l₄(l)₃f₅
(22)₂2¹222³

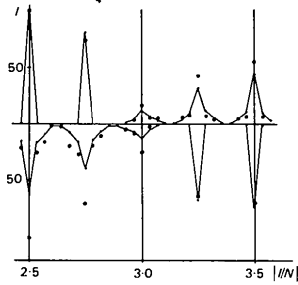


Fig. 7.

54R₃ l₁l₁f₂(o)₃l₁l₁f₅
2212¹112(11)₄

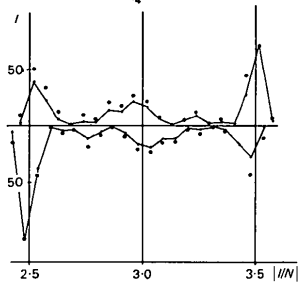


Fig. 14.

66R₁ l₁l₁(l)₅f₂l₁f₂l₂
2¹112¹(22)₃1¹

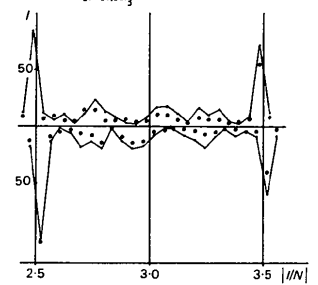


Fig. 15.

38H₂ (l)₇l₁f₂
(22)₃1¹

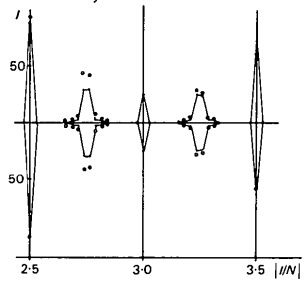


Fig. 8.

40H₂ (l)₇l₄(l)₅f₅
(22)₆2¹1(22)₂2³

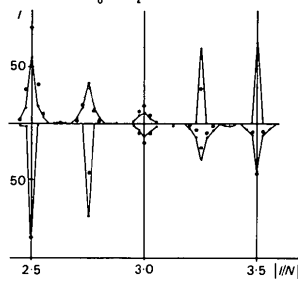


Fig. 9.

66R₂ l₁l₁(l)₅f₂o₁f₅
212¹(22)₃(11)₂

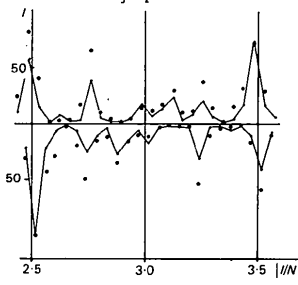


Fig. 16.

84R₃ l₁l₁(l₂l₁)₂(l)₄f₂f₂
2¹112¹(22¹)₄(22)₂

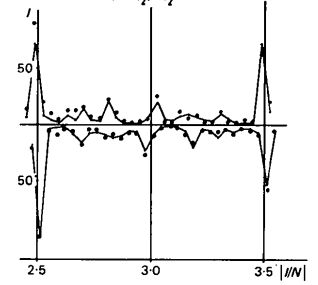


Fig. 17.

40H₃ l₁l₁(o)₂f₁(l)₃f₂f₂
(22)₂1¹122¹(11)₂1

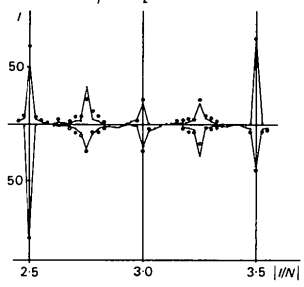


Fig. 10.

24R₃ l₁l₁f₂f₂
2112¹

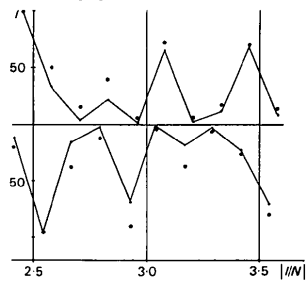


Fig. 11.

84R₄ l₁(o)₆l₁(l)₄f₂f₂
(22)₂2¹112¹(11)₃1

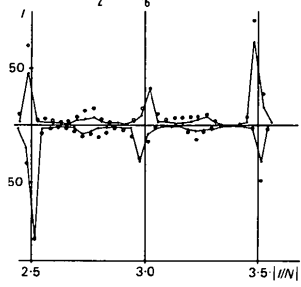


Fig. 18.

96R₁ (l)₈l₄(l)₆f₅
(22)₆1¹(22)₃3

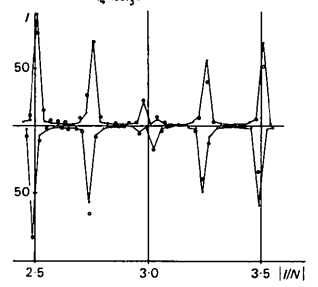


Fig. 19.

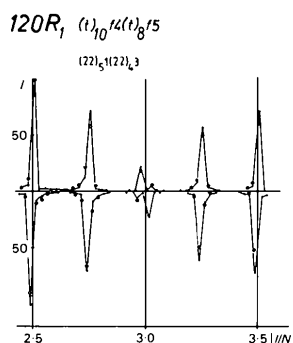


Fig. 20.

Table 3. Structural series of polytypes of CdI₂

Group of polytypes	Symbol of series	<i>t-o-f</i> sequence of unit cell
I	SI-1	(<i>t</i>) _{2N} ∩(<i>o</i>) _n f2(<i>t</i>) _{2N} ∩(<i>o</i>) _n f2
II	SII-1	(<i>t</i>) _{2N+1} ∩(<i>o</i>) _n f2
III	SIII-1	(<i>t</i>) _{2N+1} f4(<i>t</i>) _{2N+1} f5
	SIII-2	(<i>t</i>) _{2N+1} ∩(<i>o</i>) _n ∩(<i>t</i>) _{2N+1} f2(<i>o</i>) _n f2
	SIII-3	(<i>t</i>) _{2N+1} f4(<i>t</i>) _{2N+1} f2(<i>o</i>) _n f2
	SIII-4	(<i>t</i>) _{2N+1} f5(<i>t</i>) _{2N+1} ∩(<i>o</i>) _n ∩
IV	SIV-1	(<i>t</i>) _{2N} f4(<i>t</i>) _{2N} f5
	SIV-2	(<i>t</i>) _{2N} ∩(<i>o</i>) _n ∩(<i>t</i>) _{2N} f2(<i>o</i>) _n f2
	SIV-3	(<i>t</i>) _{2N} f4(<i>t</i>) _{2N} f2(<i>o</i>) _n f2
	SIV-4	(<i>t</i>) _{2N} f5(<i>t</i>) _{2N} ∩(<i>o</i>) _n ∩

Discussion. The construction of polytype cells and the results for 20 new polytypes of CdI₂ are considered below.

Construction of polytype cells of the MX₂-type lattice

Recently we introduced two new forms for the symbolic description of polytypic structures of MX₂; these new forms are based on the notation of the molecular layers *X-M-X*: the *xyz* and *t-o-f* notations (Pałosz & Przedmojski, 1980; Pałosz, 1980). In the *xyz* notation the structure is presented as a sequence of molecular layers *AγB*, *BαC*, *CβA*, *CaB*, *AβC* and *BγA* denoted by the symbols *x*, *y*, *z*, \bar{x} , \bar{y} and \bar{z} , respectively. In the *t-o-f* notation we used the symbols *t*, *o*, *f*1, *f*2, ..., *f*8 which correspond to ten specific arrangements of the *xyz* layers in three-layer sequences. To determine a *t-o-f* sequence for a given structure, a special diagram given by Pałosz (1980, 1982) must be used. With the molecular-layer notation we formed two levels of classification for the MX₂ polytypes:

(1) Groups I-IV, corresponding to the classification of the *a*-axis oscillation photographs on the basis of the symmetry of the 10.*l*/10. \bar{l} diagrams (Pałosz & Przedmojski, 1980).

(2) structural series: the polytypes of each group were divided into structural series. The structures of the different polytypes of a series may be described by the general formula giving the *t-o-f* stacking of the layers (Table 3). The polytypes belonging to the same series are constructed of similar *f* layers, but have different numbers of *o* and/or *t* layers. For a given number of layers in the cell, the *o*, *t* and *f* layers may be arranged in several ways (Pałosz, 1982).

As noted earlier by Pałosz (1982), the distributions of the 10.*l* and 10. \bar{l} reflexion intensities in the diagrams of the different polytypes of the same series exhibit distinct regularities which make the diagrams similar to each other, while the diagrams of different series are different. By comparing the experimental diagram with the diagrams calculated for structural models of different series, the series is directly identified and the general formula for the cell of the polytype

under consideration can be determined. So, the identification of the polytype is reduced to the determination of the coefficients occurring in the general cell formula of the series (see Table 3). Independently, the number of models needed for a unique determination of a polytype structure may be reduced with the help of the known rules for constructing polytype cells, e.g. Verma & Krishna (1966), Dubey (1975), Jain & Trigunayat (1978), Pałosz (1980, 1982). The regularities of the 10.*l*/10. \bar{l} diagrams may be easily used in recognizing the polytypes having simple cells, i.e. those constructed of one cell of a given series. A number of multilayer polytypes, which may occur in real crystals, have cells composed of several simple cells. For the identification of such complex cells of polytypes one needs to consider the number of structural models relatively greater than that necessary in the case of simple polytypes. Of the 20 new polytypes of CdI₂ reported in this paper, 14 belong to a single series and only six have complex cells, c.f. Table 1.

Results: the structures of 20 new polytypes of CdI₂

The symmetry and shape of the experimental and theoretical diagrams in Figs. 1-20 agree satisfactorily. Some differences between experimental and calculated intensities occur for several diagrams. These discrepancies seem to be due to the coexistence of several polytypes in one crystal, and to a small degree of disorder observed in some cases:

- polytypes observed with 2H: 22H₇, 22H₈, 40H₃, 54R₃, 66R₂, 84R₃, 84R₄;
- polytypes observed with 4H: 16H₈, 20H₁₂, 22H₆, 28H₅, 48R₂, 96R₁;
- polytype 48R₃ occurred together with 12R;
- a small amount of disorder accompanied the polytypes 20H₁₂, 28H₅, 48R₂, 66R₁, 84R₄.

Polytypes belonging to a single series

The probable cells for simple polytypes were deduced after determining the series to which they belong. Examples are as follows:

Polytype 16H₈: Fig. 1, group III, series SIII-4: (*t*)_{2N+1}f5(*t*)_{2N+1}∩(*o*)_n∩. The cell 16H is formed of

eight molecular layers. From the general formula of the SIII-4 series it follows that, of the eight layers in the cell, three are f layers (namely $f1$, $f1$, $f5$), and the total number of the o and t layers is five. The number of the t layers must be even, so the number of the t layers can be four or two, with one or three o layers, respectively. For such a construction of the $16H$ cell only two different models are possible: $(t)_3f5t1of1 = tf5(t)_3f1of1 = (t)_3f1of1tf5$ and $tf5t1(o)_3f1$. The first corresponds to that investigated.

Polytype 28H₅: Fig. 7, group III, series SIII-1: $(t)_{2N+1}f4(t)_{2N'+1}f5$. 14 molecular layers occur in this cell. Of these, two are $f4$ and $f5$ which occur together with 12 t layers (see Table 3). As the t layers occur in two odd sequences, only three models of the $28H_5$ cell are possible: $tf4(t)_{11}f5 = (t)_{11}f4tf5$, $(t)_3f4(t)_9f5 = (t)_9f4(t)_3f5$ and $(t)_5f4(t)_7f5 = (t)_7f4(t)_5f5$, the second corresponding to the $28H_5$ polytype under consideration.

Polytype 24R₃: Fig. 11, group IV, series SIV-2: $(t)_{2N}f1(o)_n f1(t)_{2N'}f2(o)_{n'}f2$. The smallest polytype possible for the SIV-2 series is $24R$ with the cell $f1f1f2f2$, when all the coefficients in the general formula of this series are zero, see above.

For the 14 simple polytypes presented in this paper, the following numbers of models were considered: $16H_8$: 2; $20H_{12}$: 2; $22H_6$: 6; $22H_7$: 6; $26H_5$: 8; $28H_5$: 3; $38H_2$: 2; $40H_2$: 5; $40H_3$: 6; $24R_3$: 1; $48R_3$: 2; $84R_4$: 53; $96R_1$: 4; $120R_1$: 5. For some of these polytypes the number of all possible models given above is larger than is needed. For example, to identify the polytype $84R_4$ only 16 of the 53 cells possible for the SIV-2 series need to be considered.

Polytype 84R₄: Fig. 18, group IV, series SIV-2: $(t)_{2N}f1(o)_n f1(t)_{2N'}f2(o)_{n'}f2$. From the diagram obtained for this polytype one may conclude that this structure is based on the sequences corresponding to the basic $2H$ polytype. This means that a number of o layers occur in the $84R_4$ cell. Because of this, we considered cells having six or eight o layers. The following values of (N, n, N', n') for $n + n' = 6$ were considered: (2, 6, 0, 0), (2, 5, 0, 1), (2, 4, 0, 2), (2, 3, 0, 3), (2, 2, 0, 4), (2, 1, 0, 5), (2, 0, 0, 6), (1, 6, 1, 0)*, (1, 5, 1, 1)*, (1, 4, 1, 2)*, (1, 3, 1, 3)*, (1, 2, 1, 4)*, (1, 1, 1, 5)*, (1, 0, 1, 6)*.

Taking into account the fact that in the cells of all known polytypes of the SIV-2 series (Pałosz, 1980, 1982) all the t layers occur in a single sequence (this means that N or $N' = 0$), the cells denoted by asterisks were not considered. For the eight o layers in the $84R$ cell ($n + n' = 8$), the following values of (N, n, N', n') were considered: (1, 8, 0, 0), (1, 7, 0, 1), (1, 6, 0, 2), (1, 5, 0, 3), (1, 4, 0, 4), (1, 3, 0, 5), (1, 2, 0, 6), (1, 1, 0, 7), (1, 0, 0, 8).

From these sequences $f1(o)_6f1(t)_4f2f2$ (2, 6, 0, 0) corresponds to that found in the $84R_4$ polytype investigated.

Polytypes with complex cells

The structures of nearly all of the identified complex-cell polytypes of CdI_2 are constructed from one cell of the SI, SIII or SIV series and from one or several cells of the SII series (Pałosz, 1980). An analysis of these models which are possible for the $22H$ complex cell is presented below.

Polytype 22H₈: Fig. 5, group III, series SIII-2 + SII. After determining that this polytype does not belong to a single series, we considered the cells composed of one cell of SII type $[(t)_{2N'+1}f1(o)_n f2]$ and one of SIII-2 type $[(t)_{2N'+1}f1(o)_{n'} f1(t)_{2N''+1}f2(o)_{n''} f2]$. Among the 11 molecular layers in the $22H$ cell, six are f layers ($f1$, $f2$, $f1$, $f1$, $f2$, $f2$) which are intermixed with five o and t layers. The sum of the t layers in the cell can only be odd ($2N+1 + 2N'+1 + 2N''+1$ is always an odd number). It follows that zero or two o layers can be present in the complex $22H$ cell:

—when no o layers occur in the $22H$ cell, the complex cell may be constructed of two simple cells: $tf1f2 = tf2f1$ and $tf1f1(t)_3f2f2 = (t)_3f1f1tf2f2$. In this case the possible complex cells may be the following: $tf1f2tf1f1(t)_3f2f2$, $tf1f1tf2f1(t)_3f2f2$, $tf1f1(t)_4f2f1f2f2$, $(t)_2f1f2f1f1(t)_3f2f2$, etc.

—when two o layers occur in the $22H$ cell, the complex cell may be constructed of the following simple cells:

$tf1(o)_2f2$ and $tf1f1tf2f2$
 $tf1f2$ and $tf1(o)_2f1tf2f2$
 $tf1f2$ and $tf1f1tf2(o)_2f2$
 $tf1f2$ and $tf1of1tf2of2$
 $tf1of2$ and $tf1of1tf2f2$
 $tf1of2$ and $tf1f1tf2of2$.

It can be shown that the total number of the $22H$ complex cells constructed of the SII and SIII-2 cells is 27; of these, $(t)_2f1f1tf2(o)_2f2f1f2$ corresponds to the $22H$ polytype of Fig. 5.

From the above examples it follows that the use of the $10.l/10.\bar{l}$ reflexions leads to a standardization of the structural analysis of polytypes, based on sets of diagrams calculated for some typical simple and complex polytypes. From the 19 diagrams already published (Pałosz, 1982a) and the 20 described in the present paper for the CdI_2 polytypes, the diagrams for the simple SI–SIV series can be completed as follows:

SII: $14H_6$, $22H_5$, $38H_2$, $50H_1$;
 SIII-1: $20H_{12}$, $24H_7$, $24H_8$, $28H_5$, $32H_2$, $40H_2$;
 SIII-2: $40H_3$;
 SIII-3: $22H_7$, $26H_5$;
 SIII-4: $12H_7$, $16H_8$, $22H_6$;
 SIV-1: $48R_3$, $72R_2$, $96R_1$, $120R_1$;
 SIV-2: $24R_3$, $84R_4$;
 SIV-3: $54R_2$;
 SIV-4: $54R_1$, $60R_2$.

Taking into account that nearly all the known polytypes of CdI_2 , which do not belong to a single

series, are constructed of one or several cells of the SII series and of only one cell of another series, a set of a few tens of diagrams calculated for typical complex cells may satisfactorily solve the problem of determining the general formula for cells of complex polytypes.

Relative frequency of occurrence of polytypes of groups I–IV and its relation to the type of faulting of CdI₂

Of six types of layers which form the polytypic structure of CdI₂, the *o* and *t* layers represent the basic polytypes 2*H* and 4*H*, respectively; the *f* layers may be divided into two groups: the layers *f*₁ and *f*₂ may be regarded as faults *B*, the layers *f*₄ and *f*₅ as faults *D* (Pałosz, 1983; Pałosz & Przedmojski, 1983). By comparing the polytypes of groups I–IV one can see that in polytypes of groups I and II only faults *B* occur, while the faults *D* occur only in polytypes of groups III and IV (frequently together with faults *B*). So, the frequency of occurrence of polytypes of different groups may be related to the frequency of occurrence of faults *B* and *D* in crystals. This relation allows one to obtain some important information on the conditions of formation of faults in CdI₂ crystals not identifying the structure of polytypes completely.

To find the group to which a polytype belongs, one needs to determine the symmetry of the experimental pattern of the 10.*l* and 10.*l*̄ reflexions. In this way we found the relative number of polytypes of groups I–IV which were grown (i) in the absence of external fields, (ii) in an external electric field and (iii) in an external magnetic field. They are as follows (in %):

	Group	I	II	III	IV
(i)		2	29	36	33
(ii)		1	6	27	66
(iii)		6	26	15	53.

From these data it appears that the polytypes of groups I and II are approximately three times less frequent than the polytypes of groups III and IV. The relative frequency of occurrence of polytypes of groups I–II and III–IV calculated for the polytypes which have been identified completely is quite the opposite: of 87 polytypes identified up to 1980 (Pałosz, 1980) only a third were from groups III and IV. It is clear that the interpretation of the incomplete structural data and the conclusions drawn therefrom concerning the organization of polytypic structures of crystals may be erroneous. This concerns, in particular, the determination of the reasons for the faulting of crystals; as discussed elsewhere (Pałosz & Przedmojski, 1983) the division of faults into *B* and *D* is connected with the different reasons for their formation in crystals. Based on the structural data obtained for polytypes of CdI₂ already identified it was concluded that faults *D* occur in crystals far more rarely than follows from the present work – about six times. It is clear now that faults *D* do not occur only incidentally in CdI₂ crystals as was

suggested earlier (Pałosz, 1980). Also, it cannot be excluded that the true value of the ratio of faults *B* and *D* does not correspond to the value which is valid for polytypes. It should be remembered that there is practically no information on the structure of disordered polytypic modifications of CdI₂. Further studies are necessary to solve this problem uniquely.

It is clear that when studying the structure of polytypic crystals, the structures having simplest construction are first identified. By comparing the formulas possible for the group I and II polytypes with those of groups III and IV one can see that the polytypes of groups I and II are far easier to identify: to determine the structure of a group I or II polytype one needs to consider models which are all modifications of a single formula (SI or SII). In the case of group III and IV polytypes, there are four possible structural series for each group. This is why most of the polytypes of groups I and II and only a small number of polytypes of groups III and IV have been identified until now. The identification of disordered structures is relatively more troublesome than the identification of polytypes and there is practically no information on the construction of disordered CdI₂ structures. Taking this into account one may conclude that the present state of our knowledge on the structure of CdI₂, still incomplete, does not allow for the formulation of general rules governing the polytypism of these crystals.

Polytypes and disordered structures: uniqueness of the structures determined for polytypes

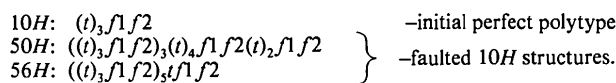
The standard method of polytype identification essentially reduces to the comparison of the reflexion intensities measured experimentally in the X-ray patterns with those calculated for hypothetical, perfectly periodic structures. Frequently, however, several polytypes coexist in one crystal with disorder. In these cases, the precise measurements of the reflexion intensities are troublesome and, in practice, the intensities of subsequent reflexions observed in the X-ray patterns are evaluated only approximately. Such a procedure does not ensure a unique determination of the structure of the polytype under consideration. Below it will be shown that, when some faults are introduced in a perfectly periodic structure of a polytype, the interference patterns of the initial perfect structure and of the faulted structure differ only slightly. This is possible not only when faults are distributed randomly, but also when faults disturb the periodic arrangement of the cells in a well defined way, e.g. periodically. It will be shown that the effect the faults have on the interference pattern of the perfect polytype may be very weak and, in some cases, it may not be revealed on the pattern. Thus, it is possible that, for a given pattern, the structure of the crystal may be classified as a polytype having a certain period, while the real period is quite different or the structure is simply nonperiodic.

Table 4. Intensities of 10.l reflexions calculated for the three polytypes

10H ₁		50H		56H	
l/N	Intensity	l/N	Intensity	l/N	Intensity
2.5	100	2.5	100	2.5	100
		2.520	0.3	2.518	0
		2.540	0.3	2.536	0
		2.560	0.3	2.554	0
		2.580	0.3	2.571	0
				2.589	0.6
2.6	3	2.6	2	2.607	2
		2.620	0.4	2.625	0.2
		2.640	0.4	2.643	0.1
		2.660	0.4	2.661	0.2
		2.680	0.4	2.679	0.6
2.7	24	2.7	26	2.696	21
		2.720	0.4	2.714	1.5
		2.740	0.4	2.732	0.4
		2.760	0.4	2.750	0.3
		2.780	0.4	2.768	0.4
				2.786	1.5
2.8	26	2.8	27	2.804	23
		2.820	0.4	2.821	0.6
		2.840	0.4	2.839	0.2
		2.860	0.4	2.857	0.2
		2.880	0.4	2.875	0.3
2.9	4	2.9	3	2.893	3
		2.920	0.4	2.911	0.1
		2.940	0.4	2.929	0
		2.960	0.4	2.946	0
		2.980	0.4	2.964	0
				2.982	0
3.0	24	3.0	24	3.0	24

Determination of the period of the structure

In Table 4 we present a comparison of the intensities of the 10.l reflexions calculated for three structural models of the unit cell:



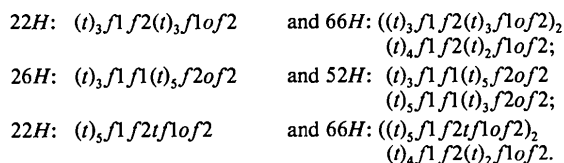
50H may be regarded as a faulted 10H in which t layers in two of each of the five 10H cells were rearranged, and now they occur in the sequences $(t)_4$ and $(t)_2$, instead of two $(t)_3$ sequences. 56H may also be regarded as a faulted 10H where, in one of six 10H cells, a single t layer occurs instead of the sequence $(t)_3$.

From Table 4 it is seen that in the case of 50H, as well as the reflexions which coincide with those of 10H (at $|l/N| = 2.5, 2.6, 2.7, 2.8, 2.9$ and 3.0), a number of additional reflexions should appear in the pattern. These 'extra' reflexions, connected with faulting of 10H, have very small intensities, however: these are always more than two orders of magnitude smaller than those for 10H reflexions. This means that, in practice, these weak reflexions may not be discerned from the background always present in X-ray patterns. The second effect faulting has on the pattern of 10H is the change of the relative intensities of the reflexions corresponding to 10H. These changes, however, are

very small. To observe this effect very precise measurements of intensities would be necessary.

A similar effect may be observed for 56H. In this case, however, the strongest reflexions of 56H, which correspond to the reflexions of 10H, are shifted a little from the $|l/N|$ positions, at which the 10H reflexions occur. The magnitude of these shifts is, however, very small and comparable with the experimental broadening of reflexions, always observed in X-ray patterns. This means that a shift of reflexions connected with a small faulting may be easily missed during the usual analysis of the pattern.

The calculations of the hypothetical patterns of perfect and faulted structures were performed for other structural models, e.g.:

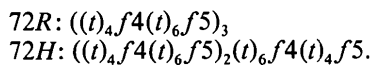


The effect of faulting observed for the diagrams calculated for these structures was similar to that described above for 10H and for 50H and 56H.

From these examples it follows that a small degree of faulting of a multilayer polytype may cause changes of the interference pattern of the perfect polytype which are so small that they cannot be observed on the α -axis oscillation photographs, which are usually used for identification of polytypes.

Identification of hexagonal and rhombohedral polytype cells

Polytypes are usually divided into hexagonal and rhombohedral on the basis of the X-ray patterns of the 10.l and 10.l̄ reflexions. It can be shown, however, that in some cases similar distributions of the 10.l/10.l̄ reflexions are possible for rhombohedral and hexagonal structures. Thus, the experimental subdivision of these polytypes into hexagonal and rhombohedral is not unique. In Table 5 we present the intensities of the 10.l reflexions calculated for two models of unit cell:



In the case of a perfect rhombohedral structure, the lattice period c is three times larger than the period calculated as the number of layers in a unit sequence [here $(t)_4 f_4 (t)_6 f_5$] multiplied by the interlayer distance. In the case of hexagonal structures the lattice period c is the same as that calculated for the unit sequence. From the two models considered here, 72R corresponds to the perfect rhombohedral polytype, and 72H represents the hexagonal structure. From Table 5 it follows that the 10.l/10.l̄ diagrams are nearly identical: very weak reflexions appear for 72H, in addition to the strong reflexions which correspond to the rhombohedral 72R

Table 5. Intensities of 10.l reflexions calculated for two polytypes

72R: $((t)_6f4(t)_4f5)_3$		72H: $((t)_6f4(t)_4f5)_2(t)_4f4(t)_6f5$			
<i>l/N</i>	72R intensity	72H intensity	<i>l/N</i>	72R intensity	72H intensity
2.486	1000	1000	2.764	0	0
2.500	0	0	2.778	9	9
2.514	0	0	2.792	0	0
2.528	9	8	2.806	0	0
2.542	0	0	2.819	4	3
2.556	0	0	2.833	0	0
2.569	4	4	2.847	0	0
2.583	0	0	2.861	1	1
2.597	0	0	2.875	0	0.1
2.611	2	2	2.889	0	0.1
2.625	0	0	2.903	1	1
2.639	0	0	2.917	0	0.1
2.653	2	2	2.931	0	0.1
2.667	0	0	2.944	6	5
2.681	0	0	2.958	0	0.2
2.694	4	4	2.972	0	0.2
2.708	0	0	2.986	1	0.2
2.722	0	0	3.000	0	0.2
2.736	69	69	3.014	0	0.3
2.750	0	0	3.028	22	21

polytype. These extra reflexions observed for 72H are three orders of magnitude smaller than the strong reflexions corresponding to 72R. Thus, in practice, they are not discernible from background in the X-ray patterns.

From Table 3 it is seen that in the polytype cells of the SIII series with hexagonal structures the *t* layers occur in odd sequences, while these layers occur in even sequences in the corresponding SIV cells of the rhombohedral polytypes (SIII-1 corresponds to SIV-1, etc.). The 10.l/10.l̄ diagrams of these two series differ very strongly (see Figs. 1–20), and the difference is connected with the ordering of the *t* layers in the structure into odd and even sequences, $(t)_{2N+1}$ and $(t)_{2N}$, and not directly with the symmetry of the unit cell. By analyzing the distribution of the reflexion intensities in

the experimental diagrams one may determine the number of the *t* layers which may occur in odd or in even sequences. Because of this, it seems to be more appropriate to classify the polytypic structure into hexagonal type [sequences $(t)_{2N+1}$] or the rhombohedral type [sequences $(t)_{2N}$]. It should be noted, however, that this classification is not always unique, because a complex cell, being a combination of one rhombohedral cell with hexagonal cells, is always rhombohedral (Palosz, 1982).

From the above discussion one may conclude that, by identifying polytypes with the standard procedures for structural analysis of polytypic crystals, the structures identified cannot be uniquely classified into 'pure' and 'faulted' polytypes. Both the lattice period and the stacking of the layers in a period, always determined for polytypes, may be regarded as parameters characterizing the average polytypic structure of the crystal.

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