

Martensitic Phase Transitions in Molecular Crystals – *p*-Dichlorobenzene

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β -Phase *p*-dichlorobenzene bicrystals, mechanically deformed β single crystals, and crystals undergoing a $\beta \rightarrow \alpha$ phase transformation have been examined optically and by X-ray diffraction. Frequently occurring boundaries between two crystals and the mutual orientations of the crystals may be explained by an *epitaxial* relation between two simple faces of each of the crystals. It is proposed that the mechanism of *nucleation* of the daughter (α) phase involves a balance between the coherence range of a series of fluctuations in molecular orientation and a critical nucleus size (determined by a further balance of bulk and surface forces in the nucleus). This is sufficient to explain α -nuclei orientations, association of nucleation with defects, and sensitivity of nucleation to temperature, doping, and deuteration. In some crystals the *growth* of daughter nuclei (both α and β) is rapid. Some crystal defects can slow growth and increase nucleation rates drastically. This work suggests that the previous distinction between martensitic and other nucleation-growth mechanisms in molecular crystals is an oversimplification. Molecular first-order phase transitions are fundamentally martensitic. Obscuring factors such as the large number of alternative pathways, and the extension in range of possible nuclei orientations caused by defects are briefly discussed.

Introduction

Phase transitions in metals are often martensitic. The characteristics of a martensitic transformation are that it is heterogeneous, involving nucleation of a crystal and its subsequent rapid growth by a mechanism involving no long-range translational diffusion. The crystal's mutual orientations, habit plane, and distortion are all crystallographically determined; as are many other crystal properties (Christian, 1965; Shewman, 1965; Bollmann, 1970).

In a series of papers on phase transitions in molecular crystals (Kitaigorodsky, Mnyukh & Asadov, 1965; Mnyukh & Petropavlov, 1972; Mnyukh & Panfilova, 1973; Mnyukh, Panfilova, Petropavlov & Uchvatova, 1975) it was concluded that the daughter crystal is apparently oriented *randomly* with respect to the parent in the great majority of cases. This is in spite of the conceptual similarity in some other respects of their proposed nucleation-growth mechanism to a martensitic transformation, such as appears to occur in at least some molecular crystals (Mnyukh *et al.*, 1975; Jones, Thomas & Williams, 1975).

We have performed experiments on the $\beta \rightarrow \alpha$ -*p*-dichlorobenzene phase transition to try to resolve why molecular crystals and metals apparently differ. We chose *p*-dichlorobenzene owing to Mnyukh's paradigmatic use of it in his argument for a non-martensitic mechanism in most phase transitions in molecular crystals.

Previous experiments have shown that *p*-dichlorobenzene at zero pressure has at least three crystalline phases β , α and γ (Figuière, 1973, and references therein). Below about 272 K the γ -phase is the thermodynamically most stable; α between 272 and 304; and β between 304 and the melting point at 326 K. In the

P-T diagram there is a triple point ($\alpha\beta\gamma$) at 1 kbar and 301 K. The crystal structures of the three phases are closely related (Croatto, Bezzi & Bua, 1952; Frasson, Garbuglio & Bezzi, 1959; Housty & Clastre, 1957; Fourme, Clech, Figuière, Ghelfenstein & Szwarc, 1974; Wheeler & Colson, 1975). We write the unit cell of β , which is of $P\bar{1}$ symmetry, $Z = 1$, as $[a, b, c, \hat{\alpha}, \hat{\beta}, \hat{\gamma}]$. The cell angles $\hat{\alpha}$ and $\hat{\gamma}$ are both nearly 90° making the cell almost monoclinic. α 's cell is almost $[2a, b, c, 90, \hat{\beta}, 90]$; and γ 's non-primitive cell is almost $[2a, b, 2c, 90, \hat{\beta}, 90]$. Both α and β are $P2_1/c$, $Z = 2$, differing from β mainly by the introduction of twofold screw axes along **b**. In crystals grown from solution or by sublimation the phase transformation is apparently initiated at specific, defective, points in the crystal. It proceeds by steps running *across* the face of the well faceted daughter crystal. The nucleation process is facilitated in β -crystals by pricking. The most perfect β -crystals cannot be induced to transform even by vigorous mechanical coercion (Kitaigorodsky *et al.*, 1965). Use of perdeutero-*p*-dichlorobenzene also slows the process of transformation markedly (Colson & Wheeler, 1974). If we cycle the crystals through the $\alpha \leftrightarrow \beta$ transition then a 'memory' is observed. Laue photographs show that the orientation of the starting α -crystal is likely to be reproduced by subsequent α -crystals.

Tseneva (1969) has observed, in β -dichlorobenzene $(100)_\beta$ plates, that the angle between $[001]_\beta$ and the projection of $[001]_\alpha$ or $[010]_\alpha$ onto $(100)_\beta$ is non-random. It clusters at values of $8\frac{1}{2}$, 17 and 32° . Mnyukh & Petropavlov (1972), by contrast, observe that the angle between $[001]_\beta$ and $[001]_\alpha$ projected onto unspecified faces, and the angle between $[001]_\beta$ and the projection of the parent-daughter interface onto $(100)_\beta$, are both apparently random. This is at first sight inconsistent with a martensitic mechanism, as

well as Tseneva's observation. Unfortunately neither specify their method of crystal preparation.

Our results reconcile these apparently conflicting results and provide firmer evidence for a mechanism allowing a large number of martensitic pathways.

Experimental

β-Crystal morphology

We prepared *β*-*p*-dichlorobenzene crystals by sublimation from a glass surface at 320 K through 5 cm on to a glass surface at 300 K. Needles grew rapidly, followed by crystals of prismatic and plate-like habit. Microscopic examination of interfacial angles and optical properties showed that the needles and prisms were *β*-phase (Colson & Wheeler, 1974). Some of the plates were *β*-phase, but most were *α*-phase. The average area of faces in the *β*-phase prisms observed was (100) ≫ (010) > (001) > (11 $\bar{1}$) > (10 $\bar{1}$), as previously observed (Manghi, De Caroni, De Benyacar & De Abeledo, 1967). The prisms sometimes had a stepped, flat pyramidal configuration. Most needles were hollow of approximately square, thin-walled-box cross-section, of long axis [001] bounded by (100) and (010). The hole was of size $\sim 10^{-4}$ m. This implies, if we assume a screw-dislocation mode of needle growth, a screw dislocation with Burgers vector of about 300 Å along [001]. The elastic stress energy around the axial screw dislocation can be minimized by the whole crystal twisting about the screw axis to become macroscopically helical (Eshelby, 1953). The size of the Burgers

vector leads us to expect a twist of several hundred degrees per metre in a $\sim 10^{-4}$ m diameter crystal with axial elastic isotropy and a circular cross-section. In these box cross-section, elastically anisotropic crystals we observe a twist of less than 100° m^{-1} . Both the (100) and (010) faces are corrugated along [001], the angle between neighbouring corrugations being about 4° . Weissenberg photographs reveal twinning commonly on (110), and once on (100). The surfaces between the twinning corrugation are still generally not flat to within 50° m^{-1} , being convex, concave or twisted. This may result from residual thermal and Eshelby stress which twinning has not relieved.

Approximately 5% of all prismatic and plate-like crystals were not single. In most cases there were two (or more) distinct, well formed, crystals. They were joined on a habit plane which was rational in *both* crystal unit-cell orientations, to within our accuracy of measurement ($\sim 3^\circ$). We have listed some 27 such hybrid crystals in Table 1. These were observed consecutively, and at random, from 10 separate sublimations. We have listed the habit plane, indexed in the two crystals *A* and *B*; and two pairs of vectors (V_1^A, V_2^A and V_1^B, V_2^B) parallel in the two crystals which define this habit plane. It will be noted that in 18 of the orientations the two crystals have a vector in common in the habit plane. In seven of these cases the crystal is twinned [on (001) and (010)]. It is apparent that these observations may be explained by predicating the necessity for an epitaxial relation between the two crystals. In all cases the two short (≤ 12 Å) vectors listed (V_1^A and V_1^B and also V_2^A and V_2^B) match in length to within 20%. The angle between the corresponding vectors in the same crystal (V_1^A and V_2^A) differs from that in the other crystal (V_1^B and V_2^B) by less than 10° . The frequency of occurrence of vector pairs is 50% identical ($V_1^A \equiv V_1^B$), 14% $[010]_A \parallel [101]_B$, 10% $[011]_A \parallel [002]_B$, 10% $[100]_A \parallel [011]_B$, and six others, individually, less than 5%. This frequency pattern suggests that there are at least four other pairs of vectors of infrequent occurrence which we did not observe. The relative frequency of observation of crystal vector pairs suggests that there are many more than 30 possible types of crystal boundary. A typical crystal boundary type may be produced by about four different crystal orientations. There are therefore in excess of 100 possible sets of Eulerian angles specifying the crystal's mutual orientations.

We have written a computer program to enumerate all the possible mutual crystal orientations in which there is an epitaxial habit plane, defined within the experimentally obtained 20% length tolerance, 10° angle tolerance and vector length less than 17 Å. We find 642 distinct orientations, of about 150 crystallographically non-degenerate types. This number may be reduced because some mutual orientations involve energetically unattainable boundary configurations. This is in agreement with the experimental result of ≥ 30 . Even such a large number of orientations is still far from non-random. If spread evenly in Euler-angle

Table 1. Grain boundaries in *β*-phase *p*-dichlorobenzene bicrystals

Habit plane		V_1^A	V_1^B	V_2^A	V_2^B
<i>A</i>	<i>B</i>				
(011)	(010)	[100]	[100]	[011]	[002]
(100)	(11 $\bar{1}$)	[002]	[011]	[010]	[101]
(011)	(010)	[100]	[100]	[011]	[002]
(10 $\bar{1}$)	(001)	[010]	[010]	[101]	[100]
(011)	(100)	[011]	[011]	[100]	[011]
(100)	(11 $\bar{1}$)	[002]	[011]	[010]	[101]
(10 $\bar{1}$)	(100)	[101]	[010]	[001]	[001]
(001)	(001)	[010]	[010]	[100]	[100]
(100)	(100)	[020]	[003]	[003]	[020]
(001)	(001)	[010]	[010]	[100]	[100]
(001)	(10 $\bar{1}$)	[010]	[010]	[100]	[101]
(010)	(010)	[001]	[001]	[100]	[100]
(001)	(001)	[100]	[100]	[010]	[010]
(001)	(001)	[100]	[100]	[010]	[010]
(10 $\bar{1}$)	(001)	[010]	[010]	[101]	[100]
(001)	(11 $\bar{1}$)	[010]	[101]	[100]	[011]
(100)	(111)	[010]	[101]	[002]	[011]
(100)	(001)	[010]	[010]	[100]	[002]
(011)	(011)	[100]	[011]	[011]	[100]
(001)	(001)	[010]	[010]	[100]	[100]
(011)	(011)	[011]	[011]	[100]	[100]
(100)	(11 $\bar{1}$)	[011]	[011]	[012]	[101]
(010)	(010)	[100]	[100]	[001]	[001]
(001)	(11 $\bar{1}$)	[010]	[101]	[100]	[011]
(100)	(010)	[010]	[101]	[001]	[001]
(010)	(100)	[100]	[002]	[002]	[011]
(011)	(111)	[100]	[011]	[011]	[101]

space the average separation of nearest neighbours is still 33° .

β -Crystal mechanical deformation

Three-point deformation, with sharp, pointed tweezers and a needle, of an untwinned optically perfect sublimation-grown needle of β -phase *p*-dichlorobenzene perpendicular to either $(010)_\beta$ or $(100)_\beta$ gives an audible click. The crystal has then formed a pair of mirror flat $(1\bar{1}1)$ planes separated by a region in which the original $[001]$ has been rotated around $[110]$ by up to about 15° . Apart from this 'kinking' the crystal remains perfect and straight edged. Gentle brushing of the crystal with a needle induces rapid motion along $[001]$ of the $(1\bar{1}1)$ boundaries. They will mutually annihilate to produce an apparently single crystal again. In crystals containing twins, or perfect crystals which have been bent and restraightened thus creating dislocations, motion of the $(1\bar{1}1)$ boundary is more difficult to produce. Sometimes other boundary planes were produced [e.g. $(1\bar{2}1)$, $(1\bar{1}\bar{1})$, $(0\bar{1}1)$, $(10\bar{1})$, $(1\bar{1}2)$], often a *different* plane at each end of the 'kink'. These other boundary planes tended to decay by growth of $(1\bar{1}1)$ from one corner of the boundary. The crystal on either side was undisturbed, apart from slight changes in the angle of tilt around $[110]$, which varied from ~ 5 – 15° . We have twice observed a phase transition from $\beta \rightarrow \alpha$ in such a kinked crystal. The phase boundary passed smoothly without any bending or hesitation through the kinked region leaving it apparently undisturbed.

We can conclude that the stress-induced deformation kinking produces a new β -crystal by a martensitic process. The angle of tilt of the kinked region is approximately consistent with an epitaxial habit plane in which $(1\bar{1}1)_{\beta_1}$ of the original crystal is stuck to $(1\bar{1}0)_{\beta_2}$; and where $[011]_{\beta_1} \parallel [002]_{\beta_2}$ and $[110]_{\beta_1} \parallel [110]_{\beta_2}$. Since $[002]_{\beta_1}$ is almost parallel to $[011]_{\beta_2}$ there are many vectors nearly parallel in β_1 and β_2 . There is the possibility of many different planar boundaries between β_1 and β_2 for the same mutual orientation, as is observed. This single mutual orientation is that almost always produced, but on two occasions a kink of $\sim 45^\circ$ not 15° was produced. This kink was too unstable to measure, recombining very speedily.

X-ray observation on the $\beta \rightarrow \alpha$ phase transition

We have grown crystals of β -phase *p*-dichlorobenzene from the melt, in thin-walled 3×10^{-4} m diameter quartz tubes. We raised them out of a water bath maintained at 328 K into air at 295 K at a rate varying between 5×10^{-5} and 2×10^{-6} m s $^{-1}$. Oscillation and Weissenberg photographs were taken on a Nonius camera with Ni-filtered Cu $K\alpha$ radiation. They revealed that the 'mosaic spread' of the resulting single crystal varied from 20° for the faster rate to a small amount ($< 0.5^\circ$) for an intermediate rate (10^{-5} m s $^{-1}$), with a corresponding improvement in optical homogeneity. The axis of the tube corresponded within 3° to

$[001]_\beta$ for the more perfect crystals. The direction of maximum thermal gradient did not affect the alignment of $[001]_\beta$ along the tube axis. The mosaic spread of less perfect crystals was elongated along $[001]_\beta$, suggesting that tilt boundaries involving dislocations of Burgers vectors $[001]$ are easily formed. These more rapidly grown crystals occasionally contained a number of β -crystals. The relative mutual orientations could be explained in a similar way to sublimation-grown bicrystals as being epitaxially determined. For example we have seen a twin on (110) ; $(10\bar{1})_{\beta_1}$ attached to $(001)_{\beta_2}$ ($[101]_{\beta_2} \parallel [010]_{\beta_2}$ and $[010]_{\beta_1} \parallel [001]_{\beta_2}$); and $(10\bar{1})_{\beta_1}$ attached to $(100)_{\beta_2}$ ($[101]_{\beta_1} \parallel [100]_{\beta_2}$ and $[001]_{\beta_1} \parallel [001]_{\beta_2}$).

To demonstrate unambiguously the crystallographic relation between parent β -phase and daughter α -phase it is necessary to induce a phase transformation after alignment of the parent β -phase. We find that β -crystals of acceptable mosaic spread ($\sim 2^\circ$ or better) cannot be induced to transform. Cycling rapidly 10 times between 273 and 313 K, followed by smashing the crystal tip with pliers, and then leaving for 3 months would not induce transformation. In one case we have observed a $\beta \rightarrow \alpha$ transformation in an aligned crystal out of a dozen or more trials. We have found that if we dope the melt with $\frac{1}{4}$ at.% of *p*-dibromobenzene then transformation is much facilitated. As soon as the local temperature drops below ~ 304 K an audible click is heard and phase transformation is later found to have occurred. We assume, as will be discussed later, that the doping facilitates nucleation without affecting the growth, orientation, or perfection of the crystal significantly. We are then able to extract, to an accuracy of $\sim 3^\circ$, the orientation of $[001]_\beta$ (*i.e.* the tube axis) relative to the daughter α -crystal. We have lost one degree of freedom, out of three, in specifying the mutual crystal orientations. Increase of *p*-dibromobenzene to 10 at.% produces no further changes. A transformation still occurs to similar mutual orientations. This strengthens our belief that doping, grossly, only alters the nucleation probabilities.

We have examined 15 crystals, doped with $\frac{1}{4}$ at.% *p*-dibromobenzene, which had transformed to optically homogeneous and transparent α -phase. We observed six orientations of the α -lattice with respect to the tube axis. In undoped crystals which are grown at the same, slow, rate and also have a good mosaic spread ($< 0.5^\circ$) the tube axis corresponds to $[001]_\beta$ in all of the more than twenty cases studied. This leads us to presume that in the doped crystals the parent β -crystal initially grows from the melt with $[001]_\beta$ also corresponding to its tube axis. The orientations listed in Table 2 make this assumption. We are able to rationalize the observed directions of $[001]_\beta$ in the α -lattice in terms of the simple epitaxial relations listed. We have written the α -vectors in terms of the β -cell *i.e.* $[200]_\alpha = \text{unit-cell } a \text{ axis in } \alpha\text{-phase}$.

The epitaxial relations we have listed are not unique but are ones which will satisfy the habit-plane criteria

found for β -phase bicrystals. The last case listed was also observed for the pure *p*-dichlorobenzene for which we were able to completely fix the crystals' mutual orientations. We have calculated whether the epitaxial relations we have found are also endotaxial: *i.e.* if there is a pair of simple crystal vectors, out of the habit plane, which match within observed criteria. In the first, fourth and fifth case observed this is so, but not in the other three cases. We have computed the number of endotaxial relations possible. Of the 642 possible epitaxial relations only 188 have out-of-plane matching vectors. Many have more than one such vector, producing a total of 766 endotaxial relations. It thus appears that it is epitaxy which is favoured in the phase transformation, and that simple endotaxy does not play a role.

Case No. 4 is endotaxial, and the observed epitaxial relation is that most commonly observed in mechanical deformation. We may speculate that we do not observe many other epitaxial relations since they imply a substantial crystal strain (rotating about $[001]_{\beta}$) which cannot occur in a crystal confined in a quartz tube. Some transformations shatter the tube when they occur. The crystallographic relationship required probably generates an unsupportable stress, even in this soft molecular crystal. The angles between $[001]_{\beta}$ and $[001]_{\alpha}$ which we have observed are consistent with Tseneva's high frequency of observation of 17 or 73°, and 35 or 55°. We did not observe any 8 or 82° values, perhaps because our linear crystal growth and confinement was more restrictive than the unconfined plates which Tseneva used.

Discussion

Crystal boundaries

We postulate three ideal types of crystal boundaries. (a) Fully coherent, with dislocations whose Burgers vectors are in the habit plane. Atomic positions across the habit plane are related. The habit plane will have rational indices in both crystals. (b) Fully coherent, with dislocations whose Burgers vectors are both in and out of the habit plane so as to produce the best possible 'matching' (Bollmann, 1970). The dislocation content will cause the habit plane to be irrational in either or

both the crystals. It will be crystallographically determined by ratios of appropriate vector lengths in each crystal. (c) Fully incoherent, no dislocations. The dislocation core of case (a) is so diffuse as to cause the mutual molecular distances across the habit plane to be random. The habit plane will be rational in both crystals.

In an incoherent boundary we would not expect that each crystal's vectors in the habit plane should match in lengths. We do observe such matching lengths which suggests at least partial coherence across the habit plane. The habit planes we observe in mechanical deformation are not quite rational. The habit plane and associated rational planes in each crystal are always nearly parallel under our experimental conditions – much more so than the ratios of vector lengths would predict. The real system appears to most closely approximate ideal case (a).

Crystal phase transformation

Crystal transformation appears to proceed by a slow process of nucleation (Kitaigorodsky *et al.*, 1965) whether it is recrystallisation ($\beta_1 \rightarrow \beta_2$) or phase transformation ($\beta \rightarrow \alpha$). Once this occurs (*i.e.* when there is an observably large transformed region), the rate of transformation of the remainder of the crystal is faster.

1. *Nucleation.* The faster the parent crystal is grown the more likely is phase transformation. The nucleation process therefore involves lattice defects. This is also shown by the need for a needle-prick to induce recrystallization in mechanically deformed β -crystal needles, and nucleation nearly always occurring at the same site in a crystal repeatedly thermally cycled through the transformation (Kitaigorodsky *et al.*, 1965).

The mutual orientation of the parent and daughter crystals is apparently determined when the daughter crystal is small, probably during the process of nucleation. We postulate that a nucleus is produced by a series of fluctuations of a large number of molecules over a large angle. The energy of the nucleus depends on the energy of the parent–daughter interface (proportional to $+ \text{Volume}^{2/3}$), and the stress energy and transition energy released (proportional to $- \text{Volume}$).

Table 2. Mutual orientation of α and β -crystal lattices

Direction of $[001]_{\beta}$ in lattice	Angle between $[001]_{\beta}$ and $[001]_{\alpha}$		Habit plane		Epitaxial relation		
	Observed frequency		α	β	V_{α}^1	V_{β}^1	V_{β}^2
$[001]_{\alpha}$	0	2	(001)	(001)	$[020]$	$[202]$	$[202]$
$[0\cdot15,0,1]_{\alpha}$	16	2	(20 $\bar{1}$)	(20 $\bar{2}$)	$[010]$	$[010]$	$[201]$
$[0\cdot3,0,1]_{\alpha}$	35	6	(20 $\bar{2}$)	(001)	$[010]$	$[010]$	$[202]$
$[011]_{\alpha}$	55	2	($\bar{2}20$)	(1 $\bar{1}1$)	$[220]$	$[220]$	$[002]$
$[021]_{\alpha}$	73	2	various		$[011]$	$[011]$	$[211]$
						or	or
							and
$[010]_{\alpha}$	87	1	(001)	(010)	$[020]$	$[003]$	$[212]$
							$[200]$
							$[203]$
							$[202]$

This quantity reaches a maximum as the nucleus grows. A nucleus reaching this 'critical' size is likely to continue its growth to produce a macroscopic daughter crystal. This critical size must be small in order that it can be reached by fluctuations. This resembles the standard nucleation theory of liquids (Strickland-Constable, 1968). We estimate the interfacial Helmholtz free energy of an epitaxial face as 5 kJ mol^{-1} and of a 'bad' incoherent face as 15 kJ mol^{-1} at 294 K, 10 K away from the transition temperature. These have been calculated by assuming: (1) Dislocation-core Helmholtz free energies per molecule length are given by twice the sublimation Helmholtz free energy; (2) Interfacial free energies are given by the sum of the core free energies of the dislocations required to construct the interface; (3) On an epitaxial face there are, on average, 10 molecules between each dislocation core (*i.e.* a lattice vector match of 10%). Correspondingly on an incoherent face the cores are separated by three molecules. These assumptions are sufficiently gross that the energies obtained are only 'order of magnitude' accurate – good enough for our purposes here.

We further estimate the Helmholtz free energy of the $\alpha \rightarrow \beta$ transition as $-0.05 \text{ kJ mol}^{-1}$ at 294 K (Figuière, 1973; Walsh & Smith, 1961). On minimizing the Gibbs free energy these give a critical nucleus size of $\sim 5 \times 10^8$ molecules for an arbitrarily oriented nucleus. Orienting the nucleus so that two faces are epitaxial reduces this by a factor of 10 also giving a spheroidal nucleus of oblateness 3:1. The surface energy needed in nucleation can be reduced by moving those dislocations needed on the nucleus faces from a nearby suitable dislocation for little energy cost. This may give a further factor of 10 reduction in nucleus size. Only some nucleus orientations have faces in which a given dislocation is necessary to give coherence. If nucleation reduces local stresses we may gain another $\sim 10^3$ in size. We now have a critical nucleus size of $\sim 10^3$ molecules which may just be obtainable by thermal fluctuations. The nucleus *must* now be (*a*) epitaxially aligned (*b*) of suitable orientation. It must also be near enough to a dislocation that local stress relief and dislocation 'borrowing' occur significantly. These conditions are very restrictive. The transition free energy plays little significant role. We therefore expect recrystallization ($\beta_1 \rightarrow \beta_2$) to occur in a similar way.

This mechanism explains why β -deutero-*p*-dichlorobenzene has a smaller nucleation rate (Colson & Wheeler, 1974), whereas $\frac{1}{4}$ at. % doping with *p*-dibromobenzene increases it. Deuteration, by increasing the molecular moments of inertia, decreases the frequency of attainment of a given excursion in molecular orientation. An appropriate series of fluctuations to produce the critical nucleus, whose size is not changed significantly by deuteration, thus becomes less likely. If we dope a small percentage of *p*-dibromobenzene in the crystal it is likely to interact with any defects present. Around a dislocation the local impurity concentration

may be substantially increased. This has two effects. The increased 'average' moment of inertia will decrease the nucleation frequency. Opposing this, the stable phase of dibromobenzene is α -phase of similar unit cell to α -*p*-dichlorobenzene (β -*p*-dibromobenzene is not known). We postulate, for illustrative purposes only, an $\alpha \rightarrow \beta$ transition Gibbs free energy of 4 kJ mol^{-1} and a local concentration of 10%. The critical nucleus size is reduced by a factor of 10^3 at 20°C. The critical nucleus size is now of the order of 10 molecules, an easily attainable figure. Lastly the nucleation rate decreases rapidly away from the transition temperature. The transition may be regarded as a typical order (β) \rightarrow disorder ($\alpha + \beta$) \rightarrow order (α) transition, which is never attained because thermal expansion causes a prior first-order transition, as in adamantane (Reynolds, 1975*b*). Large 'critical' fluctuations from local β to local α may be expected which decrease very rapidly with temperatures away from the transition. The necessary critical volume of the nucleus needed exceeds the size of fluctuations only near the transition temperature. We might expect that solution-grown crystals, which contain a wide range of large Burgers vector growth dislocations, arising from the initial 'seed' of the crystal, would exhibit more variation in parent-daughter orientations than either sublimation or melt-grown crystals where there are fewer types of dislocations and where the stress field near each dislocation is not as variable. This, besides the insensitivity of the type of measurement (projection of three Euler angles into a single line in Euler space, as opposed to our plane), may be another reason for previous failure to observe special mutual orientations (Mnyukh & Petropavlov, 1972).

2. *Crystal growth.* As the $\beta \rightarrow \alpha$ transformation progresses the area of the 'epitaxial' matching may increase at the expense of other faces in the nucleus, until the parent and daughter crystals are only separated by this face. Growth of α perpendicular to this face will be slow owing to facial coherence causing an activation energy of the order of 50 kJ mol^{-1} . A step may be produced in the face by nucleation of a small area of a new layer; or a step may already exist by virtue of a screw dislocation passing through the nucleus. The barrier to rotation of molecules at that incoherent face may be less than that at a coherent face. There is also no necessity for long-range translational diffusion at the face. The step-face may therefore move at speeds up to vibrationally determined speeds ($\sim 10 \text{ m s}^{-1}$). Perhaps this involves motion of partial dislocations as suggested in other crystals (Parkinson, Thomas, Williams, Goringe & Hobbs, 1976). Such steps are observed and they do move rapidly. Stress-induced recrystallizations of sublimation-grown nearly perfect needles ($\beta_1 \rightarrow \beta_2$), and phase transformations in melt-grown crystals of low mosaic spread doped with small amounts of *p*-dibromobenzene ($\beta \rightarrow \alpha$), both give audible clicks. This implies that growth steps attain a speed of greater than 0.1 m s^{-1} , and therefore that the moving crystal

boundary does not interact strongly with the types of crystal defect in these crystals. However, sometimes growth is less rapid ($\sim 10^{-5} \text{ m s}^{-1}$) and shows a large activation energy ($\sim 70 \text{ kJ mol}^{-1}$) (Kitaigorodsky *et al.*, 1965). We assign this to growth occurring in crystals which contain more types of defects such as dislocations. The activation energy then arises from the necessity for jogging, kink motion, climbing, *etc.* of some of these types of dislocations when the boundary moves through the crystal; for which $\sim 70 \text{ kJ mol}^{-1}$ is a reasonable value for the activation energy. Further evidence comes from cycling a given crystal through the transition. Initially the rate of transformation increases, presumably as a result of some imperfections being easily swept out of the crystal. However, the rate soon begins to decrease again, perhaps because each transformation creates a number of relatively fixed defects by interaction of the dislocations in the boundary with others already in the crystal.

Conclusions

1. Boundaries

Boundaries between crystals occur more frequently and may have lower energy if they can be interpreted in terms of an epitaxial fit ($\pm 20\%$) between two simple planes in each crystal. Boundaries produced during sublimation growth, mechanical deformation, and $\beta \rightarrow \alpha$ -phase transition in *p*-dichlorobenzene crystals all support this hypothesis. As the experiments become more 'drastic', and the crystals less perfect, the boundary can occur in a wider and wider angular variation about the rational planes in each crystal. The condition of epitaxy implies some coherence between molecular positions in each crystal across the boundary.

2. Crystal nucleation

The observed crystallographically defined 'epitaxial' orientation of α or β -daughter nuclei in a parent β -lattice, and also the effect on the nucleation rate of doping with *p*-dibromobenzene, use of perdeuterio-*p*-dichlorobenzene, temperature and mechanical 'pricking', may be explained in terms of a necessary 'critical size' of nucleus being exceeded by a 'fluctuation' in molecular coordinates.

Large thermal fluctuations may occur since the transition can be likened to an order (β) \rightarrow disorder ($\alpha + \beta$) \rightarrow order (α) transition, although the lattice expansion causes a discontinuity which skips most of the disorder regime (Reynolds, 1975*b*). The extent of the typical fluctuation depends sensitively on proximity to the transition temperature, and also, depends on molecular moments of inertia.

The critical size is determined by a balance between surface energy needed in nucleation and bulk energy gained. In *p*-dichlorobenzene the fluctuation size is generally only just able to exceed the critical size when the following conditions minimize the critical size: (a) orientation of the nucleus to form a large epitaxially

fitting area; (b) borrowing from existing crystal dislocations those dislocations needed to fit the nucleus to the parent lattice; (c) increasing the bulk transition energy by nucleation near a defect where strain-energy can be large and suitable dopants may be concentrated.

In less perfect crystals the larger variety of dislocations and stress environments available both increase nucleation rate and relax the restrictive conditions on nucleus orientation.

3. Crystal growth

If nucleation can be induced then growth to a macroscopically transformed crystal in a good crystal is rapid ($> 0.1 \text{ m s}^{-1}$), which implies a diffusionless process with a small activation energy. The growth induces a crystallographically determined distortion. This is typical of a martensitic transformation.

In less perfect crystals the boundary and its associated dislocations interact strongly with other crystal defects. This produces a substantial activation energy and a slowing in transformation rate by $\sim 10^5$.

4. Attainment of crystal equilibrium

It has been postulated (Reynolds, 1975*a*) that near the transition substantial molecular orientational disorder is needed to minimize the Gibbs free energy. However, attainment of such orientational equilibrium will be as difficult as the phase transition. Experimental observation of orientational disordering will thus depend on whether nucleation is feasible, and may require substantial straining or doping of the crystals.

5. Relevance to other crystals

The conclusions which we have drawn for *p*-dichlorobenzene are well known in metallic systems. The only substantive difference is that the range of *alternative* martensitic pathways available increases by a factor of, perhaps, one hundred. This is because of the change from simple cubic or hexagonal systems to monoclinic or triclinic, with the associated reduction in symmetry. We expect that discontinuous transitions in all molecular crystals proceed by martensitic mechanisms. This has already been recognized in a minority of molecular crystals in which only a few martensitic pathways occur. This happens either because more symmetric unit cells appear, or because asymmetry in forces or structure in the crystal favours particular nuclei orientations, with favourable epitaxial faces. In other crystals there is already some circumstantial evidence for martensitic transitions. Examples are *p*-nitrophenol where there are rapid polycrystal \rightarrow single-crystal phase transitions (Cohen, Coppens & Schmidt, 1964); and in anthracene dimerization the daughter crystal orientation is epitaxially determined (Julian, 1972). Use of very imperfect crystals may mask this mechanism by altering rates of transformation and relaxing the mutual orientation requirements of parent and daughter crystals.

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Representation of the Fast-Rotation Function in a Polar Coordinate System

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Crowther's fast-rotation function [Crowther (1972), *The Molecular Replacement Method*, edited by M. G. Rossmann, pp. 173–183. New York: Gordon & Breach] expression has been modified in a manner in which it is convenient to explore spherical polar coordinates rather than Eulerian angles.

The 'rotation function' (Rossmann & Blow, 1962) has been widely used in the initial stages of the solution of protein structures. The computation of this function (Tollin & Rossmann, 1966) is, however, exceedingly time consuming. Crowther (1972) has shown that the same function can be computed very much faster in Eulerian space when each Patterson function is expanded as a product sum of spherical harmonics and spherical Bessel functions. It is, however, often convenient to plot the rotation function in terms of spherical coordinates where specific sections represent searches for specific rotation axes (*e.g.* diads, triads *etc.*). Shown here is how Crowther's fast-rotation function can be easily recast in terms of spherical coordinates, necessitating only minor changes in the corresponding computer program. This is done by applying Eulerian rotations to *both* Patterson functions such that the third rotation is relative to a polar axis.

Rossmann & Blow (1962) defined the rotation function as the integral of the product of the Patterson

function $P_1(\mathbf{x})$ and the rotated Patterson function $\mathcal{R}P_2(\mathbf{x})$ such that

$$R(\Omega) = \int_U \{P_1(\mathbf{x})\} \{\mathcal{R}P_2(\mathbf{x})\} dV,$$

where Ω is the angle of rotation, the integral is evaluated within a volume U , and dV is an elementary unit of volume. If the rotation \mathcal{R} is expressed in terms of Eulerian angles α, β, γ as defined by Rossmann & Blow (1962), and if the first Patterson function is also rotated by $\alpha, \beta, 0$ then

$$\begin{aligned} R(\alpha, \beta, \gamma) &= \int_U \{\mathcal{R}(\alpha, \beta, \gamma=0)P_1(\mathbf{x})\} \{\mathcal{R}(\alpha, \beta, \gamma)P_2(\mathbf{x})\} dV \\ &= \int_U \{P_1(\mathbf{x})\} \{\mathcal{R}^{-1}(\alpha, \beta, \gamma=0)\mathcal{R}(\alpha, \beta, \gamma)P_2(\mathbf{x})\} dV. \end{aligned}$$

But

$$\mathcal{R}^{-1}(\alpha, \beta, \gamma=0)\mathcal{R}(\alpha, \beta, \gamma) = \mathcal{R}'(\gamma, \beta, \alpha) \equiv \mathcal{R}_p(\varphi, \psi, \kappa)$$