inférieure à 90° lorsque les composés possèdent les groupes spatiaux $R3m$ ou $R3c$ (Megaw & Darlington, 1975).

La valeur de la distance Al—O trouvée égale à 1,892 Å, permet de calculer le paramètre a d'une maille cubique perovskite hypothétique: $a = 2d(\text{Al—O}) = 3,784$ Å. On en déduit dans ce cas la distance Nd—O $= a/\sqrt{2} = 2,676$ Å dans un cubo-octaèdre NdO$_{12}$ régulier ainsi qui les douze distances O—O dans l'octaèdre AlO$_6$, égales aussi à 2,676 Å. La déformation de la structure conduit à observer deux sortes de distances O—O. La première, égale à 2,696 Å, concerne les atomes situés dans des plans perpendiculaires à l'axe [111]; la seconde, égale à 2,655 Å et relative à des distances entre ces plans, est plus courte et caractérise l'aplatissement de l'octaèdre.

Le cubo-octaèdre NdO$_{12}$ est également déformé et on observe trois types de liaisons Nd—O. Perpendiculairement à l'axe [111], il existe six oxygène qui forment avec le néodyme un plan. De plus, trois oxygène sont situés dans un plan supérieur et trois autres dans un plan inférieur. La distance entre Nd et ces six derniers oxygène est égale à 2,656 Å. Dans le plan médian, on observe trois distances Nd—O plus courtes $= 2,406$ Å et trois oxygène significativement plus éloignés $= 2,914$ Å. Il en résulte que la coordinence du néodyme tend vers neuf, valeur qu'on retrouve dans le composé Nd$_2$AlO$_3$N

(Marchand, Pastuszak, Laurent & Roult, 1982) qui possède une structure de type K$_2$NiF$_4$, donc apparentée à la structure perovskite.

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Structures of Five Large-Period Polytypes of Cadmium Iodide

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Abstract. The crystal structures of the five new large-period polytypes $16H_{10}$, $18H_7$, $24H_{10}$, $30H_6$ and $32H_3$ of cadmium iodide have been determined. The structures are represented as 2112 $(11)_5$, 222112 $(11)_4$, $(22)_3(11)_31221$, $22(11)_522(11)_6$ and $(22)_6112211$ in Zhdanov notation. They all belong to the space group $P3m1$.

Introduction. The phenomenon of polytypism exhibited by a large number of substances has attracted solid-state physicists because different polytypic modifications of a substance possess different semiconducting, dielectric, optical and photovoltaic properties, which depend upon the crystal structures of the various modifications. With the determination of the complete crystal structures for a large number of polytypes of prominent polytypic compounds like silicon carbide and cadmium iodide, a vast amount of precise structural data has accumulated, which has already found use in several ways in understanding the formation of polytypes and the phase transitions observed in them. From the analysis of the known crystal structures, the existence of structural series was pointed out by Mitchell (1955, 1956, 1957) in the polytypes of SiC and CdI$_2$, *viz* the series $[(33)_n32]_3$ and $[(22)_n11]$, respectively, the implications of which were discussed later by Trigunayat (1971). The structural data available on the polytypes of SiC, ZnS and CdI$_2$ have been employed by Srinivasan & Parthasarthi (1973) for a statistical analysis of Zhdanov sequences, to yield semi-empirical, semi-theoretical rules regarding the occurrence and distribution of polytypes. Similarly,

based on the examination of similar data on CdI_2 polytypes, Jain & Trigunayat (1977a,b) and recently Wahab & Trigunayat (1980b) have formulated empirical guidelines, which can help to reduce the number of probable structures for a given polytype drastically and thus considerably facilitate future crystal structure determinations. From the crystal structure data on the polytypes of SiC, ZnS and CdI_2, Srinivasan & Parthasarthi (1974) have evaluated the relative proportions of cubic and hexagonal packing in these polytypes and have concluded that they are governed by changes in internal energy, arising from interaction at the atomic level. Similarly, making use of the vast amount of structural data available on the same compounds, Wahab & Trigunayat (1980a) have quantitatively estimated the stacking-fault energies and entropy contributions and hence the specific surface free energies of the faults.

So far nearly 289 polytypes of CdI_2 have been reported, of which complete crystal structures of more than 132 polytypes have been worked out (Wahab & Trigunayat, 1980b; Chadha, 1982; Pałosz, 1982, 1983). In the course of a recent comprehensive study of the influence of impurities on the growth of CdI_2 polytypes, we have discovered several new polytypes. It has been possible to work out complete crystal structures of five of them. The c dimensions of these polytypes are relatively large, ranging from 55·68 to 109·38 Å.

Experimental. The crystals were grown by evaporation of an aqueous solution of reagent-grade cadmium iodide. Details of growth procedure, the selection of crystals and X-ray methods employed are available elsewhere (e.g. Chadha & Trigunayat, 1967). The method of structure determination, together with various refinements, has been described earlier by Jain & Trigunayat (1978), Wahab & Trigunayat (1980b) and Chadha (1980).

Discussion. Complete crystal structures of five new CdI_2 polytypes, all hexagonal, have been determined. The X-ray oscillation photographs of the polytypes are reproduced in Fig. 1 and the calculated and observed intensity values of their 10.l reflections are listed in Tables 1 to 5.* To ensure uniformity of comparison in these tables, the calculated intensity values have been so adjusted that the reflection $l = 5n/2$ has the value 1000 units for each polytype, where n is the number of layers in the unit cell. The crystal structures, finally arrived at on the basis of obtaining a satisfactory agreement between calculated and observed intensities for 10.l reflections, are given in Table 6.

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* Tables 1–5 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38365 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
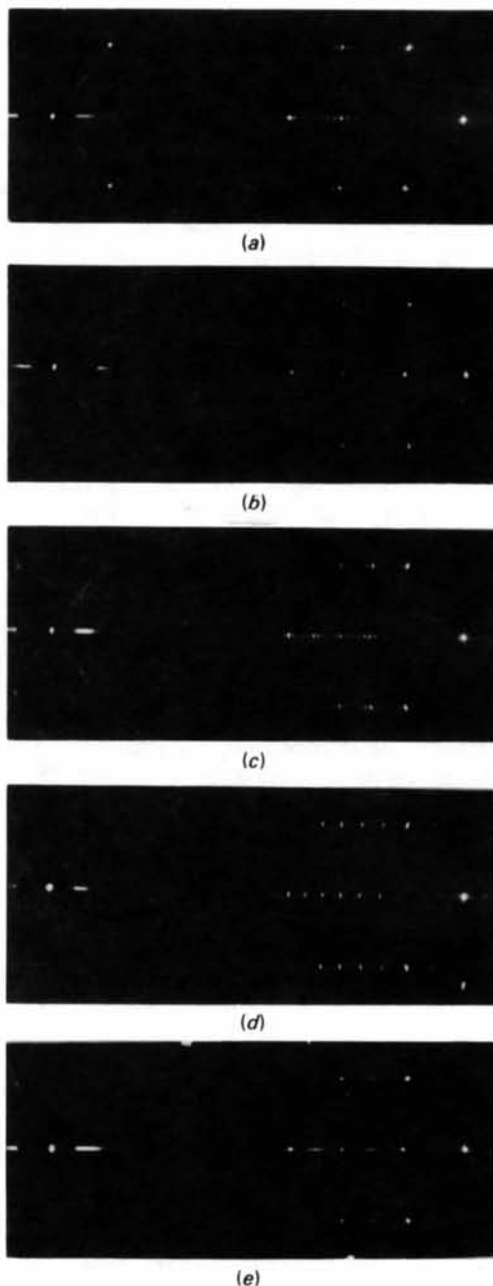

(a)

(b)

(c)

(d)

(e)

Fig. 1. 15° a-axis oscillation photographs of the polytypes (a) $16H_{10}$, (b) $18H_7$, (c) $24H_{10}$, (d) $30H_6$, (e) $32H_3$; 3 cm camera; Cu Kα radiation. The first most intense spot from the centre on the zero layer has $l = 5n/2$ for all five nH polytypes.

Table 6. Detailed crystal structures of new polytypes (space group P3m1 and a=b=4·24 Å, for all polytypes)

No.	Poly-type	Zhdanov symbol	ABC sequence	c(Å)
1	$16H_{10}$	$2112(11)_5$	$A\gamma B\ (C\alpha B)_2\ (A\gamma B)_5$	55·68
2	$18H_7$	$222112(11)_4$	$(A\gamma B\ C\alpha B)_2\ C\alpha B\ (A\gamma B)_4$	61·52
3	$24H_{10}$	$(22)_3(11)_3 1221$	$(A\gamma B\ C\alpha B)_3\ (A\gamma B)_4\ A\beta C\ A\gamma B$	82·02
4	$30H_6$	$22(11)_5 22(11)_6$	$A\gamma B\ C\alpha B\ (A\gamma B)_6\ C\alpha B\ (A\gamma B)_6$	102·54
5	$32H_3$	$(22)_6 112211$	$(A\gamma B\ C\alpha B)_6\ (A\gamma B)_2\ C\alpha B\ A\gamma B$	109·38

Polytype $16H_{10}$. This new polytype existed on one basal pinacoidal face of a well developed hexagonal crystal. Though a few-hundred probable structures exist for a 16-layered CdI_2 polytype, the number of possibilities was drastically cut by the observation that the intense reflections lie on or around $2H(11)$ positions (Fig. 1a), thus suggesting that the Zhdanov sequence of the polytype necessarily contains many (11) units. Further, the intensity distribution closely resembled that of $10H_4$, worked out earlier by Jain & Trigunayat (1975). Therefore, the following structures were postulated:

    (1) $22(11)_6$
    (2) $(22)_2(11)_4$
    (3)·$2112 (11)_5$
    (4) $2(11)_22(11)_4$.

A satisfactory agreement between the calculated and the observed intensities was found for structure (3) (see Table 1).

Polytype $18H_7$. The crystal structures of six $18H$ polytypes have been reported earlier by various workers. This new modification existed on one of the basal faces of the crystal. The other pinacoid was found to be $4H$ with some streaking. The a-axis oscillation photograph of the polytype is shown in Fig. 1(b). The strong reflections lie on or around $4H$ positions and the distribution of the reflections is not symmetrical. A large number of stacking sequences are possible for an 18-layered polytype. Intensities were computed for several such sequences, consisting of (22) and (11) units. Of these, the sequence $222112 (11)_4$ gave a satisfactory agreement with the observed intensities (Table 2).

Polytype $24H_{10}$. This structure was found on one of the pinacoids, while the other one showed the reflections of the common polytype $4H$. It was observed that the strong reflections either coincided with the $4H$ positions or lie near them, thus indicating that the unit cell of the structure mainly consists of (22) units. Consequently, a large number of probable sequences containing (22) units were tried. The best matching between the calculated and the observed intensities was found for the structure $(22)_3(11)_31221$ (Table 3).

Polytype $30H_6$. This polytype existed in coalescence with a much smaller polytype $6H$, the crystal structure of which is already known, *viz* (2211). Thus it was suspected that its crystal structure would be based on $6H$. A large number of sequences of Zhdanov symbols containing (2211) units were tried, out of which a good agreement between I_{calc} and I_{obs} for 10.*l* reflections was found for the structure $22 (11)_522 (11)_6$ (Table 4). It was not possible to compare I_{calc} and I_{obs} for reflections with $l = 75, 80, 85, 90, 100$ and 105, because of their superposition with the reflections of polytype $6H$. However, this was not a serious handicap, since because of the large unit-cell size of the polytype

the total number of reflections available for intensity comparison is still large.

Polytype $32H_3$. So far complete crystal structure determinations for only two 32-layered polytypes of cadmium iodide have been reported (Prasad & Srivastava, 1970; Pałosz, 1982). Fig. 1(e) shows the a-axis oscillation photograph of the present 32-layered polytype, which was present on one of the pinacoidal faces of a CdI_2 crystal. The other face was identified as $4H$. It was observed that strong reflections of $32H$ either coincide with $4H$ positions or lie around them, thus indicating that the unit cell consists mostly of (22) units. The following possibilities were tried:

    (1) $(22)_7(11)_2$
    (2) $(22)_6(11)_4$
    (3) $(22)_6121121$
    (4) $(22)_6112211$
    (5) $(22)_5(11)_6$
    (6) $(22)_511(22)_211$
    (7) $(22)_512211221$
    (8) $(22)_5(11)_222(11)_2$
    (9) $(22)_51122(11)_3$
    (10) $(22)_5112112(11)_2$
    (11) $(22)_5112(11)_2211$
    (12) $(22)_512(11)_321$
    (13) $(22)_51112112111$.

Excellent agreement between the observed and calculated intensities was obtained for structure (4) (Table 5).

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