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The structure of PbI_2 polytypes 2H and 4H: a study of the 2H–4H transition

B Palosz[†], W Steurer[‡] and H Schulz[‡]

[†] High Pressure Research Centre of the Polish Academy of Sciences, 'Unipress', ul. Sokolowska 29/37, 01142 Warszawa, Poland

[‡] Institut für Kristallographie und Mineralogie der Universität, Theresienstrasse 41, D-8000 München 2, Federal Republic of Germany

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Abstract. The structures of 2H PbI_2 , grown from a gel, and of 4H PbI_2 , obtained by thermal transformation of 2H at 423 K, have been determined by single-crystal x-ray analysis. The space groups are $\text{P}\bar{3}\text{m}1$ for 2H and $\text{P}3\text{m}1$ for 4H. The occupancy of the atomic sites in the 2H and 4H structures is only about 80–85%, indicated by an observed density D_m of 5.0(1) Mg m^{-3} versus a crystallographic density D_x of 6.09 Mg m^{-3} . The density of the polytype 12R grown by the *Bridgman* method is $D_m = 6.19(5) \text{Mg m}^{-3}$. The initial 2H and the transformed 4H structure have been refined to $wR = 0.021$ and 0.049, respectively. A strong modulation of the occupancy of the Pb and I layers (for 2H the occupancies are 0.8 in both layers) along c has been derived for 4H. The occupancies vary between 0.7 and 0.9. The atomic layers with the highest occupancies in the 4H stacking are split into double layers with z coordinates differing by about 0.4 Å. For 2H PbI_2 , $M_r = 461.01$, $a_{2\text{H}} = 4.558\,0(5)$ Å, $c_{2\text{H}} = 6.986(3)$ Å, $V_{2\text{H}} = 125.69(8)$ Å³, $Z = 1$, $D_{x2\text{H}} = 6.09 \text{Mg m}^{-3}$, $\text{Mo K}\alpha$, $\lambda = 0.710\,61$ Å, $\mu = 45.2 \text{mm}^{-1}$ and $F(000) = 188$. For 4H PbI_2 , $a_{4\text{H}} = 4.554(1)$ Å, $c_{4\text{H}} = 13.962(5)$ Å, $V_{4\text{H}} = 250.80(9)$ Å³, $Z = 2$ and $F(000) = 376$.

1. Introduction

Although the origin of polytypism and the physical reasons for the formation of polytypes have been discussed for several decades, the nature of the phenomenon is still not fully understood. In recent years, however, much progress has been made towards understanding the physical meaning of polytypism, which seems to be a common behaviour of crystals. Traditionally polytypism is related to the changing of stacking sequences of layers which are assumed to be fully compatible units; all layers have the same chemical composition and are geometrically identical whatever the layer stacking might be. Although the effect of chemical factors on the polytype structure is observed in various materials (effect of impurities, crystallisation environment, stoichiometry, etc), e.g. in SiC (Vodakov *et al* 1983, Sorokin *et al* 1983), CdI_2 (Gierlotka and Palosz 1985), PbI_2 (Hanoka and Vand 1968, Palosz *et al* 1985) and SnS_2 (Palosz *et al* 1986), the way in which the chemical factors influence the layer stacking of the crystals is unclear. If we assume that the composite atoms (the atoms of a given compound, impurities or dopands, lattice defects such as vacancies, etc) are distributed randomly in the layers and in the bulk, then every compatible unit (e.g. the double layer Si–C in SiC, the triple layer

I–Pb–I in PbI_2 , etc) should have a given average composition. If it is so the layers are identical as in a perfect polytype structure. Trying to answer the question of why the layers combine in specific stackings, we shall face again the ‘classical’ problem of polytypism of why identical units combine in different stackings.

If we look at the literature published on polytypism, we see that the identity of the stacking layers was tacitly assumed and has never been proven. However, if the layers are not identical, because of their construction or composition or specific distribution of the atoms in the layers, the question of ordering of identical layers and of the stacking stability of the layers is *not* the question that we have to answer to understand the polytypic behaviour of the crystals. The variation in the chemical composition and in the construction of the layers which we may expect to occur between polytype phases is certainly very small. There is a small chance of observing differences between the layers directly, e.g. by the HRTEM technique. We cannot also expect the detection of any differences between individual layers by measuring physical properties which always reflect an average property of the material.

Recently we successfully used single-crystal x-ray structure analysis to detect differences between simple polytypes of SnS_2 ; there is a strong modulation of occupancies of S and Sn layers along the stacking direction (Palosz *et al* 1989a). The polytypes 2H, 4H and 18R of SnS_2 which we have examined were grown at different temperatures and crystallisation environments (Palosz *et al* 1986) and have different densities which means that different polytypes are qualitatively different materials. The experiment with SnS_2 is not enough to decide whether the chemical composition determines the structure of the crystals and the temperature is of secondary importance or the polytypes (given layer stackings) have well defined thermal stability regions independent of chemical composition. To solve the problem, additional thermal investigations would be necessary, e.g. the occurrence of an interpolytype transformation upon heating would show whether, within a given chemical composition of the crystal structure, different stacking sequences can be formed. Unfortunately SnS_2 is not a simple material to be examined at elevated temperatures because of its sublimation, oxidation and decomposition at high temperatures. For that reason we have chosen another polytype material PbI_2 in which to study the phase transition.

The polytype 2H of PbI_2 is known to undergo a reversible phase transition: 2H to 4H or 12R in the temperature range 273–423 K (Minagawa 1979, 1981). The structural, thermodynamical and dielectric aspects of this transition have widely been discussed by Salje *et al* (1988). For unknown reasons, some 2H samples transform into 4H, and others into the structure 12R. In our experiment the structure 2H transformed into the polytype 4H.

Before studying the transition of 2H we tried to refine the structures of pure as-grown polytypes 4H and 12R but we did not find good-quality single crystals which could be used. Our study, therefore, is limited to the refinements of the structure of the pure as-grown polytype 2H and of the structure obtained after transformation from 2H to 4H.

2. Experimental details

2.1. Sample preparation

Because of very strong absorption of x-rays in PbI_2 ($\mu = 45.2 \text{ mm}^{-1}$ for Mo $\text{K}\alpha$) the samples used for the structure analysis should have a diameter of about 0.02–0.04 mm

to minimise the effect of absorption on the measured intensities. Crystals of PbI₂ grown from a gel are thin hexagonally shaped platelets and have to be etched. They are extremely soft and cannot be treated mechanically. The cleaning of the samples was performed in two steps. First they were treated with an aqueous solution of potassium iodide. PbI₂ is partly dissolved in this solution and, because potassium iodide dissolved in water penetrates the crystal volume, the samples become covered with a thin surface layer of a polycrystalline material. This surface layer was removed by putting the sample into acetone. This procedure was repeated several times to obtain samples of desired size. Unfortunately potassium iodide (KI) penetrates the crystal volume very easily, probably along defects, leading to a strong deformation of the samples when the solvent dries out. The structure and quality of the crystals were examined by Laue and precession photographs. Of more than 20 samples prepared, only one was acceptable for the intensity data collection (size about 0.02 mm × 0.05 mm × 0.24 mm). We also tried to prepare a sample of the polytype 12R grown by the Bridgman technique but the qualities of the samples were always very poor.

2.2. Density measurements

The density of PbI₂ single crystals has been measured by hydrostatic weighting in iso-octane. The crystals of PbI₂ grown from a gel (particularly the large crystals) very often contain cavities in the bulk where gas or liquid is trapped during the crystal growth. Only small crystals were used for density measurements and they were examined under an optical microscope to select samples free of cavities. Two sets of 2H single crystals grown from a gel each of mass about 20 mg and one sample of the 12R polytype were measured. As-grown crystals of 2H were annealed at 423 K for 24 h and measured again. No change in the density was observed upon annealing.

The measured density D_m of the 12R polytype of 6.19(5) Mg m⁻³ agrees very well with the crystallographic density D_x of 6.09 Mg m⁻³. The density of the 2H polytype was found to be $D_m = 5.0(1)$ Mg m⁻³ corresponding to only 80% of the crystallographic density. It should be noted that a similar discrepancy was observed for the 2H polytype of SnS₂ (Palosz *et al* 1989a).

2.3. Intensity data collection

Data collection was carried out with the following experimental details: Enraf-Nonius CAD-4 four-circle diffractometer, Ω - 2θ scans, one intensity-control reflection per hour, constant within counting statistics; three orientation-control reflections; $\theta_{\max} = 30^\circ$; for 2H 1352 ($-5 \leq h, k \leq 5, -8 \leq l \leq 8$), 4H 2686 ($-5 \leq h, k \leq 5, -18 \leq l \leq 18$) reflections collected, 163 and 492 unique reflections, respectively, after averaging ($R_{\text{int}} = 0.065$ and 0.069 for 2H and 4H, respectively); lattice parameters from least-squares fits of 25 reflections in both cases; weights proportional $1/\sigma^2(I)$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); Lorentz-polarisation factor L_p correction, numerical absorption correction, secondary extinction correction (Becker and Coppens 1974); ratio of maximum least-squares shift to error in the final refinement cycles, for 2H, -0.69 and, for 4H, -0.39. The structure refinements were performed using the program PROMETHEUS (Zucker *et al* 1983).

Because of strong absorption and a needle-like shape of the sample used for the intensity data collection, the absorption correction is the critical factor deciding on the accuracy of the intensities used for computing. To minimise the effect of the absorption

Table 1. *R*-values for refined structures 2H and 4H of PbI₂. Models (a)–(e) are described in the text.

Sample	Space group	Number of measured reflections	Number of unique reflections, unrejected	<i>wR</i>
2H	P $\bar{3}$ m1	1352	163–141	0.036–0.021
4H, model (a)	P6 ₃ mc	2686	173–160	0.253–0.160
2H, model (b)	P3m1	2686	496–464	0.271–0.197
2H, model (c)	P3m1	2686	496–464	0.145–0.084
2H, model (d)	P3m1	2686	496–464	0.128–0.064
2H, model (e)	P3m1	2686	496–464	0.115–0.049

on the refinement a χ^2 -test has been performed for all measured reflections after the absorption correction. From the list of symmetrically equivalent reflections those with the largest deviations of the intensities from the average value were rejected. The numbers of measured, unique and unrejected reflections are given in table 1.

The density measurements of gel-grown crystals of 2H showed that the measured density is only 80% of the crystallographic density. This value says nothing, however, about the chemical composition of the samples. We have to consider the structural models with a stoichiometric composition but with Pb and I sites filled in only 80%. We must also take into account that the crystals can be non-stoichiometric with an excess of Pb or of I atoms. The chemical analysis which we performed using a microprobe analysis did not give us an unequivocal result concerning the stoichiometry owing to the instability of the samples of PbI₂ under the electron beam. Not having the chemical composition defined unequivocally we considered the structure models with different compositions.

3. Theory

3.1. Refinement of the polytype 2H

Three models of 2H were tried:

- (a) with occupancies of Pb and I sites constrained to unity (stoichiometric structure);
- (b) with occupancy of Pb constrained to unity and refined occupancy of I;
- (c) with occupancy of I constrained to unity.

The refinements of models (b) and (c) showed that the structure is stoichiometric within an accuracy to better than 0.5% and model (a) was accepted. Taking into account the density of the crystals, we conclude that the layers of Pb and of I are occupied to only 80% by the atoms. The vacancies are distributed randomly in the layers.

The structure 2H has been refined in the space group P $\bar{3}$ m1 to *wR* = 0.021. The stacking sequence is given in figure 1, the inter-layer distance in figure 2, and the atomic coordinates, occupancy factors and thermal parameters in tables 2 and 3†.

† Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No SUP 70040 (7 pages).

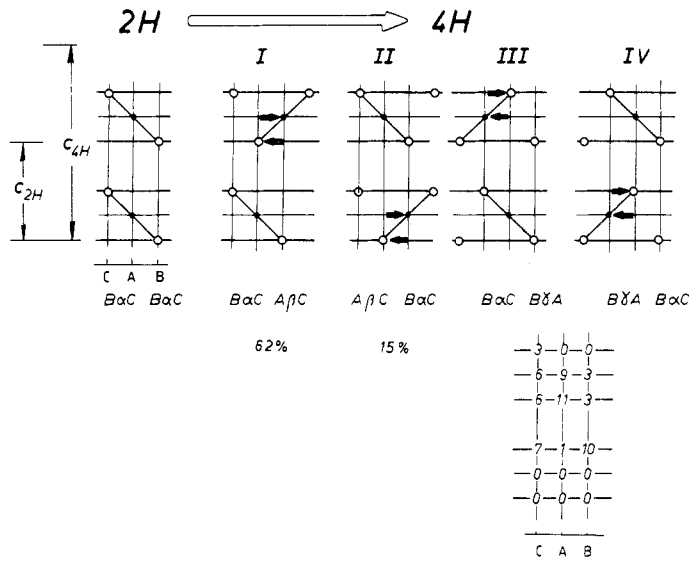


Figure 1. Mechanism of the reconstruction of the stacking sequence of 2H PbI_2 in the 4H stacking; four equivalent stacking sequences of the 4H unit cell are shown schematically. The average unit cell of 2H transformed to 4H is a combination of stacking I (62%) and II (15%).

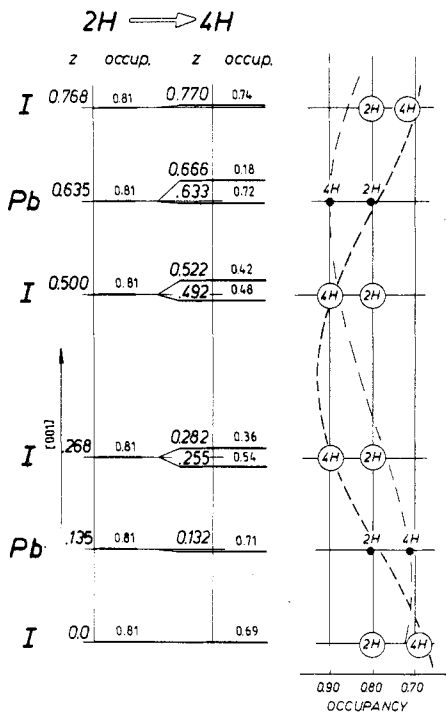


Figure 2. Inter-layer distances in the 2H and in the transformed 4H structure. The modulation of the occupancies of the atomic layers (○, I; ●, Pb) in the stacking direction is shown schematically.

Table 2. Atomic coordinates and occupancy factors of 2H and 4H PbI₂.

	2H				4H			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>p</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>p</i>
Pb(1)	0	0	0	1	$\frac{2}{3}$	$\frac{1}{3}$	0.1325(6)	0.635(5)
Pb(2)					$\frac{1}{3}$	$\frac{2}{3}$	0.1325(6)	0.152(4)
Pb(3)					$\frac{1}{3}$	$\frac{2}{3}$	0.6336(8)	0.609(4)
Pb(4)					$\frac{2}{3}$	$\frac{1}{3}$	0.6336(8)	0.151(5)
Pb(5)					0	0	0.6656(21)	0.079(15)
Pb(6)					$\frac{1}{3}$	$\frac{2}{3}$	0.6656(21)	0.045(15)
Pb(7)					$\frac{2}{3}$	$\frac{1}{3}$	0.6656(21)	0.117(7)
I(1)	$\frac{1}{3}$	$\frac{2}{3}$	0.2675(2)	1	$\frac{1}{3}$	$\frac{2}{3}$	0	0.58(1)
I(2)					$\frac{2}{3}$	$\frac{1}{3}$	0	0.17(1)
I(3)					0	0	0.255(2)	0.47(6)
I(4)					$\frac{1}{3}$	$\frac{2}{3}$	0.255(2)	0.14(1)
I(6)					0	0	0.283(3)	0.23(1)
I(7)					0	0	0.283(3)	0.15(1)
I(8)					0	0	0.492(2)	0.08(1)
I(9)					$\frac{1}{3}$	$\frac{2}{3}$	0.492(2)	0.04(1)
I(10)					$\frac{2}{3}$	$\frac{1}{3}$	0.492(2)	0.44(3)
I(11)					$\frac{2}{3}$	$\frac{1}{3}$	0.522(2)	0.30(1)
I(12)					$\frac{1}{3}$	$\frac{2}{3}$	0.522(2)	0.15(19)
I(13)					0	0	0.770(1)	0.66(1)
I(14)					$\frac{2}{3}$	$\frac{1}{3}$	0.770(1)	0.16(1)

Table 3. Thermal parameters of 2H and 4H PbI₂ polytypes.

	2H	4H
		Pb
u_{11} (10 ⁴ Å ²)	246(4)	205(6)
u_{33} (10 ⁴ Å ²)	468(6)	236(23)
		I
u_{11} (10 ⁴ Å ²)	305(3)	308(9)
u_{33} (10 ⁴ Å ²)	305(7)	263(40)

3.2. Refinement of the transformed-structure polytype 4H

While the stacking sequence of the polytype 2H is unequivocally defined, the transformed structure is not necessarily a one-domain polytype 4H. There are different stacking sequences describing the 4H cell (figure 1). The transformed structure may, in general, be made up of 4H domains having different stacking sequences. We can also expect that some disorder will accompany the multidomain structure of the transformed phase. In such a case a broadening of reflections or continuous streaks should occur on the x-ray patterns along the *c** direction. Therefore, before the intensity data collection was performed, the crystal was examined by photographic methods; Laue and oscillation methods were used. The reflections were reasonably sharp and it was assumed that the transformed structure is the polytype 4H, predominantly.

3.3. Tentative models of the reconstruction of the layer stacking 2H to 4H

Comparing the stacking sequences of 2H and 4H polytypes one can deduce the rearrangement of the layers associated with the transformation. Four different stacking sequences, each of them describing the polytype 4H, are presented in figure 1. Additionally, there are three translationally equivalent stackings for each of the stackings I–IV, e.g. $B\alpha C A\beta C = C\beta A B\gamma A = A\gamma B C\alpha B$. If we consider the polytype 2H to be transformed into a perfect structure 4H free of stacking disorder, one domain with the stacking I, II, III or IV should occur in the whole volume of the transformed crystal only. Considering the transition of 2H we must also take into account structures with not fully transformed stacking 2H and structures which are combined of different stacking domains of 4H.

3.4. Refined models of the 4H transformed polytype

Five models were used to refine the transformed structure 4H; the results are summarised in table 1.

3.4.1. Model (a). The model presents a perfect structure 4H which belongs to space group $P6_3mc$ with only three non-equivalent atomic sites in the unit cell to be refined. This model did not converge, however, and has been rejected (extinction parameter refined to a negative value).

3.4.2. Model (b). The stacking sequence of the transformed structure was a combination of the untransformed structure 2H (stacking $B\alpha C B\alpha C \dots$) and of the stacking $B\alpha C A\beta C$ representing the polytype 4H, e.g. the stacking I (figure 1). In other words the model presents domains of 2H combined with those of 4H. The total occupancy of each layer was constrained to 1.0 and the relative occupancies of the positions $B\alpha C$ (untransformed 2H) and $A\beta C$ (transformed 2H) were refined. (Note that according to the density measurements there are only about 80% of the atomic sites occupied but the absolute value of the occupancy of the individual layers has an effect only on the scale factor and not on other refined parameters.) This model including nine occupied atomic sites has been refined to $wR = 0.197$ and is a very poor approximation of the transformed structure.

3.4.3. Model (c). Two alternative stacking sequences of the polytype 4H, domains I and II, are combined in this model (figure 1). In this case we assumed that either the first (I) or the second (II) sandwich of every two subsequent sandwiches I–Pb–I of the 2H stacking $B\alpha C B\alpha C$ is reconstructed to the stacking $A\beta C$ (figure 1). The model includes 12 atoms. The relative occupancies of the atomic sites belonging to the stackings I and II were refined with the total occupancy of every layer constrained to unity. The *R*-factor dropped drastically compared with that of model (b), namely to 0.084. Difference Fourier maps showed, however, extra densities (up to 12% of the highest maxima of the Fourier map) in some sites $ABC\alpha\beta\gamma$ which are not occupied in the stackings I and II, suggesting positional disorder in the layers.

3.4.4. Model (d). This model is a modification of the model (c) for which the occupancies of all hexagonal sites in each layer were refined. The layer sequence is combined from four 4H-type stackings, I–IV (figure 1), each stacking consisting of six atoms. The occupancies of the atomic sites of one given 4H stacking I, II, III and IV were constrained

to one common value; three independent occupancy factors were refined for the domains I–IV. Additionally, the occupancies of the atomic sites which have been unoccupied in the domains I–IV were refined independently. The model includes 24 atomic sites in the 4H unit cell. The fact that $wR = 0.064$ shows that the model is a reasonably good approximation of the crystal structure. There is again a residual electron density in the difference Fourier maps up to 12% of the highest maxima of the Fourier maps.

3.4.5. Model (e). In this final model the occupancies of all the atomic sites permitted for P3m1 were refined independently, as well as the z coordinates of the sites with the largest occupancies. This resulted in a splitting of the atoms in the domains I and II of 4H. Note that, in models (a)–(d), only one coordinate z was refined for every layer in the 4H cell.

The results of the refinement are presented in figure 1 and figure 2; the atomic coordinates, occupancy factors and thermal parameters are listed in tables 2 and 3. The residual difference electron densities dropped to a maximum of 5% of the highest peaks of the Fourier maps. Note that, because of very strong correlations between occupancies, atomic coordinates and anisotropic temperature factors, the thermal parameters of all the Pb and all the I atoms were constrained to one common value, respectively.

The average chemical composition calculated from the layer occupancies in the refined model (e) (the occupancies of all ABC \leftrightarrow $\alpha\beta\gamma$ sites in each layer were included) refers to stoichiometric PbI_2 with an accuracy to better than 0.5%. Taking into account that the model includes 24 independent atomic sites, the good agreement between the chemical composition of model (e) and of stoichiometric 2H is a very strong indication for the correctness of the model.

3.5. Mechanism of the 2H–4H transition

The transition between the stackings 2H and 4H is associated with a very complicated pattern of atomic shifts necessary for achieving the transformation (cf 2H–12R transition (Salje *et al* 1988)). In the analysis of the polytypic transitions it is tacitly assumed that the atoms rearrange within single layers. With this assumption it is difficult to explain the transformation of the crystal from one into another strictly periodic layer stacking in the whole volume. If we like to transform 2H PbI_2 into single-domain 4H, the structural changes nucleated in different parts of the crystal have to be synchronised. Thus the information about the reconstruction of a given layer has to be transferred over tens and hundreds of ångströms to other layers. If it is not so, the equivalent but geometrically different domains (figure 1) would grow independently, and the transformed structure would be heavily disordered. If the crystal structure is to be transformed into one domain, then either the transformation spreads over the whole crystal from a single nucleation centre or the whole structure becomes unstable and the atoms are mobile enough at the transition temperature to create a new stacking which is the most stable among others at given temperature. In practice we always observe disorder accompanying the polytype transitions; an exception is the transition of some large-period polytypes of CdI_2 where the layers to be reconstructed (2H-type stackings) are uniquely defined and ordered periodically (Gierlotka and Palosz 1985).

Recently the transformation of 2H into 12R polytypes in PbI_2 has been discussed by Salje *et al* (1988) as an equilibrium phase transition. It was suggested that the transition looks like a 'knitting' process where the layers or packages of the layers transform subsequently one after another. It was concluded that the process is extremely fast which

probably limits the number of different domains of 12R in the transformed structure with some inter-domain boundaries which can never be removed from the structure.

It is common to accept that ordinary crystals have nearly the crystallographic density. This assumption was the base for the models and mechanisms proposed for the polytype transitions. The reconstruction of the whole structure was considered to occur through reconstruction of individual layers which takes place within the layers owing to and along the dislocations such as Shockley partials (see, e.g., Rai *et al* 1976, Gierlotka and Palosz (1985). The real crystal structure of the 2H polytype of PbI₂ is, however, far from being fully occupied; every fifth atomic site in the Pb and I layers is unoccupied. One could expect that the atoms surrounded by a number of vacancies should be very mobile in the layer planes as well as in the direction perpendicular to them. The activation energy calculated for the transition of 2H into 12R is surprisingly 3.8 eV (Salje *et al* 1988). It suggests a rather high stability of the structure, even when only 80% of the atomic sites in the 2H structure are occupied. Another proof of the high stability of the polytype structures, which is insensitive to the site occupation, comes from the lattice constants measurements; the lattice parameters in the layer plane of different polytypes with different stacking sequences and different densities are similar to within $\pm 10^{-3}$ Å. A relatively weak dependence of the lattice parameter *c* on the polytype structure is observed for various MX₂ polytype materials (Palosz and Salje 1989). Because the close packing in the layers is preserved in any layer stacking, the latent heat for the transformation is expected to be very small. The value of $L = 300$ J mol⁻¹ has been measured for the 2H–12R transition (Salje *et al* 1988) and a similarly small value of *L* can be expected for the 2H–4H transition.

The present work shows very clearly that during the polytype transition not only are the atoms rearranged within single layers, which we tacitly assumed previously, but the Pb and I atoms jump from one I–Pb–I sandwich to the neighbouring ones; the occupancies of some atomic layers decrease from 0.8 to 0.9 (figure 2). At the transition temperature the whole structure of 2H becomes unstable and mobile, and it tends to reconstruct. One cannot expect that the stacking sequence will be free of disorder but the structure may be combined of a rather small number of different domains, possibly; the inter-domain boundaries obviously increase the lattice energy and the number of domains which are in contact should be small. As presented in figure 1, the transformed structure 4H is formed mostly of two kinds of 4H domain: I and II, the stacking I dominating the crystal structure. Domains I and II are formed through reconstruction of single sandwiches BαC of the initial 2H stacking (AβC) in the package. In domain I this sequence is the upper sandwich of the 4H unit cell (the bottom sandwich is BαC as in 2H); in II it is the bottom sandwich. It means that, even when BαC sandwiches of the initial 2H structure reconstruct (second, fourth, etc) then domains I form; when odd sandwiches reconstruct (first, third, etc), domains II result. The relative number of domains I and II varies probably from crystal to crystal and the relative occupancies of domains I and II (0.65 : 0.15) has no particular meaning.

As observed for various polytypic materials the polytype transformations occur in a stepwise fashion. This can be understood as being due either to a pinning of the transformation front on lattice defects or, what seems a more reasonable explanation, the growth of the domains created at the beginning of the transformation is stopped when two domains meet (see discussion of solitons and polytype transformation by Salje *et al* (1988)). At early stages, strongly disordered structures form, indicated by intensity streaks and reflection broadening observed on x-ray patterns (see, e.g., Mingawa 1981, Gierlotka and Palosz 1985, Salje *et al* 1988). When the transformation occurs, the

reflections sharpen corresponding to the growth of some domains at the cost of others. Initially, the domains nucleating spontaneously have very different stackings: altogether there are 12 equivalent stacking sequences in the 4H unit cell (figure 1). The growth process of only some domains could not be understood if one assumes that the lattice reconstruction occurs within single layers only. It is obvious that the stability of the stacking 4H is higher than that of the 2H stacking at the transition temperature, and this is where the driving force for the transformation of the 2H stackings comes from. However, the stacking 2H once transformed in a 4H domain, whatever the particular layer stacking in the domain may be, has no reason to transform again into another 4H stacking; a single layer with its nearest surrounding cannot 'feel' a need to reconstruct again. So it is clear that there are other reasons and forces running the layer reconstruction of the domains created at early stages of the transformation. The experiment shows that polytypes never transform immediately but stepwise or continuously depending on heating conditions. The transformed structure results as a compromise between different domains already existing in the crystal and which must be matched together in a uniform structure having the lowest lattice energy. The interaction between the domains is possible because the atoms can move freely along and across the layers owing to vacancies and the high temperature. We suggest that the density of the structure and the modulation of the layer occupancies determine the final structure of the crystal. Different domains of 4H may have the layer occupancies modulated differently (figure 2). The modulation waves of the domains which make up the final structure are superposed and in the transformed crystal there is only one periodic modulation of the layer occupancy. The stackings superposed in the crystal are among 12 equivalent stackings 4H which consist of the same sandwiches: I \equiv (B α C)(A β C); II \equiv (A β C)(B α C). It should be noted that, if the modulation of the densities in the 4H domains are not 'in phase' (figure 2), a superposition of the modulation waves of different domains would give us the same average occupancy factor for each layer. The transformed structure is dominated by the sequences I and II but there are atomic sites occupied which belong neither to domains I nor to domains II (5–7% of the total number of the atomic sites) (figure 1). We suggest that these atoms occur at the interfaces between the domains which are residuals after the domains created at the early stage of the transformation and subsequently eliminated during growth of domains I and II. As seen in figure 2, two layers of I and one of Pb which have the largest occupancy of 0.9 are split into two sublayers spaced about 0.4 Å apart. This is probably due to the relatively high occupancy of the layers and the density gradient in the stacking.

The present study does not allow us to conclude that the modulation of the occupancy of the atomic layers is an invariable property of 4H PbI₂, as has been observed earlier for SnS₂ polytypes (Palosz *et al* 1989a) but not for the polytype 4H of CdI₂ (Palosz *et al* 1989b). If the density of the polytype crystals and the occupancy modulation of the layers do have a strong influence on the stability of the structure, we can expect the polytype phases with small occupancy to transform under pressure into phases with larger occupancies. High-temperature and high-pressure experiments on SnS₂ and PbI₂ polytypes are currently being performed.

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References

- Becker P S and Coppens P 1974 *Acta Crystallogr. A* **30** 129–53
Gierlotka S and Palosz B 1985 *Cryst. Res. Technol.* **20** 47–52
Hanoka J I and Vand V 1968 *J. Appl. Phys.* **39** 5288–97
International Tables for X-ray Crystallography vol IV 1974 (Birmingham: Kynoch)
Mingawa T 1979 *J. Appl. Crystallogr.* **12** 57–9
—— 1981 *J. Phys. Soc. Japan* **50** 902–6
Palosz B, Gierlotka S, Wiktorowska B and Dziag D 1985 *Acta Crystallogr. C* **41** 1407–9
Palosz B, Palosz W and Gierlotka S 1986 *Bull. Mineral.* **109** 143–50
Palosz B and Salje E 1989 *J. Appl. Crystallogr.* **22** 622
Palosz B, Steurer W and Schulz H 1989a *Acta Crystallogr.* at press
—— 1989b to be published
Rai A K, Tiwari R S and Srivastava O N 1976 *Phys. Status Solidi a* **35** 719–24
Salje E, Palosz B and Wruck B 1988 *Adv. Phys. Geochem.* **7** 217–39
Sorokin N D, Tairov Yu M, Tsvetkov V F and Chernov M A 1983 *Sov. Phys.–Crystallogr.* **28** 539–42
Vodakov Yu A, Lomakina G A and Mokhov E N 1983 *Sov. Phys.–Solid State* **24** 780–4
Zucker U H, Perenthaler E, Kuhs W F, Bachmann R and Schulz H 1983 *J. Appl. Crystallogr.* **16** 11–6