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X-ray Diffraction Study on the Polytropic Structural Transformations Induced by Annealing in Cadmium Iodide Single Crystals

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Abstract

The thermal transformations produced by annealing in CdI_2 single crystals have been investigated. The mechanism of the structural changes has been analysed from the point of view of generation and/or elimination of two kinds of stacking faults of I–Cd–I molecular layers identified in the polytypic structure of CdI_2 : faults *B* and *D*. It has been established that two thermal barriers for the nucleation of the structural changes in CdI_2 may be distinguished: 353–383 and 463–503 K. The rules found for the polytypic transformation of CdI_2 crystals allow one to predict the way in which a definite structure may transform by annealing.

Introduction

Preparation of samples of desired structure remains one of the basic problems since polytypism was discovered 70 years ago. A complete list of the geometrical, chemical, thermodynamical and kinetic factors which determine the polytypic structure of a crystal is still not known. Two ways of controlled preparation of polytypic crystals are possible: controlled crystallization or modification of the structure of a crystal by inducing structural changes in the crystal.

Crystals growing at similar conditions, even in one crystallization run, may each have a different structure and single crystals with a uniform structure in the

whole volume form rather occasionally. Recently some papers have appeared on the effect of growth conditions on the polytypic structure of CdI_2 (Gyaneshwar & Trigunayat, 1975; Sharma, Sharma & Agrawal, 1980; Jain & Trigunayat, 1980; Pałosz, 1980; Pałosz & Przedmojski, 1982*a, b*; Chaudhary & Trigunayat, 1982; Gierlotka & Pałosz, 1983), but the relations found experimentally between some of the crystallization factors and the structure of the crystals have a rather qualitative meaning. An alternative way of obtaining crystals with a uniform well defined structure is thermal transformation of polytypic crystals. In this case the conditions of crystal structure formation are easily reproducible: to repeat a given transformation process one needs to control the temperature and the time of annealing of the crystal. This process does not seem to be very sensitive to accidental factors such as impurities or thermal fluctuations, the influence of which on crystal growth may be very large. Polytropic transformations have been investigated many times for different polytypic materials (Baars & Brandt, 1973; Steinberger, Kiflawi, Kalman & Mardix, 1973; Minagawa, 1975; Verma & Trigunayat, 1976; Bind, 1978, 1979) but no conclusive study on the application of this method to control the crystal structure has been reported. To use transformation for the preparation of samples of a desired structure one should know the rules which govern this phenomenon; this will enable one to predict the structure which forms from a given initial structure upon heating at a defined temperature.

In this work some experimental data on the thermal transformation of CdI_2 polytypes are presented. By using some rules established therefrom the effect of heating of crystals on the generation and elimination of faults from the crystals may be easily predicted.

Polytypic transformations of CdI_2 ; present state of investigations

The annealing of CdI_2 crystals for several hours under a vacuum of about 1.3×10^{-2} Pa at a temperature of 423–553 K was used by different investigators to induce structural changes in CdI_2 polytypes (Lal & Trigunayat, 1971, 1974; Tiwari & Srivastava, 1972, 1973, 1975; Rai & Srivastava, 1974, 1977; Rai, Tiwari & Srivastava, 1976*a, b*). The structures chosen for investigation, however, did not have a clearly visible order and the results reported in the literature on the structural changes in different polytypes cannot be summarized in the form of a rule. The discussions of the experiments were focussed on the role of dislocations in the structure transformation of the crystals (Lal & Trigunayat, 1970, 1974; Rai & Srivastava, 1974, 1977; Tiwari & Srivastava, 1975; Rai *et al.*, 1976*a, b*; Agrawal, 1979, 1981; Prasad, 1976; Arora & Trigunayat, 1976). The analysis of the mechanism of the structural changes was performed from the point of view of the dislocation and/or of Jagodzinski's theory of polytypism. No quantitative relations describing the transformation of CdI_2 polytypes were found.

A systematic study of the effect of annealing temperature and of annealing time on the structure of $2H\text{-CdI}_2$ was performed by Minagawa (1978). He ascertained some important facts: (1) the polytype $2H$ transforms gradually into the structure $4H$ beginning at 323 K; (2) the structural changes occurring in the crystals do not depend appreciably on the different heating times; (3) the intermediate faulted phases $2H\text{-}4H$ have structures depending on the maximum heating temperature and not on the heating process (on the times of annealing and quenching); (4) two temperature barriers may be distinguished in the gradual transformation of $2H$ into $4H$: 323–373 and about 473 K.

Experimental data

The CdI_2 crystals used for transformations were grown from aqueous, ethanol-water and isobutyl alcohol solutions by slow evaporation (Pałosz, 1981; Pałosz & Przedmojski, 1982*a, b*; Gierlotka & Pałosz, 1983). The structure of the crystals was determined from intensity measurements of $10.l$ and $1\bar{1}.l$ X-ray reflexions registered in the a^* oscillation photographs (Pałosz & Przedmojski, 1980*b*; Pałosz, 1980, 1982). The crystals were annealed using two methods: (1) the crystals were heated in a high-temperature X-ray

cylindrical camera and the photographs were registered at subsequent temperatures without quenching the crystals; or (2) the crystals were placed in a furnace for successive heat treatments, they were quenched to room temperature after each heating run, and the photographs were registered at room temperature. It was found, however, that the reflexion intensities decrease very strongly with temperature (Gierlotka, Pałosz & Przedmojski, 1982). The photographs registered in the high-temperature camera above 373–423 K were practically illegible and, because of this, only method (2) was used.

In order to establish an appropriate annealing time for transformations the effect of heating times from 10 min to 6 h on the structures of the polytypes $2H$ and $6H$, was examined. As no appreciable differences in the structures of the crystals were observed for different heating times it was concluded that the transformations are completed immediately or nearly immediately during the initial heating and independently of the times of annealing and quenching the crystals to room temperature. The standard annealing time used in our experiments was 10 min.

All the crystals under investigation were subjected to successive heat treatments beginning at 353 K. For each subsequent annealing run the temperature was raised by 10, 20 or 30 K. The crystals were heated to 573 or 603 K. A list of the samples subjected to annealing is presented in Table 1. The structures of the polytypes employed for or obtained by annealing are described in Table 2 in both *xyz*, *t-o-f* and Zhdanov notations.

Characteristics of the polytypic structure of CdI_2 ; description of structural changes of polytypes

Among the symbolic notations which may be used to describe the structure of CdI_2 , we found the molecular layer notations *xyz* and *t-o-f* (Pałosz, 1980; Pałosz & Przedmojski, 1980*b*) to be the most appropriate for characterization of the structural changes occurring in the crystals. As discussed elsewhere (Pałosz, 1980, 1983*a, b*; Pałosz & Przedmojski, 1984), the polytypic structure of CdI_2 may be described by six *t-o-f* symbols: *o*, *t*, *f1*, *f2*, *f4* and *f5*. The symbols *o* and *t* (called *o* and *t* layers) correspond to the basic polytypes $2H$ and $4H$ (see Table 2), the layers *f1* and *f2* represent faults of type *B*, and the layers *f4* and *f5* are faults *D* (Pałosz, 1983*b*; Pałosz & Przedmojski, 1984). Polytypic modifications of CdI_2 may be presented as structures constructed of a given number of basic layers *o* and/or *t* and of a given number of faults *B* and/or *D*.

Polytypic transformations provide the means of converting one polytype (ordered or disordered) into another polytype (ordered or disordered). The transformation takes place owing to the creation, elimination (annihilation) or redistribution of the faults in

Table 1. List of crystals subjected to annealing; characteristics of the thermal structural changes of CdI₂ polytypes

T_1 : temperature of nucleation of the transformation.
 T_2 : temperature above which structural changes were no longer observed.
 T_3 : temperature of a change of arcing (if a change was observed).
 d : disorder.
 un: unidentified structure.

Sample number	Structure	Initial arcing	T_1 (K)	Intermediate structure ^a	T_2 (K)	Final structure	T_3 (K)
(1)	2H	-	353	2H+4H+d	543	4H+d	-
(2)	2H	+	383	2H+4H+d	543	4H+d	503
(3)	2H+4H+d	+	463	2H+4H+d	543	4H+d	483-503
(4)	2H+d	-	423	2H+4H+d	543	4H+d	483-503
(5)	6H ₁ +d	+	463	4H+d	503	4H+d	-
(6)	6H ₁	-	463	6H ₁ +(4H+d)	473	4H+d	-
(7)	10H ₁	-	463	10H ₁ +(4H+d)	483	4H+d	-
(8)	10H _{un} +d	-	433	10H+4H+d	583	4H+d	-
(9)	10H _{un} +d	-	473	10H+4H+d	573	4H+d	-
(10)	12R+4H	-	543	4H+12R+d	603	4H+12R+d	-
(11)	12H ₃	+	423	12H ₃ +4H	463	4H	-
(12)	14H ₄ +4H	-	423	14H ₁	473	4H+d	-
(13)	16H ₁	-	463	16H ₁ +4H	503	4H	-
(14)	18H ₆	-	443	18H ₁	543	4H+d	453
(15)	18H ₁	-	473	18H ₁ +4H	573	4H+d	-
(16)	42R ₂	-	503	42R ₂ +d	583	42R+d	513

Table 2. Structures of polytypes of CdI₂ occurring in transformations

Ramsdell symbol	Zhdanov sequence	$t-o-f$ sequence*	xyz sequence†
2H	11	<i>o</i>	$x (= \bar{x} = y = \bar{y} = z = \bar{z})$
4H	22	<i>t</i>	$x\bar{x} (= y\bar{y} = z\bar{z} = x\bar{y} = \bar{x}z = y\bar{z})$
6H ₁	2211	<i>tf2f1</i>	$xx\bar{x}$
10H ₁	(22) ₂ 11	(<i>t</i>) ₃ <i>f2f1</i>	$x\bar{x}x\bar{x}$
12H ₃	(22) ₂ (11) ₂	(<i>t</i>) ₃ <i>f20f1</i>	$x\bar{x}x\bar{x}\bar{x}$
12R	(13) ₃	(<i>f4f5</i>) ₃	$x\bar{x}y\bar{y}z\bar{z}$
14H ₁	(22) ₃ 11	(<i>t</i>) ₃ <i>f2f1</i>	$x\bar{x}x\bar{x}x\bar{x}$
14H ₄	(22) ₂ (11) ₃	(<i>t</i>) ₃ <i>f2(o)2f1</i>	$x\bar{x}x\bar{x}\bar{x}\bar{x}$
16H ₁	(22) ₂ 211211	(<i>t</i>) ₄ (<i>f2f1</i>) ₂	$x\bar{x}x\bar{x}x\bar{x}\bar{x}$
18H ₁	(22) ₄ 11	(<i>t</i>) ₇ <i>f2f1</i>	$x\bar{x}x\bar{x}x\bar{x}x\bar{x}$
18H ₆	(22) ₂ (11) ₂ 2211	(<i>t</i>) ₃ <i>f2of1tf2f1</i>	$x\bar{x}x\bar{x}\bar{x}x\bar{x}\bar{x}$
42R ₂	(21223211) ₃	(<i>f5</i> (<i>t</i>) ₂ <i>f4tf2f1</i>) ₃	$x\bar{y}y\bar{y}y\bar{y}y\bar{z}z\bar{z}z\bar{z}z\bar{z}x\bar{x}x\bar{x}x\bar{y}$

* Symbols $t-o-f$ (layers $t-o-f$) are from Patosz (1980).

† Symbols xyz correspond to the following sequences of ABCαβγ layers (molecular sandwiches):

$$x = A\gamma B; y = BaC; z = C\beta A;$$

$$\bar{x} = CaB; \bar{y} = ABC; \bar{z} = B\gamma A.$$

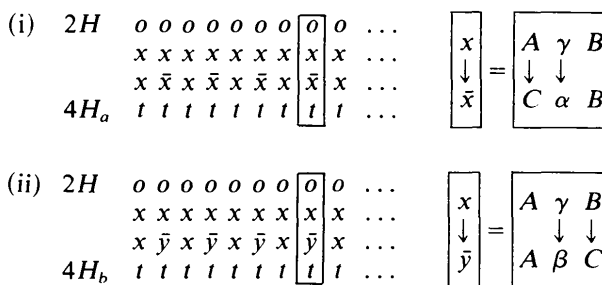
the initial structure. From the point of view of the $t-o-f$ notation the structure transformations may be considered as a process of generation and/or elimination of faults B and/or D .

Possible kinds of polytypic transformations of CdI₂; mechanism of transformation

It is well known that each polytypic structure of CdI₂ tends to transform upon heating into the basic structure 4H. In some cases the transformations lead to the creation of the polytype 4H free of faults. In other cases this polytype contains a certain number of faults. The transformations we have observed in CdI₂ may be divided into three different groups of structural changes.

Transformation 2H-4H

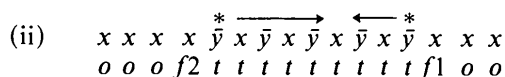
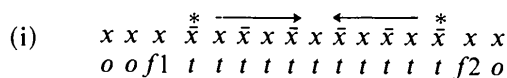
The polytype 2H is formed only of layers o . A change of the structure of this polytype may be regarded as a process of generation of faults. The polytype 2H may transform into 4H in two ways:



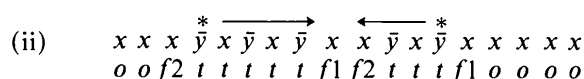
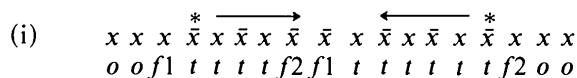
The sequences $4H_a$ and $4H_b$ are geometrically equivalent and experimentally indistinguishable (Pałosz & Przedmojski, 1980*b*). One may expect that the occurrence of the sequences $4H_a$ and $4H_b$ (called here domains $4H_a$ and $4H_b$) may have the same probability. It seems reasonable also to assume that the transformation of $2H$ may proceed through the nucleation process simultaneously in different parts of the crystal. Thus, in the crystal a number of $4H_a$ and $4H_b$ domains should appear simultaneously and, when the transformed domains expand, between the neighbouring domains some faulted arrangements of layers should appear.

(A) When the two neighbouring sequences t belong to two $4H_a$ and $4H_b$ domains then:

(1) The resulting structure may be free of faults (nucleation centres are denoted by asterisks, the directions of the expansion of the domains are marked by arrows):

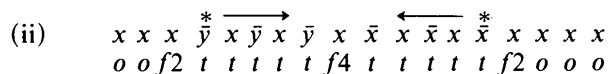
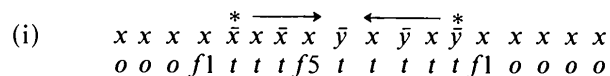


(2) In the intermediate region $4H_a$ - $4H_a$ or $4H_b$ - $4H_b$ the faulted sequence $f1f2$ or $f2f1$ may form:

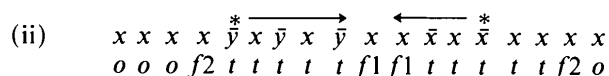
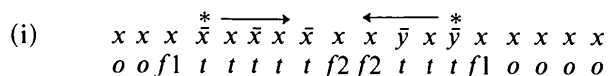


(B) When the two sequences t expand from two different centres generating neighbouring domains $4H_a$ and $4H_b$ then two other types of faults may occur:

(3)



(4)



If one assumes that the domains $4H_a$ and $4H_b$ are formed in a single crystal beginning from a certain number of independent transformation centres, the faults (1) to (4) should occur with similar frequencies. In general, the faults should be distributed randomly.

The transformation of polytype $2H$ begins at 353–383 K, see samples (1) and (2), Table 1. This temperature may be regarded as the temperature at which the first sequences t form in the crystals and simultaneously the first faults are created. This process is connected with the transformation of individual layers o into layers t . In fact the samples show different nucleation temperatures of transformation depending on the sample perfection (dislocations, boundaries, inclusions, stresses or strains). Experiment shows that the number of faults increases up to about 453–463 K. For samples (3) and (4) (see Table 1), also with structure $2H$ but initially having a certain number of faults, the structure begins to change at 423–463 K. The intensity curves observed experimentally for the initial and transformed sample (4) are presented in Fig. 1(a). The intensity curve of the initial structure of sample (4) corresponds approximately to the intensity curves obtained for samples (1) and (2) heated at about 423 K. Sample (4) began to change just at this temperature and this suggests that a well defined number of faults in the crystal might correspond to a given temperature.

The initial structure of sample (4) (the same structure has the crystal heated below 423 K) may be regarded as faulted structure $2H$. The broad intensity maximum observed in Fig. 1(a) around the position 2.75, corresponding to the position of reflexion 10.11 of $4H$, may be related to the faults present in the initial structure $2H$. Above 423 K the intensity gradually concentrates and the decrease of the streaking may be connected with a decrease of the number of faults in the crystal. The streaking of the reflexion 10.11 of $4H$, however, never disappears completely (see also Figs. 1*b* and 1*c*) and this means that a certain number of faults is always present in the final structure $4H$ obtained from $2H$. If one assumes that the mechanism of the transformation of $2H$ into $4H$ presented above does operate in the crystals it appears clear that a certain number of faults cannot be eliminated from crystals disregarding other causes, *e.g.* the annealing-temperature time, lattice defects *etc.* When two kinds of domains, $4H_a$ and $4H_b$, form during transformation of $2H$ and if the domains do not interact with each other in any particular way, there is no possibility of transforming all the domains $4H_a$ into $4H_b$ because the reverse process (transformation of $4H_b$ into $4H_a$) should occur simultaneously with equal probability. The experiments show that the final faulted structure $4H$ forms at about 543 K. The structural changes are no longer observed in the crystals annealed above 543 K.

Elimination of faults f_1 and f_2 from the structure of polytypes

In the following the structural changes of several polytypes constructed of layers o , t , f_1 and f_2 are analysed.

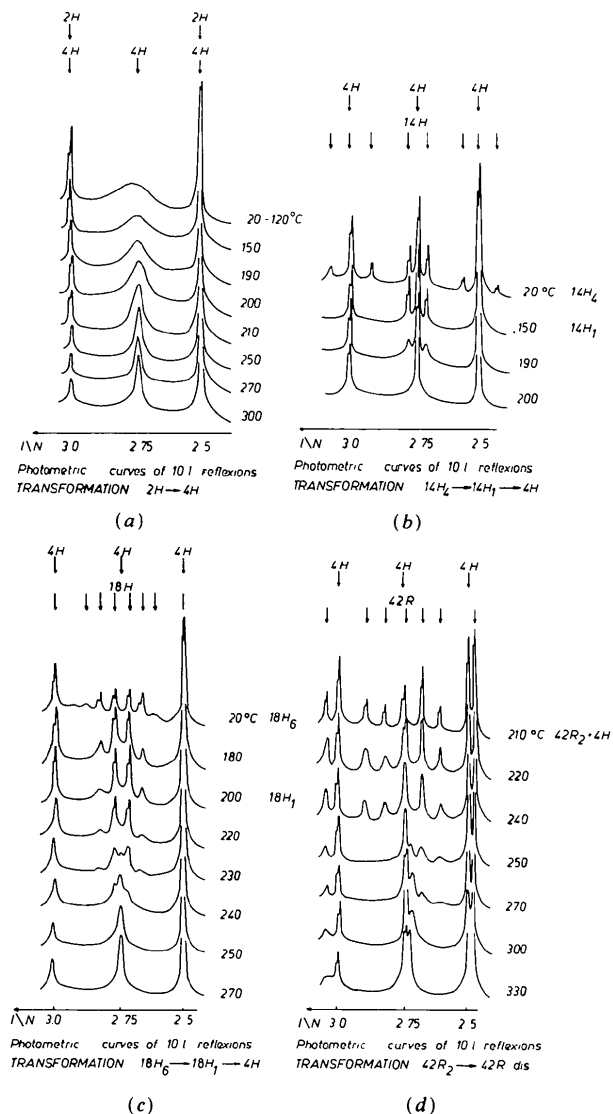
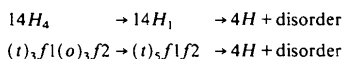


Fig. 1. Photometric curves of 10.1 reflexions for which $1/N$ varies between 2.5 and 3.0 (N is the number of iodine layers in a cell).

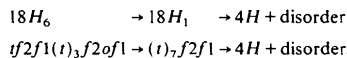
(a) Transformation of the structure $2H$ + disorder into the structure $4H$ + disorder.

(b) 'Intrapolytypic' transformation



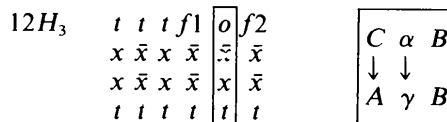
(the polytype $14H_4$ occurs in coalescence with $4H$).

(c) 'Intrapolytypic' transformation



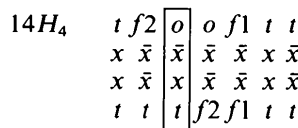
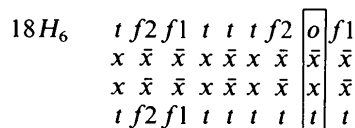
(d) Transformation of the polytype $42R_2$: $f_5(t)_2f_4tf_2f_1$ in a rhombohedral-type disordered structure with faults f_4f_5 . (The polytype $42R_2$ occurs in coalescence with $4H$.)

Polytype $12H_3$ [$(t)_3f_1of_2$, sample (11)] transforms into the pure polytype $4H$ in the temperature range 423–463 K. One may expect that the layer o in the cell $12H_3$ should transform first into the layer t , similarly as it takes place in the transformation of $2H$ into $4H$. The tentative mechanism of the transformation may be:



The transformation of o into t is, in this case, connected with the simultaneous annihilation of faults f_1 and f_2 . The temperature of this transformation corresponds to the temperature at which the polytype $2H$ transforms into $4H$, 353–463 K. Note that in order to transform the polytype $12H_3$ into $4H$ two singular layers C and α in the above model transform into the layers A and γ , respectively. This type of transformation corresponds to the transformation of $2H$ into $4H$. The energy, and thus temperature, necessary to nucleate such a transformation in $12H_3$ and in $2H$ should be similar, which agrees very well with the experiment.

Transformations similar to that observed for the polytype $12H_3$ were also found for other polytypes: $18H_6$, sample (14) and $14H_4$, sample (12):



The above transformations were observed at the temperature 423–443 K, similar to the transformation of $12H_3$ into $4H$. In these two cases, however, not pure polytype $4H$ but other polytypes having the same period as the initial structure were created. In Figs. 1(b) and 1(c), presenting the intensity curves registered at different stages of the annealing, one can observe the gradual process of the transformation of two polytypes $18H_6$ into $18H_1$ and of the polytype $14H_4$ into $14H_1$ at the first stages of the transformation and then the transformation of these polytypes into $4H$ with disorder. The polytypes constructed of layers o , t , f_1 and f_2 may or may not transform into pure $4H$. The elimination of faults f_1 and f_2 from polytypes [samples (3), (5), (6), (11), Table 1] takes place

hard to visualize forces which could cause expansion of one of them and lead to the formation of a uniform structure of t layers of one kind. The expansion of t sequences should be equally probable for $t_{x\bar{x}}$, $t_{y\bar{y}}$ and $t_{z\bar{z}}$. The expansion of one of the t sequences in one part of a crystal should always be accompanied by a similar expansion of other t sequences in other parts of the crystal. The faults $f4f5$ may move in a crystal but they can in no case be annihilated. This structure with faults $f4f5$ is an example of a polytype structure which can exist in a crystal as a stable one, but at the same time it is energetically unstable.

Role of lattice imperfections in the transformation of polytypes

The polytypic thermal transformations reported in the literature are frequently equated to the transformation (reorganization) of the dislocation network of the crystals (Lal & Trigunayat, 1974; Rai & Srivastava, 1974, 1977; Tiwari & Srivastava 1975; Rai *et al.*, 1976*a, b*; Agrawal, 1979, 1981; Arora & Trigunayat, 1976). Simultaneously it has been suggested that polytypes can undergo phase transformations because with an increase of the temperature the dislocations already present in the crystals may move freely in the lattice. There are, in fact, no well established experimental or theoretical arguments which could support this interpretation of the polytypic transformations. The present results allow one to consider the thermal structural changes of CdI_2 without reference to the dislocations: (1) The stackings of the type t may be unquestionably regarded as the most stable layer arrangements at high temperature. The stability of the layers t cannot depend on the presence of dislocations in the lattice and there are no reasons for the assumption that the transformation of a given stacking into the sequence t is conditioned by the presence of well defined dislocations in the as-grown crystal. (2) As is well known, structural changes usually begin on various lattice imperfections and this should also be valid for polytypic crystals. The dislocations present in the initial structure can affect the arrangement of layers during polytypic transformations. It is evident that some defects will promote while others, at the same time, will inhibit an expansion of the transformation. The difference in the nucleation temperatures observed for similar kinds of polytypic transformations but occurring in different samples may be related to the differences in the dislocation structures of the crystals. The occurrence of transformations in certain temperature ranges and not at fixed temperatures (e.g. 353–463 K for the transformation $o-t$) is probably also connected with the presence of dislocations in crystals. (3) Close correlation between arcing and polytypism has been suggested (Lal & Trigunayat, 1974; Agrawal & Trigunayat, 1969, 1970). It has also been suggested that the changes in the

dislocation structure of the crystals accompanying the polytypic transformations should cause generation or an increase of the arcing of the crystals. In fact, this suggestion has never been uniquely confirmed experimentally (Prasad, 1976). As seen from Table 1 the arcing, if present in the parent structure, increases in only some cases during annealing of the polytypes. Sometimes arcing arises in the initially perfect crystals whereas in others no changes in arcing were registered. Moreover, it was found that similar effects were observed in the case when a pure $4H$ polytype was heated. It should be noted that if arcing appears, or when it increases, it always occurs in the well defined temperature range of 483–523 K. So, similar to the polytypic transformations which occur in definite temperature ranges, the 'transformation' of arcing may also be regarded as a 'characteristic' phenomenon connected with some specific changes in the crystals, connected probably with dislocations (Agrawal & Trigunayat, 1970). Further discussion of a correlation between dislocations and polytypic transformations will be presented in a separate paper (Gierlotka & Pałosz, 1985).

Final remarks

Some well defined rules which govern the structural changes of CdI_2 polytypes by annealing are:

- (1) The layers o can be eliminated from the structure by annealing the crystals up to about 453 K. The reorganization of the layer arrangements connected with the elimination of layers o may cause the creation of faults $f1, f2, f4$ and $f5$, or the annihilation of faults $f1$ and $f2$. In each case, however, the structural changes are governed by the tendency to transform the layers o into layers t . The faults $f1$ and $f2$ and $f4-f5$ present in the initial structure or generated in low-temperature ranges do not transform up to 453–463 K.
- (2) The faults $f1$ and $f2$ transform into layers t when the crystals are annealed in the temperature range 463–503 K. The presence of some fault configurations of molecular layers in the crystals may cause a certain number of faults $f1$ and $f2$ to be retained above 503 K. In some cases, in particular when the initial structure is of a disordered type, the faults $f1$ and $f2$ cannot be completely eliminated from the crystal.
- (3) The faults $f4$ and $f5$ represent the arrangements of layers which can be partly eliminated only at about 573 K. There are some special fault arrangements, e.g. the sequences $f4f5$, which cannot be eliminated by annealing.

All the solid-state transformations observed in polytypic crystals of CdI_2 are governed only by the above-mentioned set of simple rules which does not depend on the theories of growth of polytypic crystals. The 'interpolytypic', 'intrapolytypic', curious and

other kinds of polytypic transformations (Tiwari & Srivastava, 1973; Rai *et al.*, 1976*a, b*) are easily explainable by simple geometrical and qualitative energetic considerations. Two basic energetic barriers which govern the structural changes in the CdI₂ crystals may be discerned:

(i) the transformation of the layers existing in the initial structure cannot proceed below 353 K (or 323 K, Minagawa, 1978);

(ii) the layers *f*₁ and *f*₂ may transform beginning from 463 K.

In some cases the faults cannot be eliminated from the crystal lattice owing to the stacking of the CdI₂ layers. Of course, different lattice imperfections (point defects, dislocations, boundaries, strains, stresses, inclusions *etc.*) affect the structural changes in the crystals. These imperfections may be determinant for the nucleation of the transformations and for blocking some transformations in domains close to them, but they do not determine either the sequence of the layer transformation or the final transformed structure.

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