Structural Thermal Transformations of Polytypes of CdI₂

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Abstract

The thermal transformations of CdI$_2$ polytypes have been investigated by X-ray diffraction. It has been established that the elimination of $2H$-type stacked layers is the constant rule governing the transformations. A tentative mechanism for the transformations through suitably spaced vacancy 'jog lines' is suggested. Two temperature barriers regarding the thermal behaviour of polytypes have been considered: T_{th} – connected with the thermodynamical stability of polytypes, and T_g – following from the geometrical conditions of the reconstruction of the crystal lattice. A possible explanation for the irreversibility of the transformation and for the variation of the transformation temperature and the dynamics between samples is given.

Introduction

A number of papers have appeared on thermal polytype transformations of CdI$_2$: Rai & Srivastava (1974, 1977), Rai, Tiwari & Srivastava (1976b), Tiwari & Srivastava (1972a, 1973, 1974, 1975), Minagawa (1978). The transformations were frequently related to changes of the dislocation network of the crystals: Lal & Trigunayat (1971, 1974). In some cases a close connection between the motion of partial dislocations and the structural changes was suggested: Rai, Tiwari & Srivastava (1976a), Tiwari & Srivastava (1972b). In a previous paper (Pałosz & Gierlotka, 1984b) the transformations of some simple polytypes of CdI$_2$ were discussed without regard to dislocations. In the present work more examples of polytype transformations of CdI$_2$ are reported. The driving force for the transformations is derived from the conditions of the thermodynamical stability of basic structures and a mechanism of the reconstruction of the crystal lattice is suggested.

Experimental results

CdI$_2$ single crystals were subjected to successive heat treatments at elevated temperatures in a high-temperature X-ray camera. The temperature was raised from 320 K in steps of 10 K up to 600 K. Two annealing runs were usually performed at each tem-

perature: a short-period one (5 min) and a long-period one (30 min). After each annealing run an X-ray pattern was registered at room temperature (Pałosz & Gierlotka, 1984a). In most cases the transformation was completed during the short-period annealing. When structural changes were observed after the long-period annealing, the crystal was subjected to further heat treatments at the same temperature until the changes had stopped. The temperature of the transformation was found to be different for different samples. Some samples transformed at well defined temperatures while others changed their structures gradually during subsequent annealings at elevated temperatures. The results are summarized in Table 1. The structures of the polytypes under consideration are given in Table 2, in both Zhdanov and t-o-f notations (Pałosz, 1980).*

As can be seen from Table 1 (*cf.* also Minagawa, 1978; Pałosz & Gierlotka, 1984b) the polytype transformations in most cases occurred in the temperature range 420-510 K. In only a few crystals were structural changes observed below 420 K. The changes observed above 540 K should not be regarded as solid-state transformations, since they were found to be connected with the sublimation of the crystal surface.

As can be seen from Table 2 (*cf.* also Pałosz & Gierlotka, 1984b) the structural changes observed in CdI$_2$ are always connected with the transformations of the layers o which are present in the initial structures into the layers t. The other layers preserve their positions and orientations in the structure. The symbols o and t describe the stacking of layers in the polytypes $2H$ and $4H$, respectively, and it is commonly known that the structure $2H$ always transforms into $4H$ upon heating. Thus, the explanation for the transformations of all CdI$_2$ polytypes can be sought in the thermal behaviour of the basic polytypes.

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* *Editorial note*: The Zhdanov notation used in this paper is a simplified version of the recommendations approved by the International Union of Crystallography *Ad-Hoc* Committee on the Nomenclature of Disordered, Modulated and Polytype Structures [Guinier, Bokij, Boll-Dornberger, Cowley, Ďurovič, Jagodzinski, Krishna, de Wolff, Zvyagin, Cox, Goodman, Hahn, Kuchitsu & Abrahams (1984). *Acta Cryst.* A**40**, 399-404].

Table 1. *Transformation characteristics of the polytypes under investigation*

Sample number	Initial structure	Temperature range of transformation (K)	Intermediate structure	Temperature range of transformation (K)	Final structure
1	$2H$	420	$2H\dagger$	460–540	$4H\dagger$
2	$2H$	480–490*			$4H\dagger$
3	$8H_1$	380–420*			$4H$
4	$8H_1$	460–490			$4H$
5	$8H_1$	480	$8H_3$	570–590*	$8H_3 + 4H$
6	$12H_7$	450–480*	$12H_1$	560–570*	$12H_1 + 4H\dagger$
7	$14H_7$	470–510	$14H_3$	550–600*	$14H_3 + 4H\dagger$
8	$36R_9$	470–500	$36R_7$	570–600*	$36R_7 + 4H\dagger$

* Structural changes were observed during long-period annealing.
† Disorder.

Table 2. *Structures of polytypes of* CdI_2 *occurring in the transformations*

Ramsdell notation	Zhdanov sequence	t-o-f sequence*
$2H$	11	o
$4H$	22	t
$8H_1$	$2(11)_2 2$	$tf2\,of1$
$8H_3$	2123	$tf5\,tf4$
$12H_7$	12211122	$f5\,tf1\,of1\,t$
$12H_1$	122232	$f5\,(t)_3\,f4\,t$
$14H_7$	1221112112	$f5\,tf1\,of1\,f2f1$
$14H_3$	12322112	$f5\,tf4\,(t)_2\,f2f1$
$36R_9$	$[131(11)_2 3]_3$	$[f5\,f4\,f2\,of2\,f4]_3$
$36R_7$	$[(13)_2 22]_3$	$[(f5f4)_2(t)_2]_3$

* t-o-f symbols are after Pałosz (1980).

Tentative mechanism for the reconstruction of the crystal lattice

The transformation of the $2H$-type stacking of layers into $4H$-type is shown in Fig. 1. As can be seen, the transformation requires a simultaneous change of the positions of the two atomic sheets: iodine from B to C, and cadmium from γ to β. It is rather improbable that the layers shift entirely as rigid structural units.
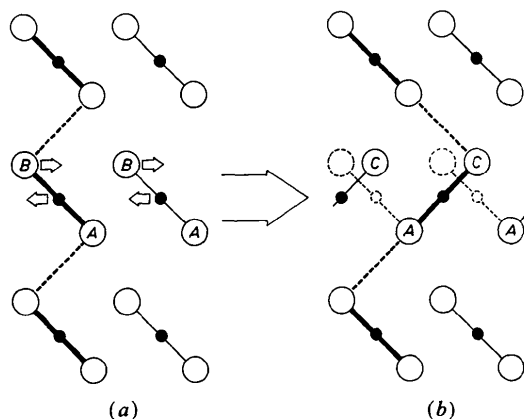
Seeking the mechanism for a step-by-step reconstruction of an I–Cd–I sandwich we came to the conclusion that it is possible when the sandwich includes a vacancy 'jog line' (v.j.l.), see *e.g.* Hirsh (1962). As shown in Fig. 2 successive jumps of Cd and I ions within the v.j.l. lead to its motion along the layer plane, which is connected with the gradual transformation of the stacking $A\gamma B$ into $A\beta C$.

It was suggested by Rai, Tiwari & Srivastava (1976*a*) that the polytype transformations of CdI_2 may be explained in terms of the motion of Shockley partials. A single Shockley partial may be considered as composed of v.j.l.'s stacked one over another. The mechanism suggested here does not require the motion of Shockley partials but only of some v.j.l.'s creating the partial. Fig. 3 presents schematically the transformation of $2H$ into $4H$, where the graphic convention is that of Verma & Trigunayat (1976). The initial structure $2H$, composed of two blocks: $2H_a$ ($A\beta C\,A\beta C\,A\beta C...$) and $2H_b$ ($B\gamma A\,B\gamma A\,B\gamma A...$) with a partial between the blocks, is given in Fig. 3(*a*). The transformation is nucleated in each second molecular sandwich and the transformed domain $4H$ expands along the layers as marked by horizontal arrows. The resulting structure is given in Fig. 3(*b*), where the domain $4H$ just created is surrounded by two domains $2H$ not yet transformed. A similar

Fig. 1. Transformation of (*a*) the stacking *o*: $A\gamma B\,A\gamma B\,A\gamma B$ into (*b*) the stacking *t*: $A\gamma B\,A\beta C\,A\gamma B$ by the simultaneous shift of I and Cd layers. Stacking of molecules I–Cd–I in the plane (11.0).
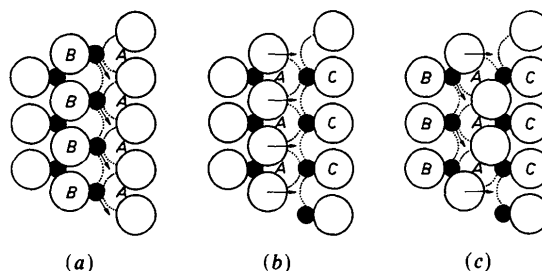

Fig. 2. Motion of the two-thirds vacancy jog line by successive jumps of Cd and I ions. Black circles represent Cd ions lying in the plane of the paper; large solid and dotted circles represent I ions above and below the Cd layer, respectively.

mechanism may be employed to explain the transformations of multilayer polytypes: the layers undergoing reconstruction are distributed less densely in the case of higher polytypes, e.g. only one layer o transforms per unit cell, in accordance with the lattice period of a polytype.

Geometrical restrictions for motion of v.j.l.'s

The axial ratio a/c for CdI$_2$ is 1·61 and the structure may be considered as a nearly perfect close-packed hexagonal structure: the I layers may be compared to hexagonal layers composed of hard equal spheres; small Cd cations are placed in the octahedral holes between the I anions, Fig. 2.
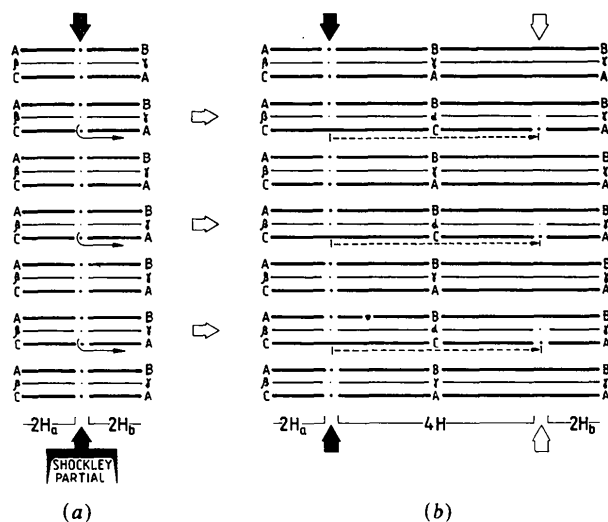

Fig. 3. Schematic transformation 2H–4H occurring by motion of v.j.l.'s: (a) 2H structure with a Shockley partial. The direction of the motion of v.j.l.'s is marked by arrows. (b) The transformed structure with the domain 4H: AγB CαB. Horizontal broken arrows indicate the transformed areas of the I–Cd–I sandwiches.

As shown in Fig. 2 small Cd cations may occupy two alternative positions within the v.j.l., denoted here by β and γ. The motion of large I ions lying close to the v.j.l. is limited by the I ions lying over and below the reference layer. To transform the stacking 2H: AγB AγB into 4H: AγB AβC the layer B should be displaced to the position C as shown in Fig. 4(a). A cross-section of three subsequent layers ABA is shown in Fig. 4(b), where it is seen that to move the ion of I from position B to C, the A ions surrounding the B ion should be drawn aside. The minimal distance at which the spheres A should be displaced is 0·18 Å, as shown in Fig. 4(c).

In real crystals the displacements of the ions are caused by thermal vibrations of the lattice. To calculate the mean-square thermal displacement $\bar{u}^2$ as a function of the actual temperature T and the Debye temperature Θ_M we have used the expression given by James (1965):

$$\bar{u}^2 = 3\hbar^2 T / mk_B\Theta_M^2, \tag{1}$$

m, $\hbar$ and k_B being the atomic mass, Planck constant and Boltzmann constant, respectively.

The characteristic Debye temperature $\Theta_M = 125 \pm 10$ K was measured by X-ray diffraction (Przedmojski, Gierlotka & Pałosz, 1985). The Θ_M values measured for 00.l and h0.0 reflections were equal within experimental error and the thermal vibrations were assumed to be isotropic.

The value of $T = T_g = 448 \pm 30$ K was obtained from equation (1) by taking $\sqrt{\bar{u}^2} = 0·18$ Å. The temperature T_g so calculated may be considered the temperature above which there are no more restrictions for the motion of v.j.l.'s within the molecular sandwiches. The calculated value of T_g satisfactorily agrees with the results of experiment: the transformations were observed in the range 420–510 K.
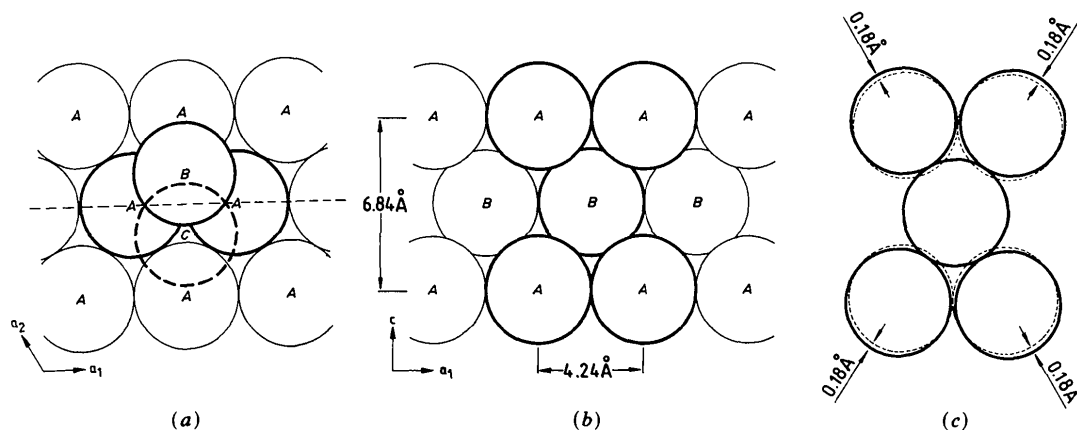

Fig. 4. Geometrical restrictions for motion of ions in a close-packed hexagonal structure. (a) A view of a hexagonal layer along the [0001] direction. The ion B lying above the reference layer A is to be moved to the position C. (b) Three sequential hexagonal layers in the stacking ABA. The [01$\bar{1}$0] direction is perpendicular to the plane of the paper. Lattice parameters are those for CdI$_2$. (c) Ions A moved 0·18 Å from the equilibrium positions (marked by broken circles) make possible the jumps of I ions from positions B to C.

Discussion

All the structural changes observed in CdI_2 polytypes follow from one constant rule: The $2H$ stackings of layers are eliminated from the crystals heated above 420 K, irrespective of the mechanism of the reconstruction of the crystal lattice. However, the transformations of CdI_2 differ from the usual phase transitions by: (i) irreversibility, and (ii) temperature and dynamics of the transformation varying between samples. The proposed mechanism may be the basis for the explanation of these phenomena.

Thermal stability of basic structures

It may be seen from the experimental data on growth (Pałosz, 1983) and transformations of CdI_2 that the $4H$ structure is stable over the whole temperature range of existence of the crystalline state. In contrast, the polytype $2H$ grows in a relatively narrow range of temperature close to room temperature, and is practically absent in the crystals obtained at 320 K (Pałosz, 1983). The transformation of $2H$ into $4H$ was observed, starting from 350 K (Minagawa, 1978).

It may be deduced from this that the temperature T_{th} above which the structure $4H$ becomes more stable than $2H$ belongs to the temperature interval between 320 and 350 K.

The difference between the temperatures T_{th} and T_g may be the reason why the transformation of $2H$ into $4H$ is irreversible. The transformation of $4H$ into $2H$ might occur below T_{th}, while the mechanism suggested here can operate only above T_g. Since for CdI_2 the temperature T_g is higher than T_{th} the reverse transformation is not possible.

The opposite situation (T_g lower than T_{th}) should lead to a reversible polytype transformation. This is probably the case for PbI_2, for which such transformations were reported by Minagawa (1979).
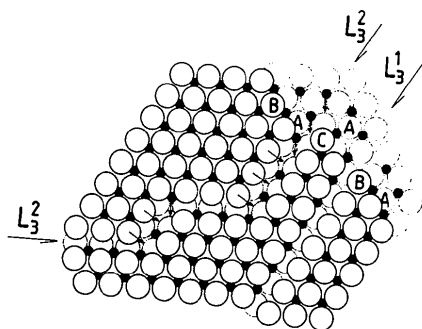
Effect of the configuration of the v.j.l.'s

As shown in Fig. 5 a single v.j.l. having an arbitrary direction is composed of a number of sections of two kinds: (i) one-third v.j.l.–L_3^1 and (ii) two-thirds v.j.l.–L_3^2 (Hirsh, 1962). Of these, only L_3^2 can move in the crystal, while the lines L_3^1 are immobile. Because of this a single v.j.l. with a given configuration may lead only to a partial reconstruction of the layer, as shown in Fig. 6. The transformation may continue until all the lines L_3^2 initially present in the crystal are removed to the crystal edges. If the number of the lines L_3^2 is large enough, the structural changes may be completed almost immediately in the whole volume of the crystal. If not, some fresh v.j.l.'s should be created, e.g. by dissociation of unit dislocations into partials. This process seems to be slower than the simple motion of the v.j.l.'s, which may be one of the reasons why in some crystals the structural changes are slow.

Role of lattice imperfections

The polytype transformations occurring according to the suggested mechanism should be strongly affected by various lattice imperfections. Since the energetic differences between polytypes are very small, lattice defects may significantly change the transformation temperature with respect to T_g. The v.j.l.'s may be held up against some obstacles, e.g. impurities, dislocations etc., at the early stage of the transformation, and to overcome the pinning forces it may be necessary to raise the annealing temperature above T_g. The v.j.l.'s held up against dislocations may be set free also by removing the dislocations from the crystal during annealing. This may be one more reason why the long-period annealing promotes the transformation in some samples. Some lattice defects may promote the transformations also by lowering the nucleation temperature. A partial transformation

Fig. 5. Two kinds of vacancy jog lines: L_3^1 (one-third v.j.l.) and L_3^2 (two-thirds v.j.l.). Small heavy circles represent Cd cations lying in the plane of the paper; large solid and dotted circles represent I ions lying above and below the Cd layer respectively. Arrows show possible directions of jumps of the ions within the lines L_3^2. I ions cannot change their positions within the lines L_3^1.
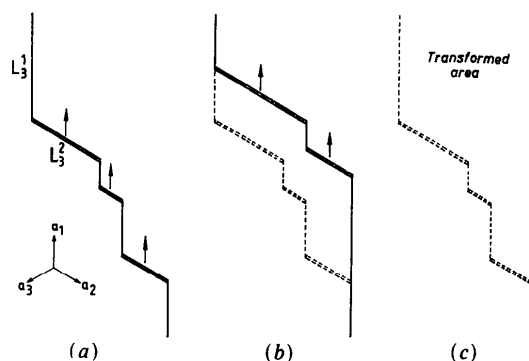

Fig. 6. Schematic reconstruction of a molecular sandwich by motion of a v.j.l. of a given configuration. Single and double lines represent sectors of one-third and two-thirds vacancy jog lines respectively. The direction of the motion of the lines L_3^2 is marked by arrows.

of the structure occurring because of some voids in the lattice (*e.g.* vacancies) is possible starting from T_{th}. However, the temperature should always be raised to T_g to induce any significant change of the structure. Two such temperature barriers occurring in the transformation 2*H*-4*H* were reported by Minagawa (1978).

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The Effect of Internal Vibration upon Deformation Densities and X-ray Scattering Intensities in H$_2$O and CO$_2$

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Abstract

The vibrational averages of electron deformation densities and molecular X-ray scattering intensities have been calculated for the bend vibration in H$_2$O and CO$_2$, and for the symmetric stretch vibration in H$_2$O. It is shown that bend mode vibrations, despite their relatively large amplitudes, have a minor effect on deformation densities and X-ray scattering intensities. Together with previous results for stretch vibration in diatomic molecules, which have been confirmed by the results in this paper for stretch vibration in triatomics, this means that all internal vibrations may be neglected except for the smearing of the high peaks very close to the nuclei. Since the X-ray intensities associated with this area will be found at high S values, the effect upon scattering intensities at low S is not important. In the valence region the effects are negligible compared to other sources of error in the comparison of calculations with experiment, such as basis set, libration [*cf.* Hermansson (1983). *Chem. Phys. Lett.* 99, 295-300] *etc.*

I. Introduction

The effect of vibrational averaging on calculated observables has been studied mostly for the stretch vibration in diatomic molecules. Among others, detailed studies have been reported for effects in both reciprocal (scattering) space (Stewart, 1977; Epstein & Stewart, 1979) and position space (Rozendaal & Ros, 1982; and references therein). The stretch vibration proved to be of minor importance, yielding only small corrections to, for example, the static deformation density at R_e due to the small weight of other internuclear distances in the vibrational average. It is possible that the influence of bend vibrations is larger, as the force constants are in general smaller and the vibration amplitudes larger. We will therefore study in this paper the internal vibration modes of the triatomic molecules H$_2$O and CO$_2$, employing the same method as used before in our study on diatomic molecules. It is interesting to consider the vibrational motion of hydrogens as the root-mean-square (r.m.s.) displacements are relatively large. Hydrogens on the