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Structures of 20 New Polytypes of Cadmium Iodide

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Abstract. The structures of 20 new polytypes of CdI_2 obtained from aqueous and from alcoholic solutions are presented: $10H_6$: $f5tf4f2f1$; $14H_7$: $f5tf1of1f2f1$; $14H_8$: $f5tf1f1(t)_3$; $18H_9$: $f5tf1of1f2f1(t)_2$; $18H_{10}$: $tf2f1f2(o)_2f1f2f1$; $18H_{11}$: $tf2of1tf2(o)_2f1$; $18H_{12}$: $f4tf2of2f1f2(t)_2$; $18H_{13}$: $tf1of1f2f1f2of2$; $26H_6$: $tf1f1(t)_5f2f1tf2f2$; $28H_8$: $(f5f4)_6(t)_2$; $30R_5$: $f5f4f2f2f4$; $36R_5$: $f5f4(t)_4$; $36R_6$: $f5f1f1f2f1t$; $36R_7$: $(f5f4)_2(t)_2$; $42R_3$: $f5f4f2f1(t)_3$; $48R_4$: $f5f4(t)_6$; $48R_5$: $(t)_2f2f2(t)_2f1f1$; $54R_5$: $f5f1(o)_2f1tf2of1$; $54R_6$: $f5f1of1f2f1f2of1$; $54R_7$: $f5f4(t)_2f2f1(t)_3$.

Experimental. The crystals of CdI_2 were grown from aqueous and from alcoholic solutions by slow isothermal evaporation (Gierlotka & Pałosz, 1983). They were examined by X-rays in a cylindrical camera with a 43 mm radius and 0·7 mm collimator. The oscillation method was used with the angle between the incident beam (Ni-filtered Cu K radiation) and the c axis varying between 21·5 and 36·5°. Previously we used a-axis oscillations (with $10.l$ and $10.\bar{l}$ reflexions; Pałosz, 1982). Now we are using a^* oscillations in which $10.l$ and $1\bar{1}.l$ reflexions are registered on the patterns (Pałosz & Gierlotka, 1984). Here the parts $(+l)$ and $(-l)$ of the intensity diagrams, Fig. 1, correspond to the reflexions $10.l$ and $1\bar{1}.l$, respectively. The method used here for the determination of the structures of 20 new polytypes of CdI_2 is similar to that described previously for the determination of 72 polytypes (Pałosz, 1982, 1983*a*,*b*; Pałosz & Gierlotka, 1984). Here we present some remarks concerning elaboration of X-ray data: the reflexion intensities, calculated as the square of the structure factor, were multiplied by the Lorentz–polarization factor; the temperature and the absorption coefficients were ignored in the calculations. The scaling of the experimental patterns is troublesome and involves several factors:

For pure polytypes the $K\alpha_1$ and $K\alpha_2$ lines of the Ni-filtered radiation are well separated on the patterns and only lines $K\alpha_1$ or $K\alpha_2$ may be measured.

When disorder occurs in a crystal the overlapping lines $K\alpha_1$ and $K\alpha_2$ form relatively broad maxima on the patterns.

The reflexions become more broadened with an increase of the Bragg angle. Because of this, integral intensities (the peak of the reflexion multiplied by its half-width) should be calculated. It should be noted that the broadening of the reflexions may change from crystal to crystal and the scaling should be performed for each pattern separately.

To establish relative intensities of weak and strong reflexions several patterns obtained for different exposure periods may be necessary.

Frequently, polytypes occur in coexistence with the basic structures $2H$ or $4H$ and the determination of exact values of the intensities may appear impossible, see Fig. 3 $14H_8 + 2H$, Fig. 5 $18H_{10} + 2H$, Fig. 10 $28H_8 + 4H$. We stress that our method of polytype identification is based on the comparison of the experimental and theoretical intensity diagrams. The analysis of the symmetry and of some characteristic regularities in the distribution of the reflexion intensities in the diagrams does not need, in fact, precise measurements of individual reflexions. Accidental errors always possible in the measurements cannot change the shape of a diagram to an appreciable extent.

Discussion. We present the structures of 20 new polytypes of CdI_2. The growth conditions of these polytypes are given in Table 1.* In this table the polytype cells are described in the t–o–f notation. The Zhdanov sequences corresponding to this notation are given in Figs. 1–20. The figures present the diagrams which compare the measured intensities of $10.l$ and $1\bar{1}.l$ reflexions with those calculated theoretically for the structural models. The series to which the polytypes given in Table 1 belong correspond to the general formulae of the t–o–f sequences classified by Pałosz (1982). As discussed elsewhere (Pałosz, 1983*a*), the polytypes may have simple cells corresponding to single series or they may have complex cells constructed from one cell of the series SI, SIII or SIV and one or several

*To apply polytypism a connexion between structure (number of layers in a period, specific stackings of layers *etc.*) and the conditions of growth of the crystals should be determined. The problem is extremely difficult because for this one should identify the structure of thousands of crystals grown in different conditions. Nevertheless, after determination of the structure of a few hundred polytypes we found some empirical semiquantitative relations describing the effect of some growth factors on the structure of polytypes of CdI_2: Pałosz & Przedmojski (1982), Gierlotka & Pałosz (1983), Pałosz & Przedmojski (1984).

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cells of the SII series. In the light of the present results it does not appear to be the rule. For example, the hexagonal polytype $28H_8$ has a cell made up of six rhombohedral cells while the unit cell of the rhombohedral polytype $30R_5$ is the combination of two different rhombohedral-type cells. It should be noted that all the known polytypes of CdI_2 consist of several simple sequences (*cf.* Pałosz, 1982); however, a complete classification of all the complex polytype cells occurring in real crystals seems to be impossible.

Table 1. *Structure and growth conditions of* 20 *new polytypes of* CdI_2

Ramsdell symbol*	*t–o–f* notation	Solvent†	Temperature of growth (K)	Series
Hexagonal polytypes				
$10H_6$	*f5tf4f2f1*	ia	298	SII + SIII-1
$14H_7$	*f5tf1of1f2f1*	ia	298	SII + SIII-4
$14H_8$	*f5tf1f1*$(t)_3$	aq + et = 1:1	323	SIII-4
$18H_9$	*f5tf1of1f2f1*$(t)_2$	aq	278	SII + SIII-4
$18H_{10}$	*tf2f1f2*$(o)_2$*f1f2f1*	pr	298	SI + SII
$18H_{11}$	*tf2of1tf2*$(o]_2$*f1*	ia + pr = 1:1	298	SII + SII
$18H_{12}$	*f4tf2of2f1f2*$(t)_2$	ib	298	SII + SIII-3
$18H_{13}$	*tf1of1f2f1f2of2*	ia	298	SII + SIII-2
$26H_6$	*tf1f1*$(t)_5$*f2f1tf2f2*	aq	298	SII + SIII-2
$28H_8$	$(f5f4)_6(t)_2$	aq + pr = 1:1	298	$(S\text{IV-1})_6$
Rhombohedral polytypes				
$30R_5$	*f5f4f2f2f4*	ia	298	SIV-1 + SIV-3
$36R_5$	*f5f4*$(t)_4$	ia	298	SIV-1
$36R_6$	*f5f1f1f2f1t*	ia + pr = 1:1	298	SII + SIV-4
$36R_7$	$(f5f4)_2(t)_2$	ia	298	SIV-1 + SIV-1
$42R_3$	*f5f4f2f1*$(t)_3$	ia	298	SII + SIV-1
$48R_4$	*f5f4*$(t)_6$	aq + ib = 1:1	298	SIV-1
$48R_5$	$(t)_2$*f2f2*$(t)_2$*f1f1*	aq + et = 1:1	323	SIV-2
$54R_5$	*f5f1*$(o)_2$*f1tf2of1*	ia + pr = 1:1	298	SII + SIV-4
$54R_6$	*f5f1of1f2f1f2of1*	ia	298	SI + SIV-4
$54R_7$	*f5f4*$(t)_2$*f2f1*$(t)_3$	aq + pr = 1:1	298	SII + SIV-1

* The indices of Ramsdell symbols are after Pałosz (1982, 1983*a,b*) and Gierlotka & Pałosz (1983).

† aq = water; pr = *n*-propyl alcohol, $CH_3CH_2CH_2OH$; ib = isobutyl alcohol (2-methylpropanol), $(CH_3)_2CHCH_2OH$; et = ethanol, CH_3CH_2OH; ia = isoamyl alcohol (3-methyl-1-butanol), $(CH_3)_2CHCH_2CH_2OH$.

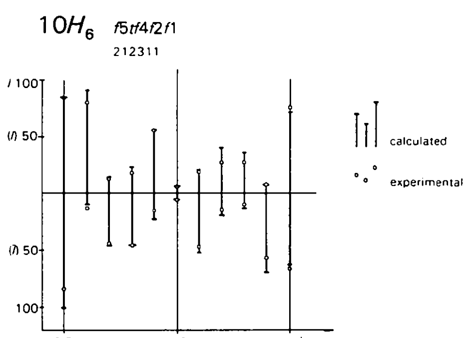


Fig. 1. Diagram of intensities of reflexions 10.*l* and 1$\bar{1}$.*l* measured experimentally and calculated theoretically for the $10H_6$ CdI_2 polytype. Figs. 2–20 show similar diagrams for other polytypes of CdI_2. *Note:* Only reflexion intensities larger than 2 of 100 are marked in the figures.

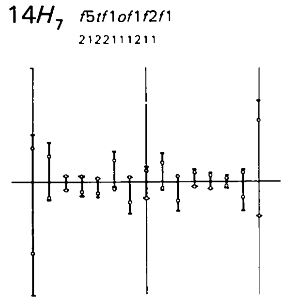


Fig. 2

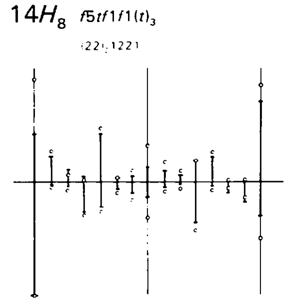
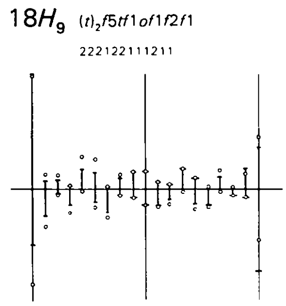


Fig. 3



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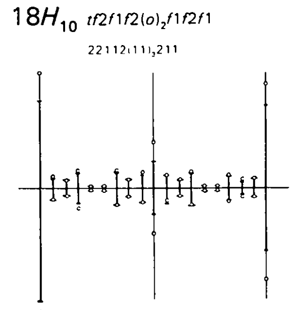
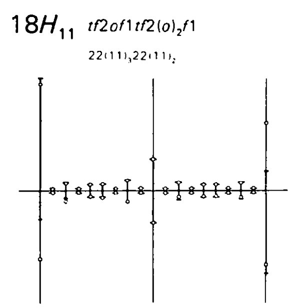


Fig. 5



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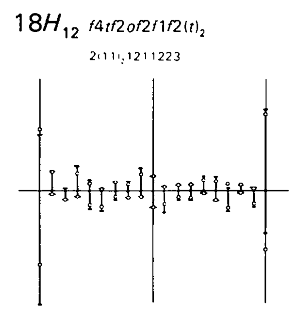
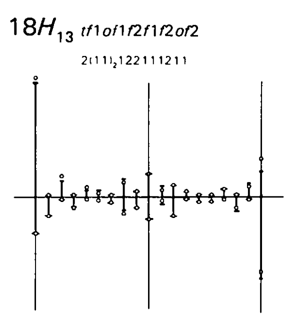


Fig. 7



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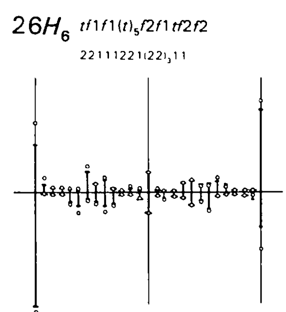

Fig. 9

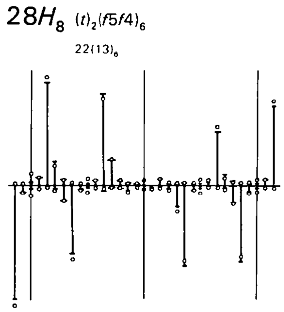

Fig. 10

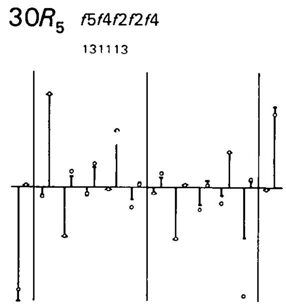

Fig. 11

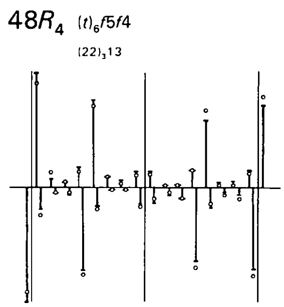

Fig. 16

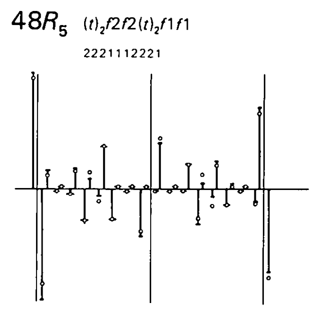

Fig. 17

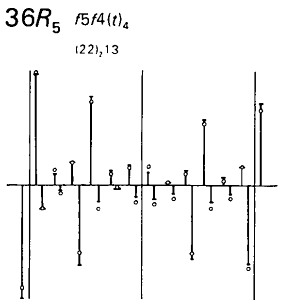

Fig. 12

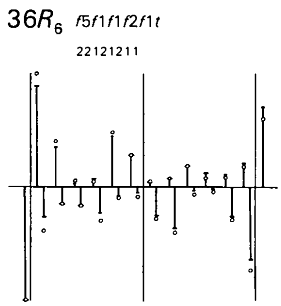

Fig. 13

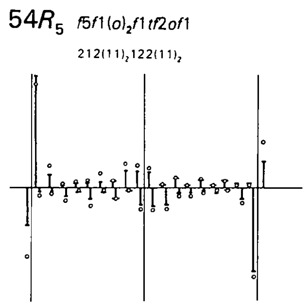

Fig. 18

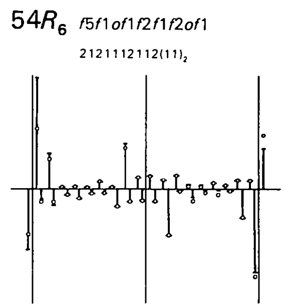

Fig. 19

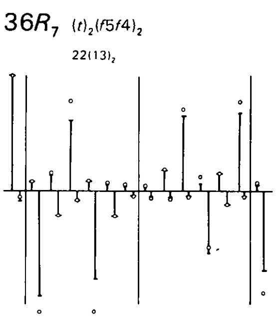

Fig.14

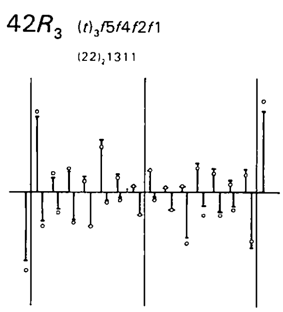

Fig. 15

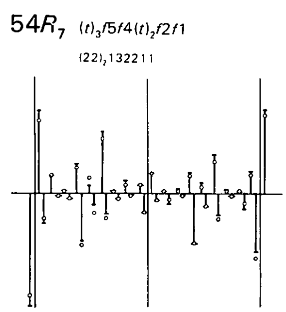

Fig. 20

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