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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 solution are presented: $18H_8$: $f5tf1f1f2(o)_3f1$; $20H_{13}$: $(t)_3f5tf1f1tf2f1$; $28H_6$: $(t)_7f1f2(t)_3f1f2$; $28H_7$: $(t)_3f1f2(t)_2f1of2(t)_2f1f2$; $30H_6$: $tf5(t)_2f1f2(t)_6f1of1$; $34H_5$: $(t)_{15}f1f2$; $34H_6$: $(t)_3f1of1tf2of2f1of2(t)_2f1f2$; $36H_2$: $(t)_8f1f2(t)_6f1f2$; $36H_3$: $tf5tf4(t)_9f2f1tf2f1$; $60R_3$: $(t)_3f5f1f1(t)_2f2f1$; $66R_3$: $(t)_4f4(t)_2f2(o)_2f2$; $72R_3$: $(t)_4f5f1f1(t)_2f5f1f1$; $78R_1$: $(t)_8f5f1(o)_2f1$; $84R_5$: $(t)_6f5(t)_2f4tf5tf4$; $90R_1$: $(t)_4f5f1f1(t)_3f2f1tf2f1$; $96R_2$: $(t)_{12}f5(t)_2f4$; $102R_1$: $(t)_{10}f4(t)_4f2f2$; $102R_2$: $(t)_6f5f1f1(t)_3f5tf1of1$; $108R_1$: $(t)_4f2f2f1(o)_4f1(tf2f1)_2$; $120R_2$: $(t)_{10}f5(t)_4f4tf5tf4$. Similarities and differences between hexagonal and rhombohedral polytypes are discussed.

Experimental. The crystals of CdI_2 were grown in the presence of external electric and magnetic fields (Pałosz & Przedmojski, 1982*a*,*b*), and in the absence of external fields in air (Pałosz, 1981), from solution by slow isothermal evaporation. They were examined by X-rays in a cylindrical camera with a 43 mm radius and 0·5 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 19 and 34° (Pałosz & Przedmojski, 1980). The intensities of $10.l$ and $10.\bar{l}$ reflexions were measured on the patterns and compared with the values computed from the formula commonly used for CdI_2 crystals (Jain & Trigunayat, 1978). The diagrams presented in Figs. 1–20 compare the measured and calculated intensities for $10.l$ and $10.\bar{l}$ reflexions in the range $2{\cdot}5 \leq |l/N| \leq 3{\cdot}5$, where N is the number of iodine layers in a polytype cell.

To identify the polytypes the molecular-layer notations *xyz* and *t–o–f* (Pałosz & Przedmojski, 1980; Pałosz, 1980) are used. In these two notations the rules for constructing the Zhdanov sequences of MX_2 polytypes found earlier by several authors – Verma & Krishna (1966), Dubey (1975), Jain & Trigunayat (1978), Wahab & Trigunayat (1980), Chadha (1981) – were rewritten in a simpler form, and some new rules were found (Pałosz, 1982, 1983*a*).

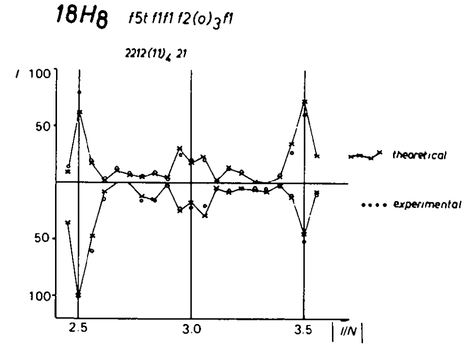


Fig. 1. Diagram of intensities of reflexions $10.l$ and $10.\bar{l}$ measured experimentally and calculated theoretically for the $18H_8$ CdI_2 polytype. Figs. 2–20 show similar diagrams for other polytypes of CdI_2.

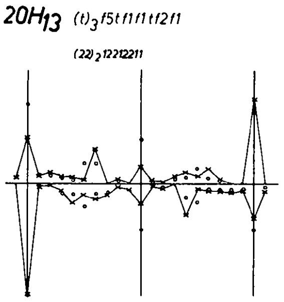
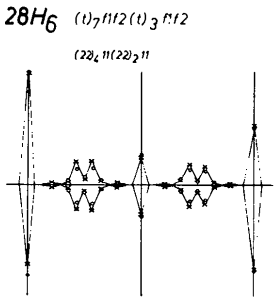


Fig. 2.



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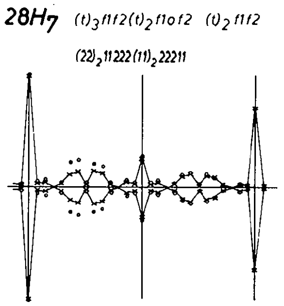

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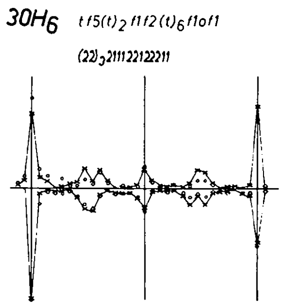

Fig. 5.

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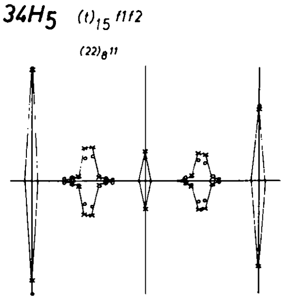

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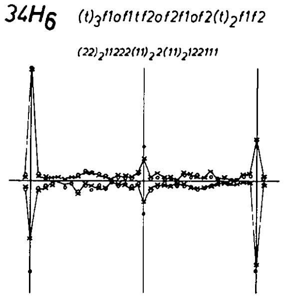

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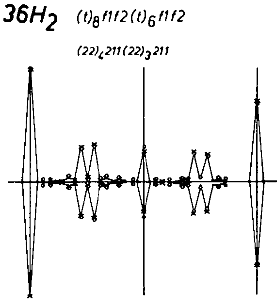

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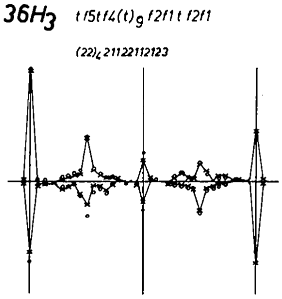

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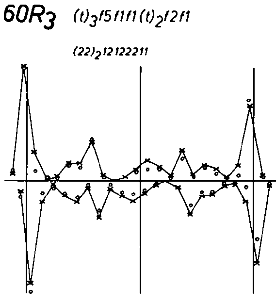

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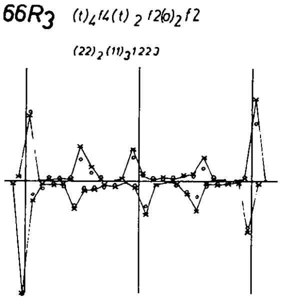

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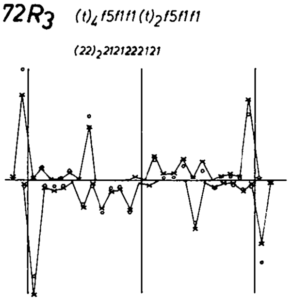

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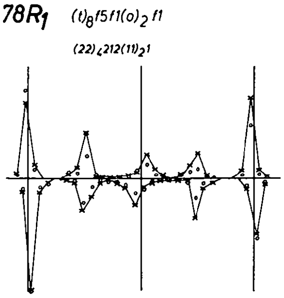

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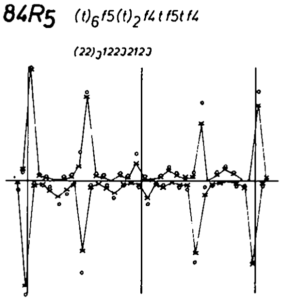

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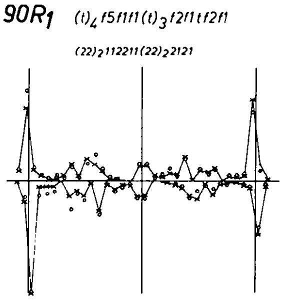

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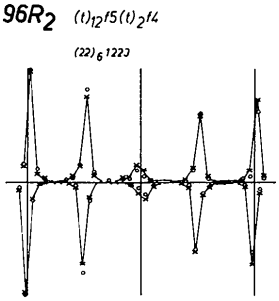

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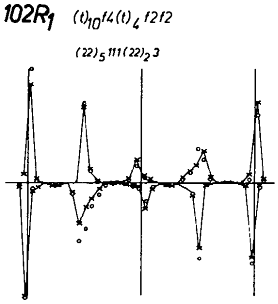


Fig. 17.

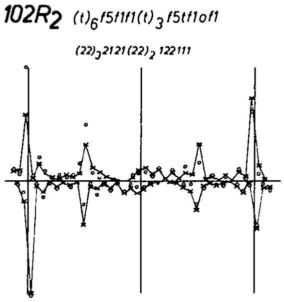
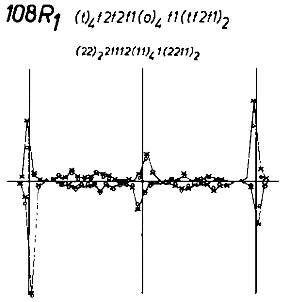


Fig. 18.



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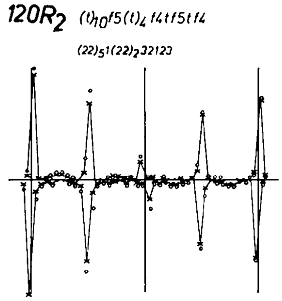

Fig. 20.

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

Ramsdell symbol*	*t–o–f* notation of a cell	Solvent H_2O: C_2H_5OH	Temperature of growth (K)	External field	Series
Hexagonal polytypes					
$18H_8$	$f5tf1f1f2(o)_3f1$	1:0	298	*H*	*S*III-4/*S*II-1
$20H_{13}$	$(t)_3f5tf1f1tf2f1$	1:0	298	*H*	*S*III-4/*S*II-1
$28H_6$	$(t)_7f1f2(t)_3f1f2$	1:1	298	*H*	$(S\text{II-1})_2$
$28H_7$	$(t)_3f1f2(t)_2f1of2(t)_2f1f2$	1:1	298	*H*	*S*II-1/*S*I-1
$30H_6$	$tf5(t)_2f1f2(t)_6f1of1$	1:0	298	*E*	*S*III-4/*S*II-1
$34H_5$	$(t)_{15}f1f2$	1:1	298	—	*S*II-1
$34H_6$	$(t)_3f1of1tf2of2f1of2(t)_2f1f2$	1:1	298	*H*	*S*III-2/*S*II-1
$36H_2$	$(t)_8f1f2(t)_6f1f2$	1:1	323	*E*	SI-1
$36H_3$	$tf5tf4(t)_9f2f1tf2f1$	1:0	298	*E*	*S*III-1/*S*II-1
Rhombohedral polytypes					
$60R_3$	$(t)_3f5f1f1(t)_2f2f1$	1:0	323	*E*	*S*IV-4/*S*II-1
$66R_3$	$(t)_4f4(t)_2f2(o)_2f2$	1:0	278	*H*	*S*IV-3
$72R_3$	$(t)_4f5f1f1(t)_2f5f1f1$	1:0	298	*E*	$(S\text{IV-4})_2$
$78R_1$	$(t)_8f5f1(o)_2f1$	1:0	278	*H*	*S*IV-4
$84R_5$	$(t)_6f5(t)_2f4tf5tf4$	3:1	298	—	*S*IV-1/*S*III-1
$90R_1$	$(t)_4f5f1f1(t)_3f2f1tf2f1$	1:1	308	*E*	*S*IV-4/*S*II-1
$96R_2$	$(t)_{12}f5(t)_2f4$	1:0	298	—	*S*IV-1
$102R_1$	$(t)_{10}f4(t)_4f2f2$	1:1	308	*E*	*S*IV-3
$102R_2$	$(t)_6f5f1f1(t)_3f5tf1of1$	1:0	278	*H*	*S*IV-4/*S*III-4
$108R_1$	$(t)_4f2f2f1(o)_4f1(tf2f1)_2$	1:1	298	*H*	*S*IV-2/*S*II-1
$120R_2$	$(t)_{10}f5(t)_4f4tf5tf4$	1:1	323	-	*S*IV-1/*S*III-1

* The indices of Ramsdell symbols are after Pałosz (1980, 1982, 1983*a*).

Discussion. Above we present the structures of 20 new polytypes of CdI_2. The growth conditions are given in Table 1. In this table their structures are presented in the *t–o–f* notation; the Zhdanov sequences corresponding to this notation are given in Figs. 1–20. The series to which the polytypes belong are also given (*cf.* Pałosz, 1982). Of these 20 new polytypes only six were 'pure': $18H_8$, $28H_7$, $60R_3$, $90R_1$, $102R_2$ and $120R_2$; four were observed in coexistence with the common polytype $4H$: $20H_{13}$, $84R_5$, $96R_2$ and $102R_1$; five occurred with $4H$ and a small amount of disorder: $28H_6$, $36H_2$, $36H_3$, $66R_3$ and $78R_1$; in five cases hexagonal polytypes occurred together with rhombohedral ones: $30H_6$ and $90R$, $34H_5$ and $102R$, $72R_3$ and $12H$ or $24H$, $34H_6$ and $102R$, $108R_1$ and $36H$. Of the hexagonal and rhombohedral pairs listed above, only one was identified; the reflexions of the second polytype of a pair observed were always very weak, giving no possibility for a unique identification. The coexistence of different structures on one basal face of a crystal does not allow a precise measurement of the reflexion intensities. This is why, in some of the diagrams presented in Figs. 1–20, discrepancies between the experimental and theoretical values of the intensities may be seen.

The mechanism of the simultaneous formation of hexagonal and rhombohedral polytypes was discussed several times in the literature from the point of view of the dislocation growth of crystals: Uma Shankar Ram (1975), Agrawal (1979, 1980). It was suggested that a given hexagonal polytype can transform into its common rhombohedral polytype (having a cell three times greater than the hexagonal one) because of twinning with orientation $[11.n]/(11.6/n)$ in the intermediate region between them (Agrawal, 1980). As discussed elsewhere (Pałosz, 1983*b*), the hexagonal and rhombohedral polytypes may be considered to be two modifications of a single structure, such that the numbers of layers occurring between sequential faults are different. In particular, the *t* layers occur in the odd or in the even sequences for hexagonal and rhombohedral polytypes, respectively (Pałosz, 1982, 1983*b*). Both when one has a dislocation-controlled transformation of hexagonal to rhombohedral polytypes and when one assumes that these two types of structure form directly during the growth of a crystal, independently of each other as equivalent structures, the rhombohedral polytypes should have cells three times larger than the hexagonal ones. The present investigations do not indicate whether the rhombohedral polytypes form in the crystals through a transformation of hexagonal structures or whether they form simultaneously as equivalent structures. The unique identification of the coexisting structures is necessary to solve this problem and this is now being investigated.

The growth of polytypes under controlled conditions reveals a correlation between the growth parameters and the polytypic structure of the crystals. Using the results of the analysis of about 350 polytypes the effect of temperature and of the external fields *E* and *H* on the type of faulting and on the construction of polytype cells of CdI_2 was analysed. The results of such an analysis are presented by Pałosz & Przedmojski (1982*c*, 1983).

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Orthorhombic Uranium(IV) Molybdenum(VI) Oxide, UMo_2O_8*

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Abstract. $M_r = 557{\cdot}8$, orthorhombic, *Pban*, $a = 20{\cdot}076\ (4)$, $b = 7{\cdot}323\ (1)$, $c = 4{\cdot}1164\ (6)$ Å, $V = 605{\cdot}2$ Å^2, $Z = 4$, $D_m = 6{\cdot}08\ (6)$, $D_x = 6{\cdot}12$ Mg m^{-3} Mo $K\alpha$, $\lambda = 0{\cdot}70930$ Å, $\mu = 367$ cm^{-1}, $F(000) = 960$, $T = 298$ K, $R = 0{\cdot}049$ for 1347 reflections. The structure consists of layers of oxide-bridged uranium and molybdenum atoms connected by infinite interlayer U—O—U and Mo—O—Mo chains. The uranium atoms have pentagonal bipyramidal coordination [U—O equatorial = 2·202 (6)–2·394 (8) Å, U—O axial = 2·0584 (3) Å]; the molybdenum atoms are in a highly distorted octahedral [Mo—O = 1·684 (7)–2·432 (7) Å] arrangement. The presence of oxide ions not connected to molybdenum suggests that this structure is better formulated as a double oxide–molybdate than as a true molybdate.

Introduction. Processing of spent Zr-clad nuclear-fuel elements can result in undesirable insoluble residues containing zirconium, plutonium and fission-product molybdenum. Zirconium and molybdenum are thought to be present in these residues as molybdate or polymeric molybdic acid species. Losses of plutonium to insoluble residues could occur because of its association with molybdenum-containing species (Penneman, Haire & Lloyd, 1980). Little reliable structural information is available on the possible plutonium–molybdenum compounds formed under nuclear-fuel reprocessing conditions. A plutonium compound claimed to be orthorhombic and isomorphous with the mineral sedovite, $U(MoO_4)_2$, has been obtained from aqueous solutions (Penneman, Haire & Lloyd, 1980). However, a single-crystal analysis has not been reported for either the Pu or U forms.

The uranium molybdate binary oxide system was first studied using powder data by Kovba & Trunov (1964). Later, Pailleret (1967) published a single-crystal structure for an orthorhombic UMo_2O_8 phase different from sedovite and also different from an orthorhombic Th compound reported by Tabuteau, Pagès & Freundlich, 1972), but the high final *R* value (0·16) suggested that further work was needed. A subsequent report by Kovba (1971) described another single-crystal structure study of this phase but again the report was exceedingly sketchy (an *R* factor was not even reported).

We have succeeded in preparing crystals of this orthorhombic UMo_2O_8 phase by skull melting (Herrick & Behrens, 1981) and, because of its relevance to the above-mentioned plutonium compounds, have carried out a definitive single-crystal X-ray diffraction study of this phase.

Experimental. D_m by flotation. Precession photographs revealed Laue symmetry and systematic absences consistent with *Pban*, crystal 80 × 80 × 180 μm, automated Picker diffractometer, cell refinement with eleven reflections, $2\theta > 55°$, quadrant of data $h, \pm k, l$ collected,

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