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Molecular Mechanism of Polymorphic Transitions

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Molecular Mechanism of Polymorphic Transitions

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It is shown that serious problems arise with the usual classification and proposed mechanisms for polymorphic transitions in crystals. On the basis of the investigation of polymorphic transitions in molecular crystals, we propose here an alternative scheme which, we believe, avoids these problems and more successfully explains the behavior of real crystals during polymorphic transitions than previous schemes have done.

1 INTRODUCTION

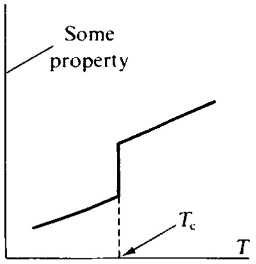
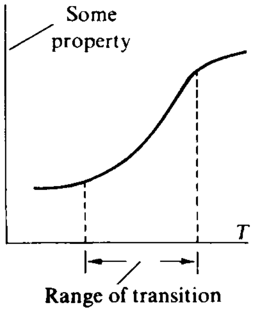
First of all, it is useful to define the two notions in the title of the paper. *Polymorphic transitions* are phase transitions involving a crystal rearrangement. *Mechanism* refers to how they occur at a molecular level, and what really happens with the molecules in time and space. It is usually believed that there are more than one, even many mechanisms. Is this so indeed? Several different classifications of the phase transitions in solids have been proposed. We will now consider briefly some of these classifications (Table I).

2 FIRST AND SECOND ORDER PHASE TRANSITIONS

Ehrenfest[1] classified phase transitions by *first order*, *second order*, and so on, on the basis of some theoretical considerations. Landau[2] built up the theory of *second-order* phase transitions. As is denoted in BI (Table I), there is a definite "temperature of transition" (or "point of transition"), T_{tr}, its position being independent of the direction of the transition; that is, hysteresis is impossible. Nothing really happens at this point. No density jump ($\Delta\rho = 0$),

TABLE I

Different classifications of phase transitions in crystals[a]

	1	2	3	4
A	FIRST ORDER $\Delta\rho \neq 0; \Delta Q \neq 0$ Heterogeneous By nucleation and growth Hysteresis is possible[b] $V_{tr} = f(T)$	DISCONTINUOUS  T_c is critical temperature	RECONSTRUCTIVE By full reconstruct Crystal structures are not "similar" Rate of transition: "sluggish" First order	"USUAL" ~~Diffusional~~ By nucleation and growth $V_{tr} = f(T)$
B	SECOND ORDER $\Delta\rho = 0; \Delta Q = 0$ Homogeneous throughout the volume By co-operative displacement Definite point T_{tr} (hysteresis is impossible) Symmetry jump	CONTINUOUS  	DISPLACIVE By displacement By distortion Crystal structures are "similar" Rate of transition: "rapid" Almost second order	MARTENSITIC $V_{tr} \neq f(T)$ V_{tr} = of sound propagation rate Definite orientational relationships Relief on surface $T_{\text{martensitic}}$

[a] T is temperature; $\Delta\rho$ is jump of density; ΔQ is heat of transition; V_{tr} is velocity.

[b] According to the present author's data this indication has to be replaced by the "hysteresis is inevitable."

no heat of transition ($\Delta Q = 0$), nor any other finite changes. Only an infinitely small co-operative displacement of all the molecules in the crystal starts, creating a jump in the crystal symmetry at this point.

On the other hand, in *first-order* transitions (A1), crystal rearrangement does not occur homogeneously, but by way of *nucleation* and *growth* of the new phase. The rearrangement occurs at the phase boundaries. In this case $\Delta\rho \neq 0$ and $\Delta Q \neq 0$. An important characteristic of a first-order phase transition in a crystal is the dependence of the interface movement on temperature. The character of the $V_{tr} = f(T)$ dependence is shown in Figure 1.

The above classification has generally been accepted as valid. It is worthwhile noting, however, that it is now impossible to find even one well documented example of a second-order polymorphic transition! Even the example chosen by Landau and Lifshitz[3] for the demonstration of a typical second-order transition, namely $BaTiO_3$, has been shown to be incorrect. While some people still believe that they know particular examples, these transitions, mostly probably, will soon be reclassified as first-order ones, as has already happened with many other so-called second-order transitions. The usual reasons for classifying a phase transition as a second-order were the seeming smooth change of a physical property, finding $\Delta Q = 0$, or a "lambda-peak" at the heat capacity curve. Later, as a rule, when the measurements were carried out more accurately, a finite jump in the physical property and values of $\Delta Q \neq 0$ were found, even if they were very small. As to the "lambda-peaks," it will be shown below that they are not real. It is interesting to note

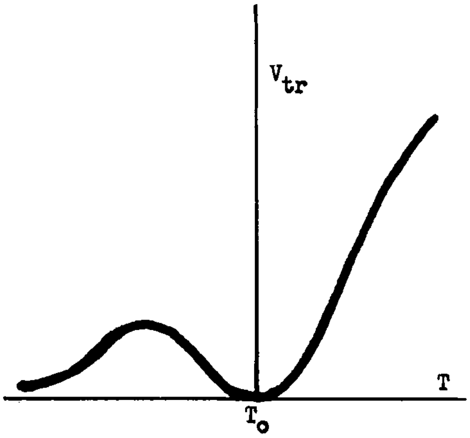


FIGURE 1 The temperature dependence of interface velocity V_{tr} characteristic of first-order phase transitions in crystal solids. T_0 is the temperature at which the free energies of the polymorphs are equal.

that those transitions that have not been reclassified usually have a very high or low T_0 where it is more difficult to make measurements.

3 DISCONTINUOUS AND CONTINUOUS PHASE TRANSITIONS

The division of phase transitions in solids by *discontinuous* and *continuous* does not rest on any theoretical considerations. There is just a widespread belief that every transition belongs to either one or the other group. In theoretical work (e.g., see Refs. 4–6), all transitions are considered, in fact, to be discontinuous (A2 in Table I). There is a definite temperature of transition, T_c, frequently called "critical"; from whichever direction this temperature is passed, the system instantly changes into the alternative phase at exactly that temperature. (The reasons for the anomalous behavior of the physical properties, which is frequently found in the vicinity of T_c, will be discussed later.) On the other hand, *continuous* transitions (B2) take place over a temperature range.

This classification has to be recognized as a very unsuccessful one. It will be shown in this paper that a smooth passage from one phase to the other has quite a different origin, and is not a result of a specific "continuous" transition mechanism. Moreover, the usual polymorphic transitions that occur by nucleation and growth do not correspond to an A2 case. A physical property is represented in these cases by two independent, partly overlapping, curves, as is shown in Figure 2, and not by a single one as is shown in A2, Table I. There is not any "critical temperature." Each individual crystal

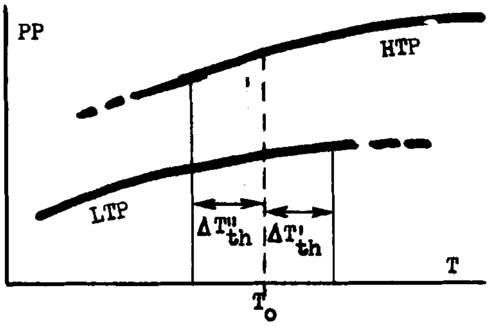


FIGURE 2 A polymorphic transition occurring by means of nucleation and crystal growth is described by two independent curves representing a physical property PP, because (1) both polymorphs are fully independent from one another, and (2) the system is heterophase at all the intermediate temperatures. $\Delta T'_{th}$ is threshold overheating needed for the polymorphic transition of the low-temperature phase, LTP, can occur (but this may not happen). The undercooling $\Delta T''_{th}$ plays the same role for the transition of the high-temperature phase, HTP, into the low-temperature phase LTP.

specimen of the same substance has its own temperature of transition which never coincides with T_0 because the system is practically stable in some finite range in the vicinity of T_0.

4 DISPLACIVE AND RECONSTRUCTIVE POLYMORPHIC TRANSFORMATIONS

The next classification (A3–B3) was suggested by Buerger.[7–9] His initial postulate was simple. If the crystal structures of the polymorphs are similar, the transition occurs by "distortion" of the starting structure without the breaking of the existing bonding, and it occurs rapidly. These are *displacive* transformations that do not involve changes in the first coordination. On the other hand, if the structures of the polymorphs are not similar, the transformation is *reconstructive*, occurring by full reconstruction, and involving changes of the first coordination; such transformations are sluggish.

All the definitions ("similar," "by displacement," "by full reconstruction," "rapid," "sluggish") are qualitative. Trying to clarify the notion "similar," Buerger related it with the changes in first and second coordination. This has led him to a much more complicated classification than simply the division into *displacive* and *reconstructive* types. *Dilatational*, *rotational*, *substitutional*, and "*of bond type*" transformations were added. But it becomes clear that the correlation with changes in first and second coordinations does not work. For example, according to the classification, *dilatational* transformations are, in fact, *displacive* transformations also, but ones that involve a change in the first coordination.

This classification is contradictory and does not reflect reality. Even qualitatively, experience does not agree with the idea of faster transitions for more similar polymorphs. It shows something else. Depending on the temperature, the rate of a transition can be anywhere in a wide range from zero to very high. Besides, if the principle of "similarity–dissimilarity" is taken as a basis for the classification, the following question arises. Since *energy of crystal state* is the only cause responsible for the crystal structure of a polymorph, the structures of both polymorphs are fully independent of each other. There can be infinite variation between the two extremes: "full similarity" and "full dissimilarity." How can all these intermediate states be classified?

5 MARTENSITIC AND NON-MARTENSITIC TRANSFORMATIONS

A martensitic transformation is believed to be a strictly ordered process. The physical interpretation of the idea itself, however, has been changing. Not so long ago it was generally agreed that the idea of a uniform deformation which occurs co-operatively in bulk had to be abandoned, and that a martensitic transformation occurs at the interfaces ("habit planes") where the two crystal lattices fit closely to each other, so that they have elastic distortions near it. This interface "slips" with a velocity of the order of that of the propagation of sound, the velocity being independent of temperature; there must be a definite orientational relationship; there is a specific temperature for a transformation, T_{mart}.

What mechanism is contrasted with martensitic? Some years ago it was believed to be *diffusional*. But diffusion is too slow a process to explain actual rates of non-martensitic transitions. Nowadays the terms "usual" and "by nucleation and growth" are frequently found in the literature. The former is not informative, and the latter is not suitable since martensitic transformations are now considered to occur also by nucleation and growth.

Here we come close to the weakest part of the classification: the more the martensitic theory is developed the less martensitic transformations differ from non-martensitic transitions. Nowadays we do not even have a single *experimental characteristic* attributed to a martensitic transformation that is sufficiently reliable to distinguish them. Characteristics such as interface propagation with the rate of an elastic wave, independence of rate on temperature, and definite orientational relationships, were abandoned.

A recent paper[10] in which the polymorphic transition in p-dichlirobenzene was affirmed to have a martensitic mechanism can serve as a typical example of some of the problems described above. The only relevant information in the experimental section is the X-ray determination of the angle between characteristic lattice directions before and after the polymorphic transition. As few as 15 crystals were used for the measurements and six different angles were found. There is no question that such data are insufficient to allow one to conclude that the transition is martensitic. The starting orientations were not precisely determined; it is noted in the paper that they were "within 3°" relative to the capillary axis. Since the X-ray patterns were taken at undetermined angles of rotation about this axis, this may lead, together with the mosaic spread ($\sim 2°$) and other sources of error, to a total measurement error of $\pm 5°$ while the entire independent angular range was 90° in a plane. The samples were crystals contained in quartz capillaries where they had been grown from the melt. Oriented crystal growth from the melt in a capillary was considered as natural, and the reasons for it are not discussed; at the same time the data on the orienting influence of a capillary and geometrical orientation selection in needle-like crystals when growing from a solid medium[11,12] were neglected. But the main weakness of the work is concealed in the absence of reliable experimental indications which could unambiguously identify the martensitic mechanism. A martensitic mechanism is defined in the paper in question as "heterogeneous, involving nucleation of a crystal and its subsequent rapid growth ...," the crystal's mutual orientations and other properties being crystallographically determined. Thus, nucleation and crystal growth themselves are used not for identification of the "nucleation and growth" mechanism (A4 in Table I), but of its antipodal (B4). At the same time such a specific indication as the "martensitic temperature" T_{mart} is not even mentioned. (By the way, nothing like this temperature is observed in the polymorphic transition in question.) Furthermore, there is no satisfactory explanation why 10 cm/sec interface movement (this value was taken without measurements or valid grounds) is enough for a martensitic mechanism while the propagation velocity of an elastic wave is 10^4 times more. As to the mutual lattice orientations, a conclusion has been drawn that a martensitic mechanism is consistent with hundreds of different orientations. It clearly makes this characteristic practically useless for identification purposes. Even if this were not so, a definite orientational relationship itself *is not a sufficient condition* for a martensitic mechanism to be identified.[12] Perhaps it would be much more important to examine the condition $V_{\mathrm{tr}} \neq f(T)$ (B4, Table I). Unfortunately, in the work under discussion no attention was paid to this point. It should be noted that the polymorphic transition in question exhibits the interface rate dependence on temperature, such as that shown in Figure 1.[13]

It seems appropriate to introduce a general remark on the indications inherent for a polymorphic transition mechanism. All the polymorphic transitions that the present author has dealt with during many years of research possessed the indications, in principle, of the same type that are possessed by crystal growth from a melt. These indications are those of a process occurring by the "molecule by molecule" principle. They are represented in Table I, A1 (with the correction: "hysteresis is inevitable") and in Figures 1 and 2; each one supposedly is a sufficient condition for the identification. The main differences, as compared to a melt crystallization, involve the possibility of reversing the process, that is, switching the roles of the "crystal" and the "medium:" the crystal growth can occur both under undercooling and overheating ΔT relative to the temperature T_0 of the energetic equality of the two crystal states.

An example of the great simplicity and unity of Nature's laws might be perceived from this fact: crystal growth occurs in vapors, solutions, melts, solids. It seems worthwhile to reexamine very attentively whether the rearrangement process by *transformation* of an initial crystal is really possible. We should keep in mind that the widely held views about the lattice transformation arose very long ago as an *idea* which seemed simple and logical, and not as a result of direct, convincing, experimental evidence. The idea of a martensitic transformation mechanism is so different from the "molecule by molecule" rearrangement principle that it *must* exhibit a characteristic experimental indication. As seen from the literature, this is the most difficult aspect to associate with martensitic theory.[14,15] Until this indication is demonstrated we do not have ways for the identification of a martensitic transformation.

6 COMPARISON OF DIFFERENT CLASSIFICATIONS WITH EACH OTHER

It is appropriate to compare the classifications Nos. 1, 3 and 4 (Table I) with each other. All of them lay claim to describe one and the same phenomenon. The items A1, A3, and A4, it is obvious, represent similar mechanisms, and also so it seems do the B1, B3, and B4. Buerger himself points out[9] the close similarity between his classification and the division into *first* and *second* order, namely A3 ≅ A1, and B3 ≅ B1. But *displacive* (B3) and *martensitic* (B4) are even more similar and are frequently noted in the literature as corresponding to one and the same mechanism. Thus, one would think,

B1 (second-order) ≅ B3 (displacive) ≅ B4 (martensitic).

However, this is not the case: martensitic are first-order phase transitions, and so we find B1 and B4 to be antipodes! Buerger defines *displacive* transitions as almost *second*-order: they are 90% second-, and 10% first-order transitions. However, it is hardly possible to imagine an intermediate mechanism between rearrangement at an interface (first-order) and rearrangement occurring cooperatively in the bulk (second-order).

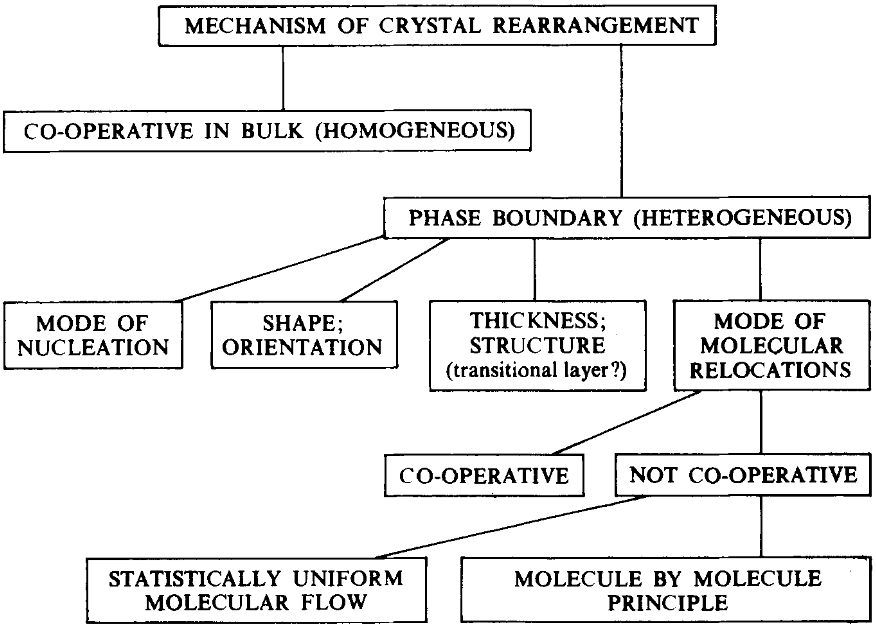
7 THE USUAL X-RAY APPROACH

To all appearance the attempts to classify polymorphic transitions were premature. To be of value the classification has to be based on high quality experimental data. Consequently, the experimental investigations of distinct characteristic examples must be carried out very carefully and in great detail. Unfortunately, contemporary experimental approaches usually do not fulfill this criterion. For example, let us consider that one which X-ray workers use worldwide. The crystal structures of both polymorphs are determined separately; the two drawings are superimposed on each other with the purpose of searching for the mutual rotation and disposition of the best fit; as a conclusion a description of the proposed molecular translations and rotations is given. There are three weak aspects to this method. (1) This is not, in fact, a study of the rearrangement process itself; the conclusions made are only suppositions as to the directions of the molecular relocations, based on the comparison of the two terminal static states. (2) The only parameter really connecting the two terminal states, namely, the lattice orientational relationship, is disregarded as a rule. (3) It has usually been considered, or merely meant, that the polymorphic transition occurs homogeneously; concrete questions of the molecular mechanism are not even put forward. These questions are summarized in Section 8.

8 SUMMATION OF ARISING PROBLEMS

The particular problems that comprise what we usually call "mechanism of polymorphic transition" are summarized in Table II. Logically, two different modes of the rearrangement could be: co-operative in bulk, or at phase boundaries. If the latter, the following four questions arise: (1) the mode of nucleation of the new phase; (2) the shape and orientation of the interfaces; (3) their thickness and structure, and (4) the mode of molecular relocations from the surface of the parental phase to that of the daughter phase. Now, there are two conceivable modes of the molecular passage: co-operative through the interface, and non-co-operative. If the latter, there could be uniform molecular flow according to the laws of statistical mechanics, or molecule by molecule building, as a house is built brick by brick.

TABLE II



9 THE CRYSTALLOGRAPHIC NATURE OF PHASE BOUNDARIES

The present author's own research in the field under discussion was started in 1960 and was aimed at a better understanding of the mechanism of polymorphic transitions as it is represented in Table II. It was noted that (a) the views and theories of the phenomenon were mainly based on terms of "natural" conjectures, rather than on hard experimental data, and that (b) most experimental work was devoted to complicated systems: nontransparent, polycrystalline, multicomponent, and those having imperfect lattices; the conditions under which the polymorphic transitions occurred were not under sufficient control. Therefore the general approach that was taken was to create conditions as "ideal" as possible for polymorphic transitions. To this end, pure, small, clean, transparent, well-shaped single crystals of several different organic substances were grown and studied, with special emphasis being placed on optical microscopy and X-ray work. *p*-Dichlorobenzene, malonic acid, glutaric acid, hexachloroethane, tetrabromomethane, octahydroanthracene and some other substances were studied in detail. The list involved aromatic and non-aromatic substances, structures with van-der-Waals and with hydrogen bonding, transitions of a "crystal to crystal" type, and from a crystal to a rotational disordered state.

As soon as the conditions favorable for very slow polymorphic transitions from one or from a few sites were created a new unforeseen phenomenon was discovered.[16–20,11] It is represented in Figure 3. *A polymorphic transition occurs by way of growth of well-shaped crystals in the parental crystal medium.* The pictures look like crystal growth in a liquid of gaseous medium. This is really crystal growth, but in a solid medium. Two striking peculiarities have been proved.

1) *The daughter crystals can have any orientations in the parental crystal.*[16,20–22] This conclusion was supported by the data on *p*-nitrophenol of Cohen, Coppens and Schmidt.[23] In fact, as far back as 1951 Hartshorne and Roberts[24] described their experiments showing the absence of definite orientational relationships in sulfur polymorphic transitions; these and some other analogous data were not in accord with the views of the traditional school and were disregarded.

2) *The interfaces are the low-index crystallographic faces of the daughter crystals.*[20,22] Table III demonstrates how this is important for a better understanding of the structure of phase boundaries. For a flat interface there are four conceivable geometries: (a) it has rational indices in both the parental and daughter lattices; (b) or only in the parental; (c) or only in the daughter; (d) or in neither of the two. It is variant (c) which corresponds to the real case: an interface is a plane oriented rationally in the daughter

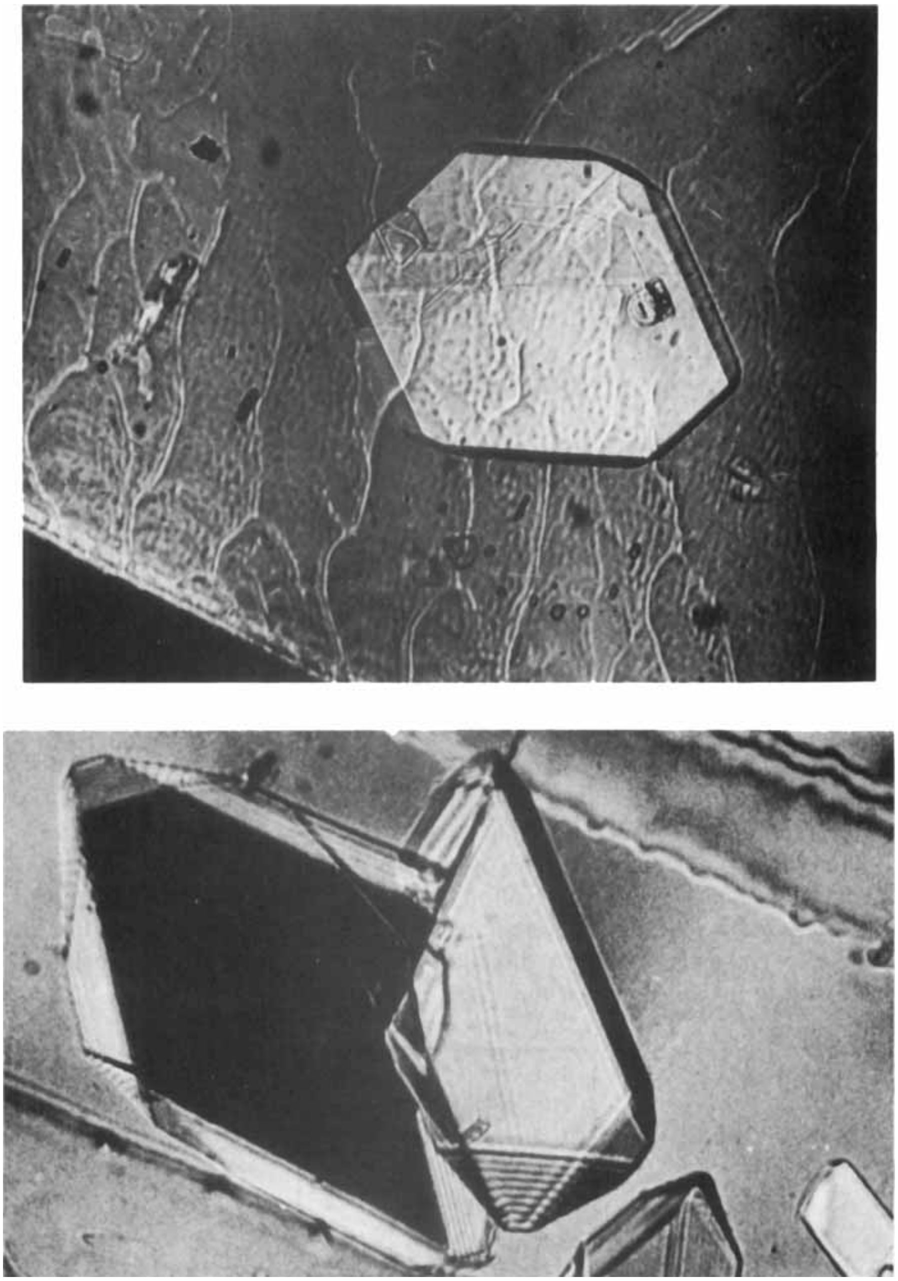
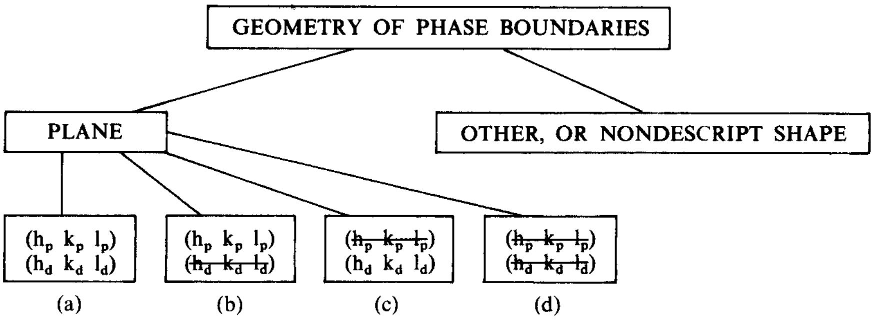


FIGURE 3 Polymorphic transition in *p*-dichlorobenzene: non-oriented growth of well-shaped crystals of the daughter high-temperature phase. (× 150)

TABLE III



"p" denotes parent, and "d" daughter crystal.

lattice and irrationally relative to the parental lattice. Of the four conceivable possibilities it is the only variant never proposed in the literature. The customary way to approach the problem is to search for the crystallographic indices of the interface relative to the parental lattice (cases (a) or (b)). The monograph by Bollmann[25] devoted to a theoretical consideration of phase boundaries in terms of a "best fit" principle is a good example of case (d).

10 LAYER BY LAYER (LEDGE) MECHANISM OF INTERFACE MOVEMENT[26]

A knowledge of the geometrical nature of the interface is a necessary step toward discovering the molecular mechanism of polymorphic transitions. The next step was made when an "alive," i.e. moving, interface was observed under the maximum optical resolution. A *layer by layer*, or *ledge*, mechanism of the interface movement was found.[26] As Figure 4 illustrates, the frontal interface movement in the $\bar{n}$ direction is the result of growth of very thin layers forming ledges which run in the $\bar{\tau}$ direction.

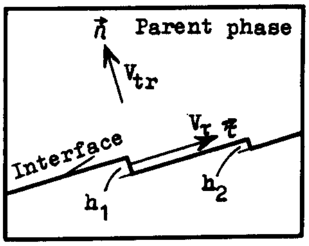


FIGURE 4 Layer by layer mechanism of an interface movement. The ledges (h_1 and h_2) visible in an optical microscope under the maximum optical resolution run in the τ direction.

It is appropriate to remember the same discovery some decades ago for the case of crystal growth in liquids and gases. That discovery led to a revolutionary change in the views on the mechanism of crystal growth. Now, the extension of the same "ledge" principle exhibits its even greater generality and leads to conclusions that change the traditional views on the mechanism of polymorphic transitions:

1) There is no equal probability for all the molecules at the interface to participate in the rearrangement.

2) The rearrangement occurs only at molecular ledges according evidently to a "molecule by molecule" principle.

3) There is no intermediate layer of excited molecules between the two phases.

11 "CONTACT" MECHANISM OF POLYMORPHIC TRANSITIONS[27]

In terms of the new data described briefly in Sections 9 and 10 a *contact* mechanism of crystal structure rearrangement has been deduced.[27]

A *contact* interface is shown in Figure 5a. Coupling forces between the two polymorphs are provided by the direct molecular contact. There is no transitional molecular layer between the two phases, but only a very little gap equal, on the average, to half a molecular layer. Such an interfacial structure does not require any matching, so that both lattices can have any relationship between the cell parameters, mutual orientation, and crystal symmetry. From the side of the daughter phase the interface corresponds to a closely packed molecular row of low indices (h, k, l). A two-dimensional net of microcavities is created. The surface energy is caused by some loss in closeness of molecular packing; however, there are no lattice distortion like those invoked in a martensitic model.

Figure 5b illustrates the molecular rearrangement at the *contact* interface when the polymorphic transition proceeds. (Figure 5 represents two shots of an animated movie modelling the process.) The rearrangement occurs according to the "layer by layer" principle. Molecule by molecule tears off from the parental crystal and relocates onto the daughter to build up closely packed layers. Some additional space is needed at a ledge (microcavity) to provide steric freedom for the molecular relocations. Thus, the phenomenon of microcavity extrusion onto the crystal surface can be forecasted. "Translation" of the interface by the width of one molecular row is a result of this building up. Many ledges evidently run simultaneously.

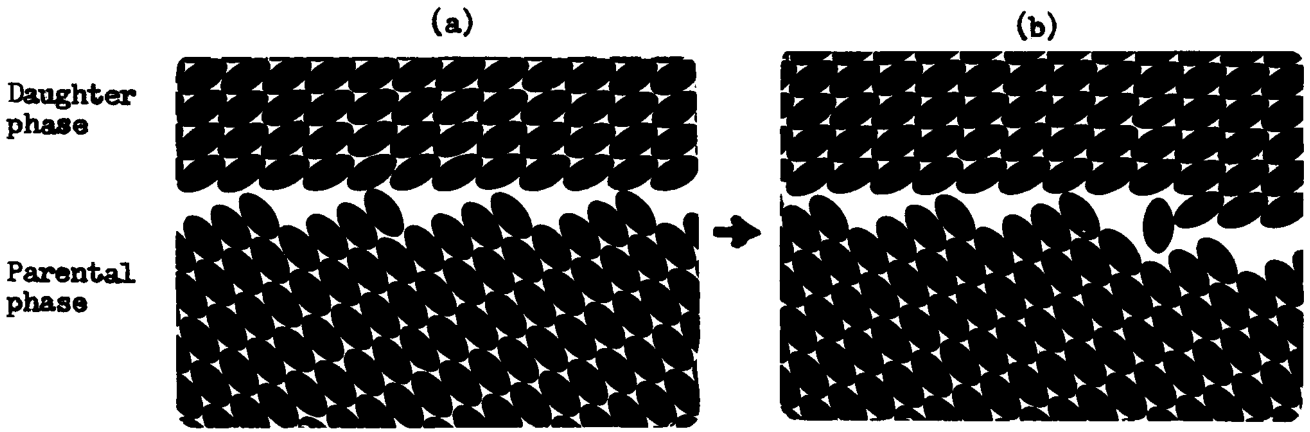


FIGURE 5 Proposed *contact* mechanism for polymorphic transitions: (a) a "contact" structure of the interface; (b) rearrangement according to the "molecule by molecule" principle.[27]

The contact mechanism is simple, universal, answers all experimental evidence, and removes the atmosphere of mysteriousness around the problem of the mechanism of polymorphic transitions. There are no limitations which could prevent this mechanism from being applied to crystals of any other type.

Now some examples will demonstrate its capability of explaining and forecasting experimental facts.

12 FORECASTING POWER OF THE CONTACT MECHANISM[27]

A Coupling force at a contact interface

The experimental fact is that fracture of the crystal under the influence of an external force always occurs along the interface. The *contact* interface shown in Figure 5 is indeed the weakest place in a crystal. It was possible to use an "atom to atom" computer calculation to estimate the coupling force as a function of the distance between the two crystal phases at the interface. Then the coupling force was measured experimentally. This measured value was found to correspond to the width of the gap between the two phases equal to 0.5 of the thickness of a molecular layer. This is a *contact* interface which has, on the average, such a gap (see Figure 5).

B Solution of Hartshorne's paradox

For more than 30 years Hartshorne and co-authors studied the polymorphic transitions in sulfur and some organic substances.[28–36,24] As a result they have come to a very interesting paradox, formulated in the clearest manner by Bradley.[37] On the one hand, a conclusion was drawn from treatment of numerous kinetic measurements that the activation energy E_a of a polymorphic transition and the sublimation energy E_s are approximately the same, $E_a \cong E_s$. Thus, it seemed natural to propose the existence of a vapor layer between the two phases, as well as the same rate for both processes. On the other hand, the following great difference was found for the velocities of the processes: $V_{tr} \cong 10^4 V_s$.

As opposed to Hartshorne's model of a vapor layer between the two phases, the molecular relocations at a *contact* interface occur under the action of attractive forces from the side of the daughter crystal (Figure 6). Computer calculations for the gap $K = 0.5$ have given the 30% lowering of E_a as compared with the energy of sublimation. Such a small difference leads to $V_{tr}/V_s = \exp(-E_a/RT)/\exp(-E_s/RT) \cong 10^4$.

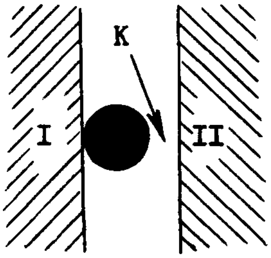


FIGURE 6 Relocations of molecules at a *contact* interface occurring under the action of the attractive forces from the side of the daughter phase. On average, K is equal to half a molecular layer.

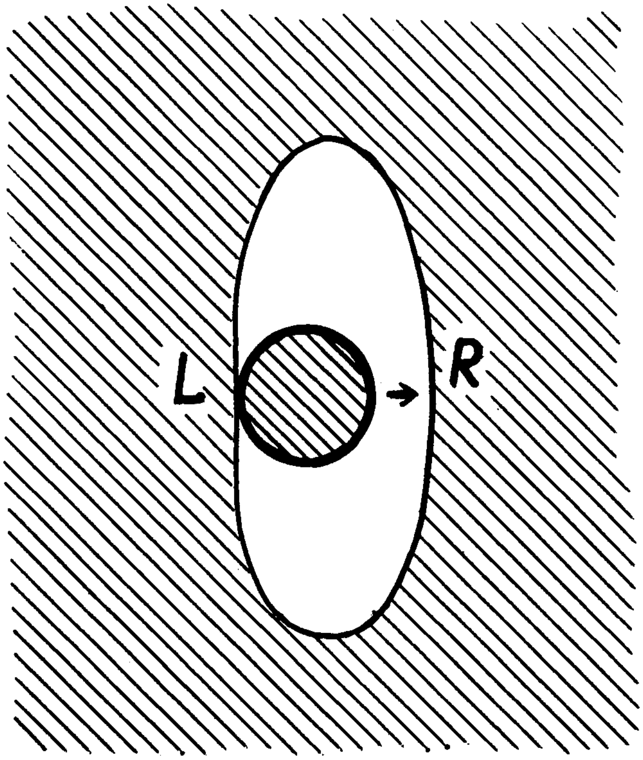


FIGURE 7 Nucleation in a microcavity of optimum dimensions can occur without steric hindrance; attractive forces from the opposite wall R help a molecule to tear off from the surface L.[38]

C Capability of explaining grain recrystallization

According to a preliminary consideration, the *contact* mechanism is capable of successfully explaining phenomena in such adjacent field as recrystallization.

13 MECHANISM OF THREE-DIMENSIONAL NUCLEATION IN A CRYSTAL[38]

The next aspect of the mechanism that will be considered is *nucleation.* Chronologically, nucleation is the first aspect of a mechanism since a polymorphic transition begins from it. According to theoretical views, a nucleus can emerge at *any* point in the crystal, as a result of a chance favorable thermal fluctuation. A quite different picture has been discovered in the present author's investigation. Small transparent single crystals of good quality were used instead of complicated systems such as polycrystalline or non-single-component ones. As a result, the following conclusions were drawn:[38]

Point 1 Nucleation occurs only when the phase equilibrium temperature T_0 has been passed. Such temperature lags for polymorphic transitions are inevitable, and differ from crystal to crystal of the same substance.

Point 2 Nucleation occurs *only* at crystal defects which were present in the crystal.

Point 3 Only defects of a particular type are suitable for nucleation. A polymorphic transition will not occur in the absence, as minimum, of one proper defect.

Point 4 It is proposed that these crystal defects are *optimum microcavities* (Figure 7); only optimum microcavities can explain all the collected experimental data. Formation of an embryo occurs, without steric difficulties, by way of molecular relocations from one wall onto the other under an attractive action from the side of the latter.

Point 5 The polymorphic transition temperature is "pre-coded" in the defect. This temperature is reproducible only relative to one and the same defect (Figure 8).

Point 6 The orientation of the daughter crystal is also "pre-coded" in the defect. This orientation can be random, but it is reproducible relative to the same defect.

A general conclusion: *nucleation is not a result of a fortunate random fluctuation; it is fully predetermined by the crystal defects.*

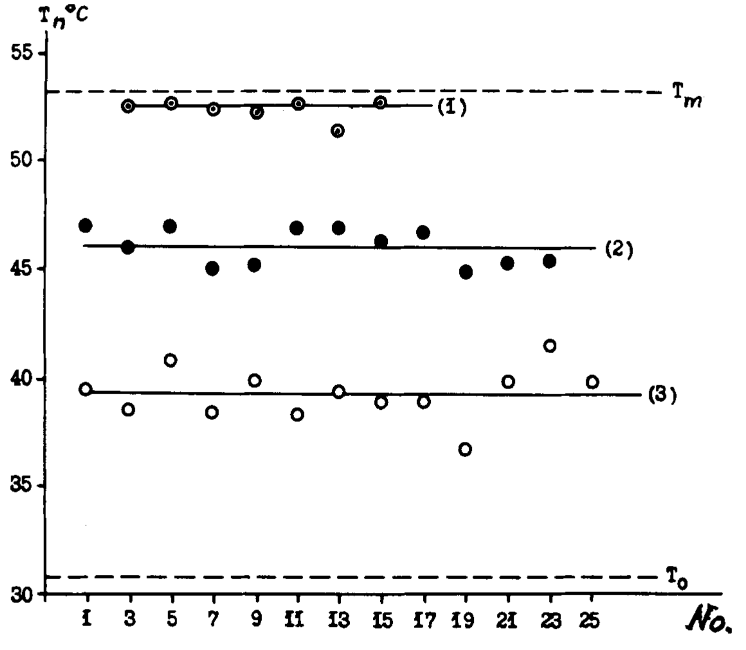


FIGURE 8 Reiteration of the nucleation temperature T_n whenever the nucleus forms in one and the same point (crystal defect). p-Dichlorobenzene. The three plots correspond to different sites. "No." is the ordinal number of transition. T_m is the melting point.[38]

14 NEW APPROACH TO THE KINETICS OF POLYMORPHIC TRANSITIONS

The new nucleation data described in Section 13 should cause a great change in our approaches to the kinetics of polymorphic transitions. Unlike nucleation, the kinetics of the process is not a part of the mechanism of polymorphic transitions, but is usually used in an attempt to elucidate the mechanism. Since a paper by the present author on the kinetics of polymorphic transitions is presented separately in this issue,† only one relevant point will be considered here.

Many articles have been published where a bulk rate for polymorphic transitions was measured in polycrystalline or powder samples. This was done either while slow, passing through the temperature range of the transition, or under isothermal conditions.‡ A physical property was re-

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† See page 201/[505].

‡ Analysis of several such works made it clear that isothermal conditions were not really provided there.

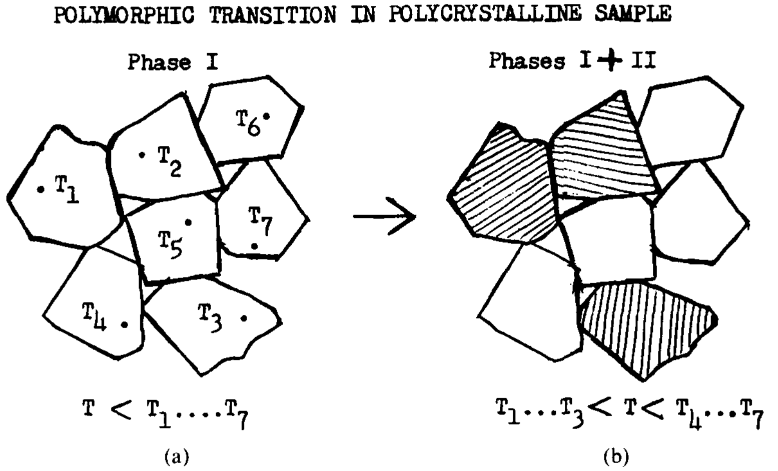

FIGURE 9 Polymorphic transition resulting from heating of a powder or polycrystalline sample is fully predetermined by the size and perfection of its crystal particles. T_1, T_2, T_3, . . . , are the "pre-coded" nucleation temperatures.

corded, such as: the optical spectrum; the NMR spectrum; the X-ray intensity; or some other. The "activation energy of the polymorphic transition" was sometimes calculated in order to draw a conclusion about the mechanism of the polymorphic transition. Figure 9 helps to clarify the fact that the bulk kinetics cannot yield sound information about the transition mechanism. Different temperatures of the transition T_1, T_2, . . . , T_n are "pre-coded" in different particles (Figure 9a). During the heating, the particle No. "n" changes the phase state as soon as its temperature T_n is reached. At an intermediate temperature T (Figure 9b) the system is heterophase: some particles have changed their state, the rest are waiting for higher temperatures. Thus, the notion "velocity of transition" is inapplicable here: the result is independent of time. It is evident from this consideration that the notion "bulk kinetics" needs reexamination.

15 HYSTERESIS OF POLYMORPHIC TRANSITIONS

According to generally held views, polymorphic transitions must occur at strictly defined temperature points. At the same time, there are numerous references to transition lags in relation to the "transition temperature" T_{tr} (or T_c). Nowadays the phenomenon of temperature lags of transition, usually refered to as *hysteresis*, is presented (sometimes indirectly) in most publications on phase transitions in solids. The hysteresis value is considered a characteristic property of one or another transition case, and can throw light on the transition mechanism. There were a few attempts to explain the cause of the hysteresis. The conception of a "hybrid crystal" involving a rejection of some fundamental thermodynamic notions was put forward by Ubbelohde;[39,40] some other workers relate this phenomenon to a martensitic mechanism[41,42] leaving the question unresolved as to what is the reason for the hysteresis in non-martensitic transitions. Parshad and Sharma in the paper "Physical basis of the mechanism of hysteresis upon phase transition"[43] take a potential barrier between the atomic arrangements in crystal phases as such a basis, an idea which is hardly valid in a process occurring by non-oriented nucleation and growth.

Meantime not only an explanation, but even the *inevitability* of hysteresis are actually contained in the nucleation conception set forth in Section 13. The reasons for the phenomenon lie in the nucleation barrier. As is known, exceeding a threshold undercooling $\Delta T_{\text{liquid}\rightarrow\text{solid}}$ is a necessary condition for melt crystallization. Temperature lags occur in this case in *one* direction only, and this fact has prevented the appearance of the term "hysteresis" in descriptions of the effect. It is used, however, in studies of polymorphic transitions since the nucleation lags ΔT_n occur in *both* directions with respect to the temperature T_0 at which the free energies of both polymorphs are equal. The ΔT_n values are "pre-coded" in the lattice defects, they are different for different nucleation sites, and cannot be smaller than threshold values $+\Delta T_{\text{min}}$ and $-\Delta T'_{\text{min}}$.[38]

Today, however, we find in the scientific literature only the recognition of the *possibility* of the hysteresis, not of its *inevitability*. The literature demonstrating this very significant point includes handbooks, monographs and review papers. Here typical examples are (some words in the quotations were italicized by us): "... The high-temperature phase *often may* be undercooled, and *occasionally* the low-temperature phase *may* be superheated";[44] (First-order transitions in solids) "occur at *precise* transition temperatures; or, rather, the free energies for the two forms become equal at a definite transition temperature, although the transition itself *may or may not* occur";[45] "... A transition from one phase to the other occurs *always at a strictly definite* temperature";[46] "... Superheatings and undercoolings are *possible* at first-order phase transitions ...";[47] "Transition points ... are *often definite* temperatures .... It is *quite possible* to superheat a polymorph without transformation taking place".[48]

In contrast to this, we would say that *it is quite impossible for a phase transition to take place without a finite superheating* (*undercooling*). This difference, as will be seen, leads to important consequences.

How the nucleation lags result in the development of a hysteresis loop will be shown in Section 18.

16 THE ORIGIN OF A TRANSITION RANGE

As is seen from the literature, "continuous transitions" (as well as "lambda-peaks" which are discussed in Section 17) were recorded with samples taken in a powdery or polycrystalline state. A substance, liquid at room temperature, is poured into an ampule and frozen, the experimental points thus refer to the solidified polycrystalline mass. In other cases powder samples or tablets pressed from the powder are used.

The following discussion is relevant independent of what a physical method is used to record a polymorphic transition (X-ray powdery photography, dilatometry, spectroscopy, etc.). Let us consider a polymorphic transition which occurs in a powdery sample upon heating. In each single microcrystal the nucleation lag ΔT_n which does not coincide with ΔT_n in other crystals is "pre-coded." Owing to the small dimensions of the crystals the nucleation temperature T_n is practically the transition temperature of the whole single crystal since very little time is needed for propagation of phase boundaries. Upon heating, the polymorphic transition in the particles takes place at different times extending over a temperature range. At each point of the "transition range" some portion of the crystals has changed its phase; the remainder has not. Upon sufficiently slow heating the shape of the curve $x = f(T)$, where x denotes a relative quantity of one phase, does not depend on the rate of heating, and a prolonged storage at any constant temperature does not change the phase ratio in the sample.

Figure 10 shows how the "transition range" and the "transition temperature T_c" depends on the crystal imperfections of the particles and on the fractional composition of the powder. The figure summarizes many experiments where the process proceeds only in one direction. The temperature corresponding to $\mathrm{d}x/\mathrm{d}T = \max$ is commonly accepted as the "transition temperature." It is shifted with respect to T_0 by not less than a threshold value $\Delta T_{\min}$, and can strongly vary depending on the sample. This effect accounts for the great scatter in the transition temperatures reported for the same substance by different authors.

A widely applied method for studying the phase transitions in solids is the recording of a physical property (PP) vs temperature through the "temperature range." If one deals with a property other than calorimetry or DTA, the curve $PP = f(T)$ within the "transition range" actually reflects the shapes of the curves PP_{I} and PP_{II} for the phases I and II in this range, and the proportion by which they are present in the sample:

$$PP(T) = x(T) \cdot PP_{\mathrm{I}}(T) + [1 - x(T)] \cdot PP_{\mathrm{II}}(T).$$

The "transition range" can also be observed in monocrystalline samples when secondary phenomena accompanying the transition bring the transi-

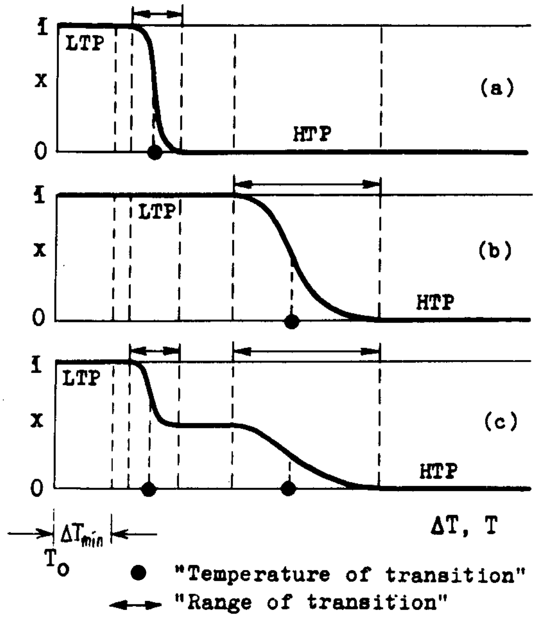

FIGURE 10 Polymorphic transition of crystalline powder from the low-temperature phase, LTP, into the high-temperature phase, HTP. The mass of the sample is 1. x is LTP portion. The "transition ranges" are indicated by bilateral arrows. The "transition temperatures" satisfying the condition $dx/dT =$ max are indicated by black circles. Nucleation lags ΔT_n "pre-coded" in individual crystals of powdery sample are responsible for the shape of curve $x = f(T)$. $\Delta T_n > \Delta T_{\mathrm{min}}$. On the average, the smaller the particle size and the more perfect its lattice, the greater is ΔT_n. Case (a) corresponds to a sample of low-quality crystal particles, and (b) to one of higher quality. Thus, a polymorphic transition in the same substance can exhibit different values and disposition of the "transition range," and different "transition temperatures" as well. Moreover, a sample consisting of both crystal fractions (case (c)) can even create the illusion of two successive polymorphic transitions.

tion to a halt. Continuation of such a transition requires new nucleation that can occur only upon some heating. After the next stop a further temperature increase is required, and so on up to complete transition.

17 "LAMBDA-PEAKS" ON THE HEAT CAPACITY CURVES

As has been shown in some previous sections, a polymorphic transition is a *non-equilibrium* process in the very nature of things. Recognition of this fact helps to disclose the origin of some mysterious phenomena, for example the "lambda-peaks" on the heat capacity curves (so called because the curves in the "transition range" often resemble the Greek letter "λ"). The numerous "λ-peaks" are demonstrated, for example, by Westrum and McCullough in a review paper,[44] as well as in Ubbelohde's book.[39] The term "λ-transitions" is frequently used. Many attempts to discover the origin of the phenomenon have already been made (e.g., see Refs. 49–52), but the literature is too abundant to be listed here.

Let us consider the usual heat capacity experiments that exhibit the λ-peaks. A clear description of the routine experimental approach is given in the review paper.[44] It is usually emphasized that the mode of measurement is on an intermittent basis, allowing time for the establishment of thermal equilibrium after each input of electrical energy into the calorimeter so that the measurements truly represent equilibrium data; in other words, if the observations span enough time, establishment of thermodynamic equilibrium can be ensured. There is a serious problem, however, with the described approach: prolonged retention of a sample at a constant temperature within the "transition range" will provide, as a matter of fact, only *thermal*, and not *thermodynamic* equilibrium.

The real situation is as follows. The sample consists of the particles of both phases. Each new portion of the energy introduced into the calorimeter provides two effects: (1) the increase in the temperature by δT, and (2) the polymorphic transition in a new portion of the particles whose "pre-coded" transition temperatures fall in this interval δT. Their latent heat of transition contributes to the value of the heat capacity. As a result, a *false peak* is superimposed on the true heat capacity curve.

18 GENERAL PICTURE OF THE "ANOMALIES" IN A CYCLIC TRANSITION

Now we can reconstruct a general picture of cyclic transition I → II → I for a powdery sample (Figure 11). The constituents of this picture are all the anomalies that are familiar to those who study phase transitions: "continuous transitions," hysteresis loop, and "λ-peaks." Each small crystal particle of the sample practically shows a hysteresis which is governed only by ΔT_n value "pre-coded" in it (plot (a)). Because ΔT_n values are not the same in different crystals, plot (b) for the whole sample differs from plot (a) by expanding the transition in each direction into a "transition range" $x = f(T)$. Plot (b) differs from Figure 10 by adding the second "transition range" shifted in the opposite direction from T_0. Both "transition ranges" taken together form one hysteresis loop. Finally, plot (c) shows a "λ-peak" in each "transition range." If there were no latent heat of transition, the arrows would follow the dotted lines conditioned by the phase ratio in each point of the "transitional range" and the shape of the curves $C_{p,\mathrm{I}}(T)$ and $C_{p,\mathrm{II}}(T)$ for both individual polymorphs. Each dotted line reflecting the true pathway of the heat capacity for the heterophase sample is superimposed by the "λ-peak" $y = Q \cdot \mathrm{d}x/\mathrm{d}T$ caused by the latent heat of the transition (Q is specific

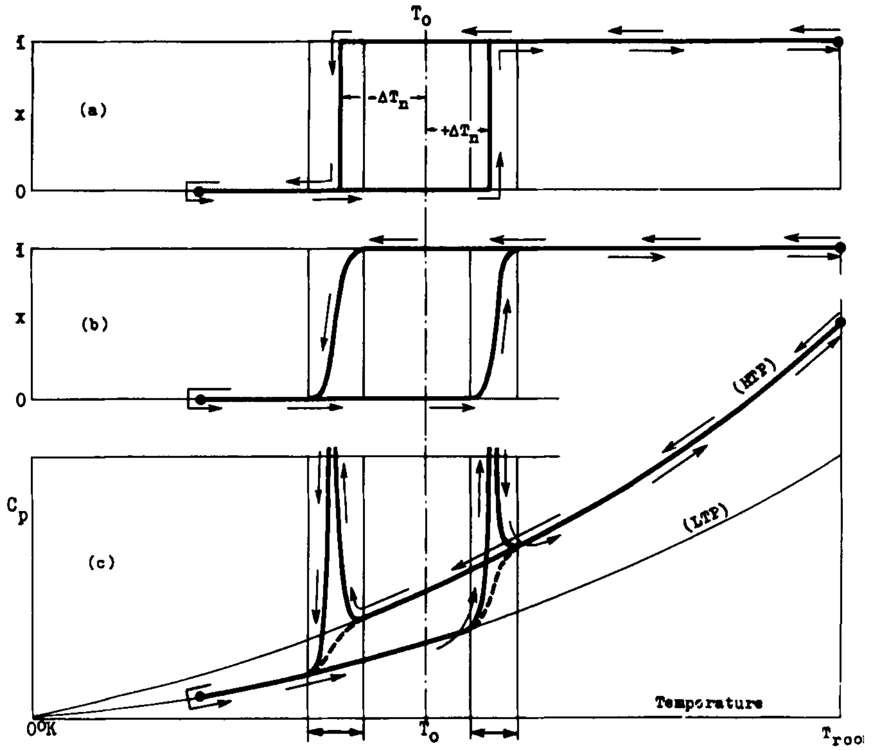

FIGURE 11 Hysteresis, "continuous transitions" and "λ-peaks" upon a cyclic (chain of arrows) transition (i.e., with return to the initial phase). "Transition ranges" are marked by bilateral arrows. The sample is a heterophase one in these ranges. x is the quantity of the initial phase. (a) Hysteresis in a single crystal of a powder sample. (b) Spread of each transition over a "transition range" for the powder sample as a whole; a common hysteresis loop is readily seen to arise. (c) "λ-Superstructure" (due to latent heat of transition) in the "transition ranges" on curves $C_p = f(T)$.

heat of transition). The equation of the experimental curve is

$$Y = C_p + y = x \cdot C_{p,\mathrm{I}} + (1 - x)C_{p,\mathrm{II}} + Q \cdot \mathrm{d}x/\mathrm{d}T.$$

Thus, the latent heat of transition is equal to the area of a "λ-peak" resting upon the dotted line, both λ-peaks have the same area.

19 OTHER SEEMING "LAMBDA-PEAKS"

Since it is generally accepted that "λ-transitions" do exist, the usual first-order phase transitions are classified frequently as "λ-transitions" if the combination of two independent curves representing a physical property for phases I and II resembles the letter "λ." This is the case even if the resemblance is rather weak. It will be noted that an arbitrary combination of two

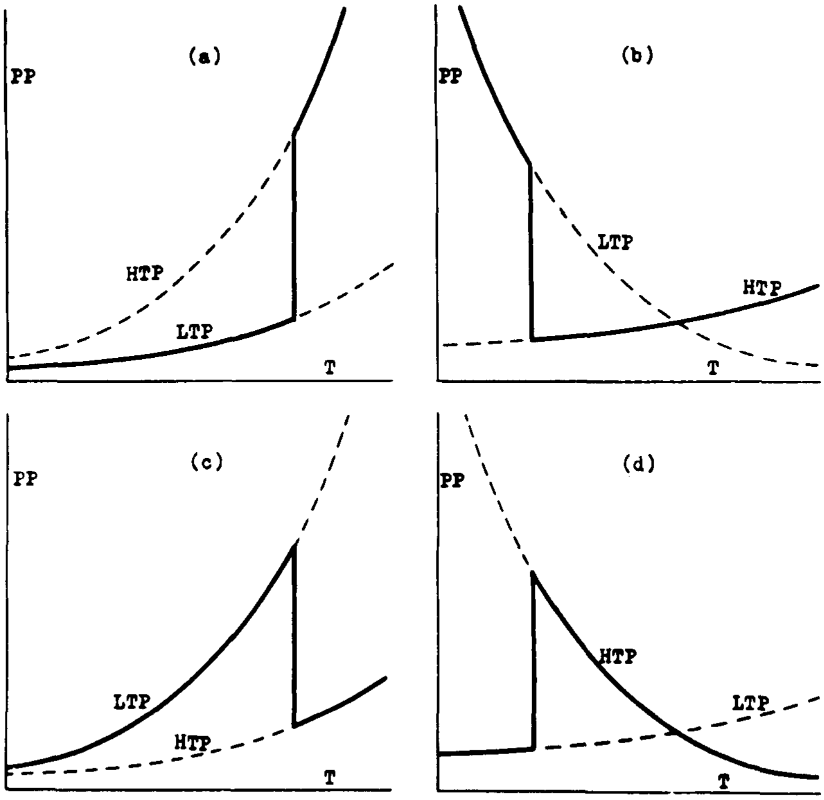

FIGURE 12 Seeming "λ-peaks" as a result of an arbitrary combination of two independent curves "physical property (PP)–temperature (T)" for the high-temperature phase HTP and low-temperature phase LTP. (a, b) The combinations do not resemble a "λ-peak." (c, d) The combinations do resemble a "λ-peak."

independent curves will give rise to such seeming "λ-transitions" in nearly 50% of all cases (Figure 12). If the physidal property is C_p, complicated cases are possible where each of the shown curves may have a "λ-superstructure" as a result of the latent heat of transition. These complicated cases support the illusion that there is a variety of mechanisms for phase transitions in solids.

20 TEMPERATURE OF TRANSITION: A MORE EXACT DEFINITION

We state that the following two rules are always valid:

1) For each reversible transition in a crystal a temperature T_0 (only one point) exists in which the free energies for the two phases coincide with one another.

2) A polymorphic transition requires an overheating (undercooling) with respect to T_0.

These simple rules, when accepted, enable one to define more exactly the concept "transition temperature" and to explain discrepancies and make corrections in the corresponding experimental data that have been reported.

The temperature known in the literature as the "temperature of transition" (or "critical point," or "Curie point") is in reality the very temperature point at which, and near which as well, the transition is impossible. The concept of a single transition temperature should be replaced by the following three temperatures:

T_0 is temperature of equality of the two free energies;
T_n is actual temperature of nucleation;
T_{tr} is actual temperature of transition.

It is only T_0 that unambiguously characterizes the polymorphic transition, not T_n or T_{tr}. T_0 cannot be determined directly, but only by interpolation as the center of some finite temperature interval. And it is impossible to avoid a systematic error in the determination of T_0 if the process is carried out in one direction only because the determined value of the "transition temperature" will be shifted by an unknown value towards lags relative to T_0 (see Section 16 and Figure 10). Nevertheless, most "transition temperatures" reported in the literature do not take account of this effect. That is why there are sometimes such great discrepancies in the data of different authors.

21 EXPERIMENTAL SIMULATION OF A "CONTINUOUS TRANSITION" AND A "LAMBDA-PEAK"

Now a special test investigation by the present author will be described. The purpose was to demonstrate a "continuous transition" for a case which is known beforehand as a "normal" transition which has a well determined temperature T_0, is initiated by nucleation of the new phase, and proceeds by moving the phase boundaries.[20,27]

Glutaric acid was chosen for these experiments ($T_0 = 64.0°C$). A great number of crystalline plates of ~ 1 mm size was grown from a solution and X-irradiated to produce a concentration of free radicals sufficient to obtain an intensive ESR signal, and 100 crystals of nearly equal size and appearance were selected for microscope study. The remainder of the crystals were studied in an ESR spectrometer. At room temperature the concentration of free radicals remained at the same level for weeks. Upon increasing the temperature the recombination rate of the free radicals was moderate enough to allow one to distinguish clearly the effect of the polymorphic transition.

The irradiated crystals, with a total weight of 80 mg, poured into an ampule, served as the ESR sample. The ampule was inserted into the ESR spectrometer and heated at the rate of 0.4°C/min. The ESR spectrum was automatically recorded every three minutes. The amplitude of the most intense line of the spectrum was taken to be proportional to the number, N, of free radicals in the sample.

The observed dependence of N on temperature T and/or time τ is shown in Figure 13a. One can see all the features of a "continuous transition" beginning at $\sim 70°$ and finishing at $\sim 79°$C. This curve is one branch of the hysteresis loop. The curve in Figure 13b obtained by graphical differentiation of the first curve shows the recombination rate of free radicals $\mathrm{d}N/\mathrm{d}T$ during uniform heating of the sample. The "transition temperature" found from the position of the maximum is $T_c = 72.3°\mathrm{C}$. It is higher by 8.3° than T_0. The plot $\mathrm{d}N/\mathrm{d}T$ is a typical "λ-peak." If temperature T_0 were not known beforehand, we would have the usual situation in which the system starts to "prepare" for the phase transition at the "transition (critical) point T_c" even before this temperature is reached (phenomenon of "pretransformation").

The following experiments clearly demonstrate a source of all these "anomalies." In each of the 100 selected crystals, the nucleation temperature of the new phase T_n was measured. Each crystal was placed in turn on the heating stage of the microscope, heated at the same rate 0.4°C/min, and the T_n was recorded. The transition itself proceeded quickly; thereby the knowledge of the nucleation lag ΔT_n in a given crystal allowed one to determine the transition lag as a whole. The temperature scale was divided into intervals $\delta T = 0.5°$ and the number of the crystals having passed into the high-temperature phase in each interval δT was calculated. The results were marked in the appropriate scale on the plot $\mathrm{d}N/\mathrm{d}T$ (Figure 13b). Excellent agreement is seen between the values for $\mathrm{d}x/\mathrm{d}T$ (points) and for $\mathrm{d}N/\mathrm{d}T$ (line). Thus the λ-peak proved indeed to be a result of nucleation occurring at different temperatures in the sample particles.

It was shown in Section 18 that "λ-peaks" on the curve $C_p = f(T)$ should be described by the equation $y = \mathrm{const} \cdot (\mathrm{d}x/\mathrm{d}T)$. The striking resemblance of the curve $\mathrm{d}N/\mathrm{d}T$ to a heat capacity "λ-peak" is explained by the fact that both cases actually represent the dependence of $\mathrm{d}x/\mathrm{d}T$ on T, the difference being only in the scale.

Thus, "λ-peaks" do not represent equilibrium states of the system.

22 TRANSITION FROM CRYSTAL TO ROTATIONAL-CRYSTAL STATE

All the data described above indicated a much greater generality in Nature's laws than could even be proposed before. Namely: there is not more than one

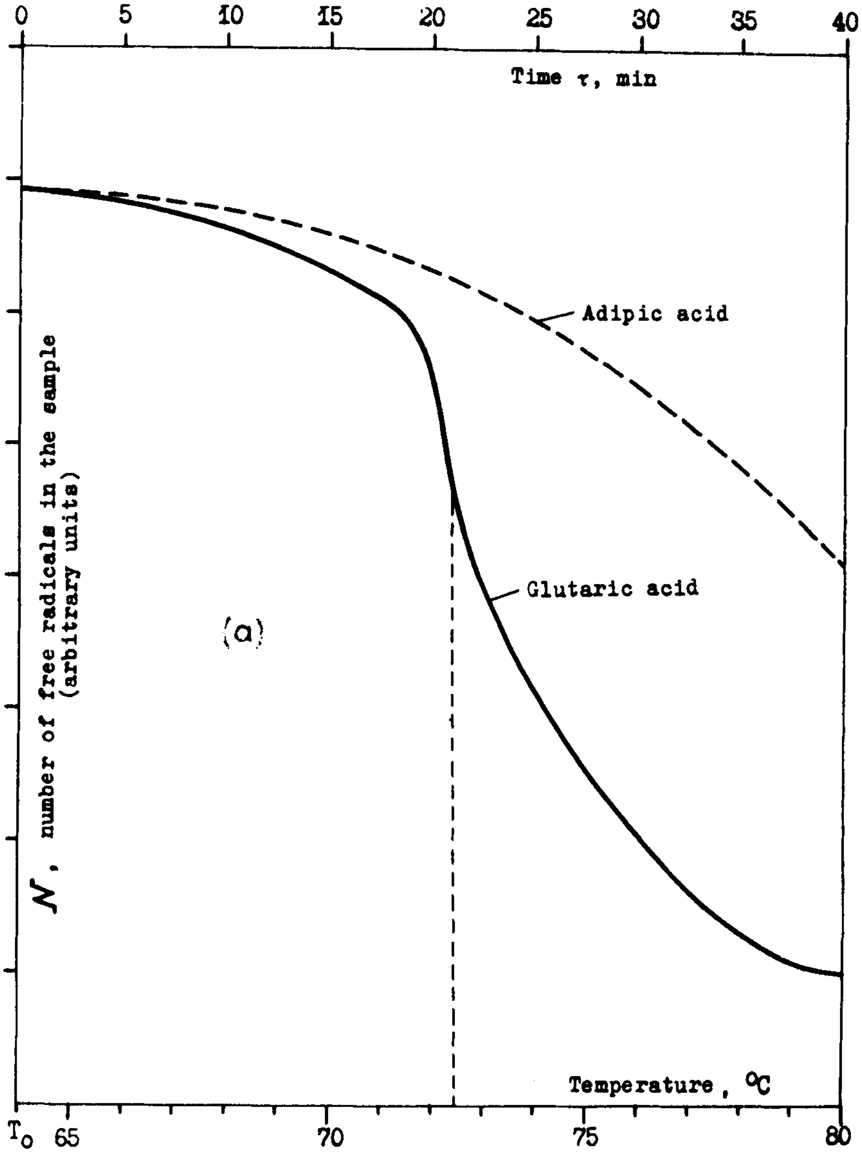

FIGURE 13. (a) Experimental simulation of "anomalies" in the region of "transition temperature T_c" for glutaric acid, and the demonstration of the reason of their occurrence. Dependence of "the number of free radicals N vs temperature T" showing a "continuous transition." The sample (coarse crystal powder) was heated at a rate 0.4°C/min. A curve for adipic acid which does not undergo a polymorphic transition is given for comparison.

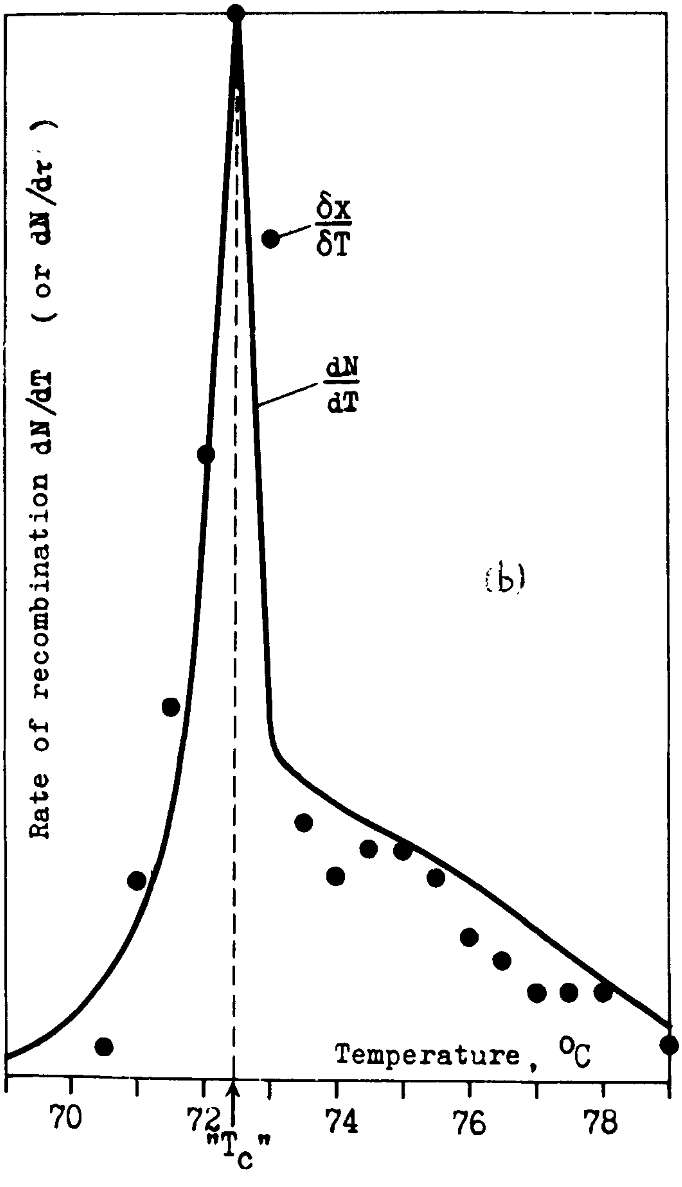

FIGURE 13 (b) Experimental simulation of "anomalies" in the region of "transition temperature T_c" for glutaric acid, and the demonstration of the reason of their occurrence. The rate of free-radical recombination dN/dT vs T: the curve showing a typical "λ-peak" was obtained by graphic differentiation of the curve (a). The black circles are the data of a parallel experiment. They show the portion δx of the crystals changing their phase in each temperature span δT ($=0.5°$). It is seen that the transition lags in these crystals are completely caused by nucleation lags.

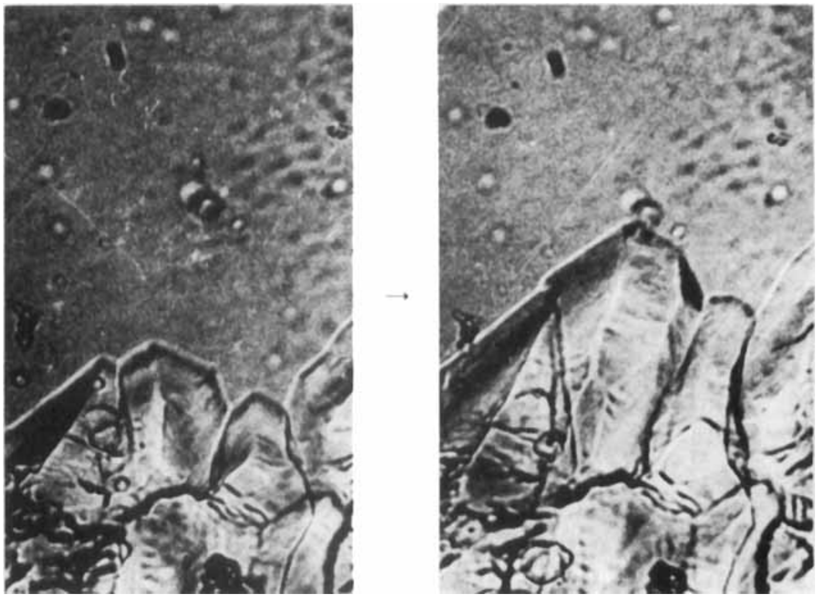

FIGURE 14 The polymorphic transition from the crystal to the rotational state in CBr_4, occurring by crystal growth (two successive stages are shown).[54] (× 100)

mechanism of polymorphic transitions; all the processes involving the creation of a new crystal structure are the same as those of *crystal growth.* Thus, polymorphic transitions do not have their own very specific transition mechanism such as *transformation* of an initial structure, nor do they represent a kind of *critical* phenomenon. They are no more than crystal growth from crystal media, similar to the related processes such as crystal growth from melts, solutions and vapors, In order to justify the above hypothesis it is necessary to examine the cases that supposedly exhibit a very different mechanism of polymorphic transitions. Polymorphic transitions of a "crystal to rotational-crystal state" (c → r) are one such case.

As is known, a rotational-crystal state is characterized by a crystalline ordered arrangement of molecular centers with, at the same time, a disordered molecular orientation because of thermal rotation. Polymorphic transitions c → r are usually considered as *co-operative* phenomena and as second-order phase transitions.[53] They are understood as the beginning of an overall molecular rotation as soon as the critical temperature is reached.[39,53] According to Buerger's classification they are "transformations of disorder," subdivision "rotational," "rapid." As Verma and Krishna comment,[48] these are phase transformations of the second order, they share almost all the characteristics of *displacive* transformations and are "speedy."

Experimental examination by the present author of two "c → r" phase transitions,[54] namely CBr_4 and C_2Cl_6, reveals complete disagreement with the above assertions: a *crystal growth* mechanism was found. All the characteristics of the mechanism coincide with those of a "c → c" type:

Nucleation: at crystal defects; there are nucleation temperature lags $\Delta T_n \neq 0$.

Rearrangement: at flat interfaces, by growth of daughter crystals (Figure 14).

Velocity: rapid, sluggish, or zero depending on the temperature.

Orientational relationship: random.

23 EPITAXIAL AND NON-EPITAXIAL POLYMORPHIC TRANSITIONS

Some polymorphic transitions in molecular crystals, among the few classified earlier as *displacive* or *martensitic* on the basis of the existence of a definite orientational relationship between the lattices of the two phases and the "instantaneous" transformation rate, have been experimentally investigated by the present author.[12]

Octahydroanthracene

The polymorphic transition in octahydroanthracene was classified[55] as *martensitic* on the basis of a definite orientational relationship and the "instantaneous" rate. As a result of the reinvestigation,[12] these data were found to be erroneous. Again all the characteristics were those of "c → c" mechanism. Figure 15 displays slow growth of a cluster of needle-like daughter crystals. These photographs demonstrate orientational scattering in a very obvious form. The statistical "orientational" diagram showed[22] that there are certainly no definite orientational relationships, although the angular distribution of the interface directions is not uniform. However, it would hardly be possible to find a truly uniform distribution of the mutual lattice orientations in any case of crystal growth in a crystal medium, because such a medium is always anisotropic. The rate of the transition is represented by the usual crystal growth temperature curve; the interface is immovable at T_0 and moves with increasing velocity upon deviation from it. If the temperature control is not good enough, the velocity can reach some millimeters a second, and the transition appears in the microscope to be "instantaneous."

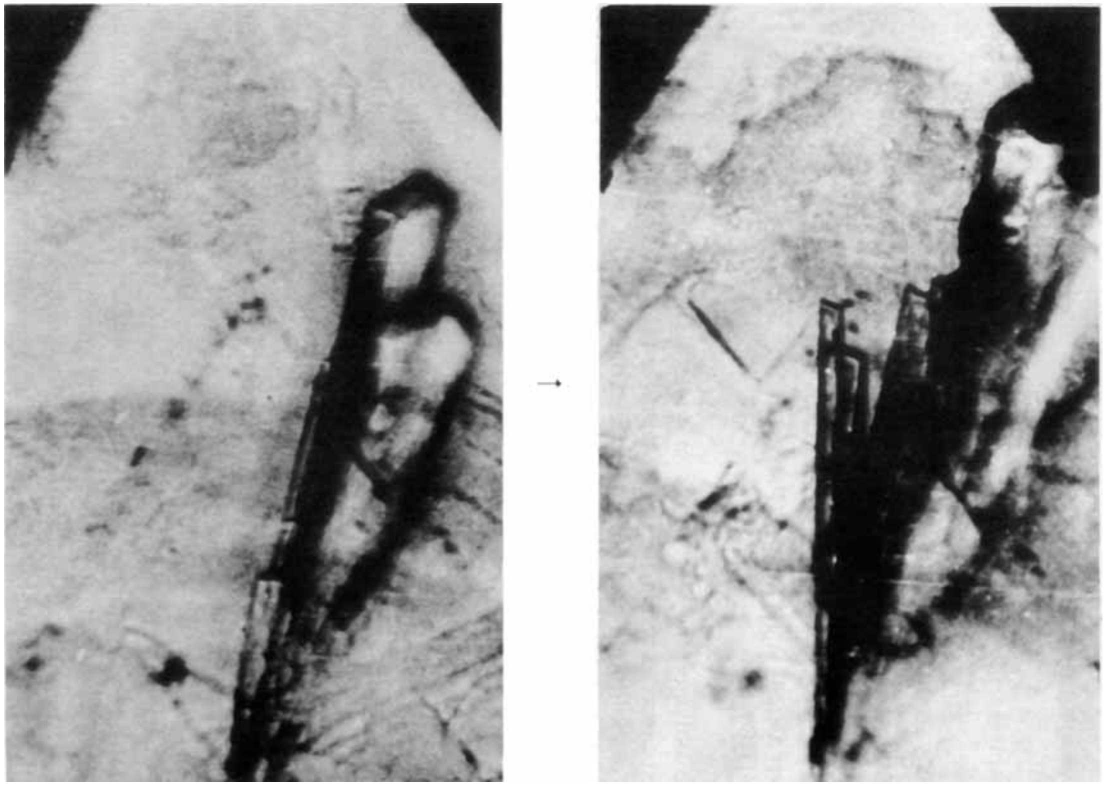

FIGURE 15 Growth of a radially diverging cluster of needle-like daughter crystals (two stages) in the octahydroanthracene polymorphic transition. (× 190)[22]

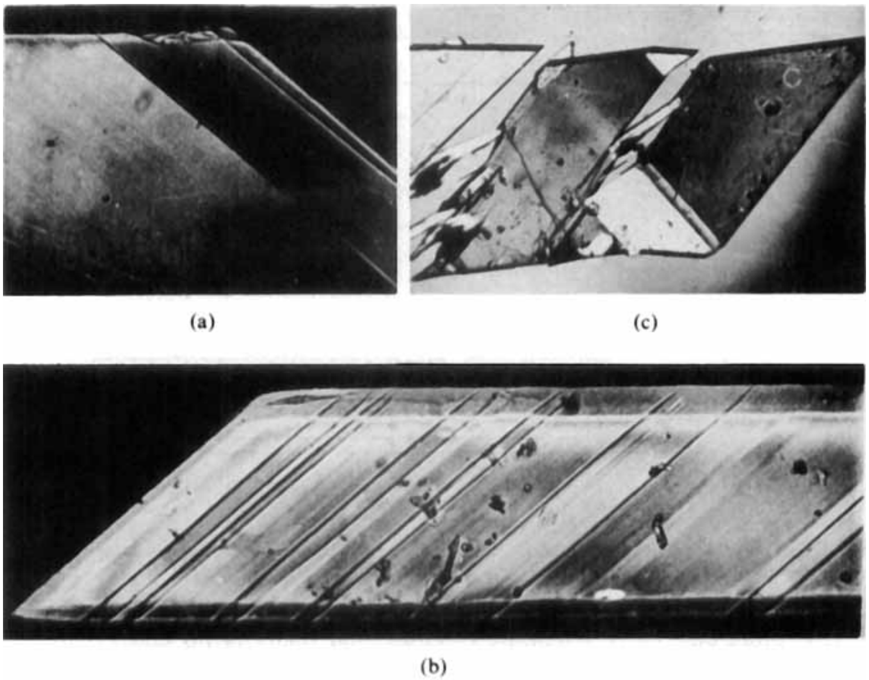

FIGURE 16 Interface propagation in the hexamethylbenzene polymorphic transition. (a) From one site. (b) From several sites. (c) Lamination of an initial crystal under the action of an outer force; the picture demonstrates that the cleavage and interface directions are the same.[12]

Hexamethylbenzene and norleucine

The polymorphic transitions in these substances were studied in great detail.[12] Indeed, a definite orientational relationship was found in both of them. Both cases differ very much from each other as regards to molecular shape and crystal packing. One similarity exists, however, namely a *layered structure* of the crystals. Both polymorphs in each case consist of nearly the same molecular layers, and differ mostly in the mode of their stacking. Geometrically the two polymorphs can be converted into each other by means of a mere shift of the layers. The study, however, made it clear that the polymorphic transitions occur not by a shift of the layers, but quite differently. At first, nucleation at a defects occurs, then the transition proceeds by interface movement (Figure 16), and the velocity of their propagation follow the usual temperature dependence; the interface direction coincides with the cleavage direction. Each layer undergoes full rearrangement, molecule by molecule, and, as a result, nearly the same molecular layer is built (Figure 17). Thus, this is an example of *oriented* crystal growth.

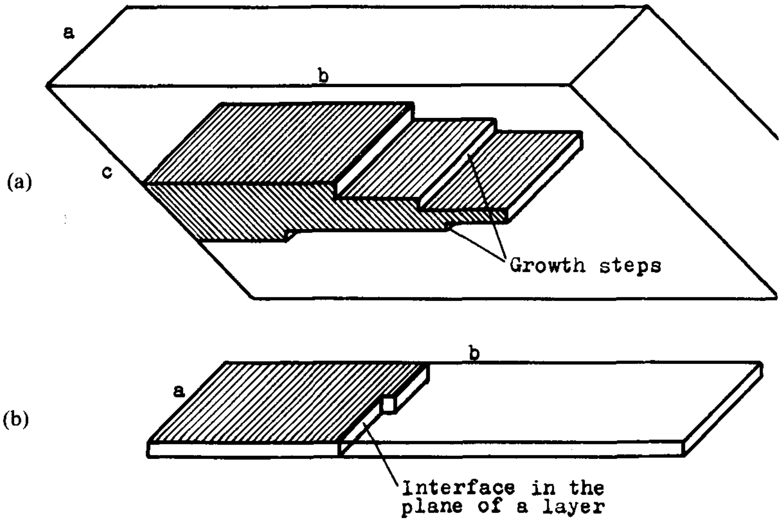

FIGURE 17 "Layer by layer" oriented crystal growth during a polymorphic transition in a layered crystal.[12]

It is quite clear why a definite orientational relationship takes place in these cases. In layered crystals there are numerous slit-shaped microcavities (splits) oriented along the cleavage. Since the crystal parameters in the layers of both polymorphs are nearly the same, there exist all the conditions for epitaxial (oriented) nucleation and growth, as is illustrated in the drawing in Figure 18.

24 CONCLUSION

A polymorphic transition can hardly be considered as a "critical phenomenon" occurring at some definite "critical temperature T_c." There is no evidence that polymorphic transitions can occur co-operatively in the sense that all molecules of the certain volume or all molecules situated at a certain interface will simultaneously participate in the transition. There is also no indication that a polymorphic transition can be achieved by any kind of a "deformation," "displacement," or "turn." Such apparently mysterious phenomena, reported in the literature, as *continuous* transitions, *lambda*-transitions, hysteresis, and some others, can be successfully explained in terms of "pre-coded" nucleation at the crystal defects and temperature-dependent growth of crystals of the new phase.

As a solution to the classification problem the author would like to propose the following: All polymorphic transitions are reduced to crystal growth

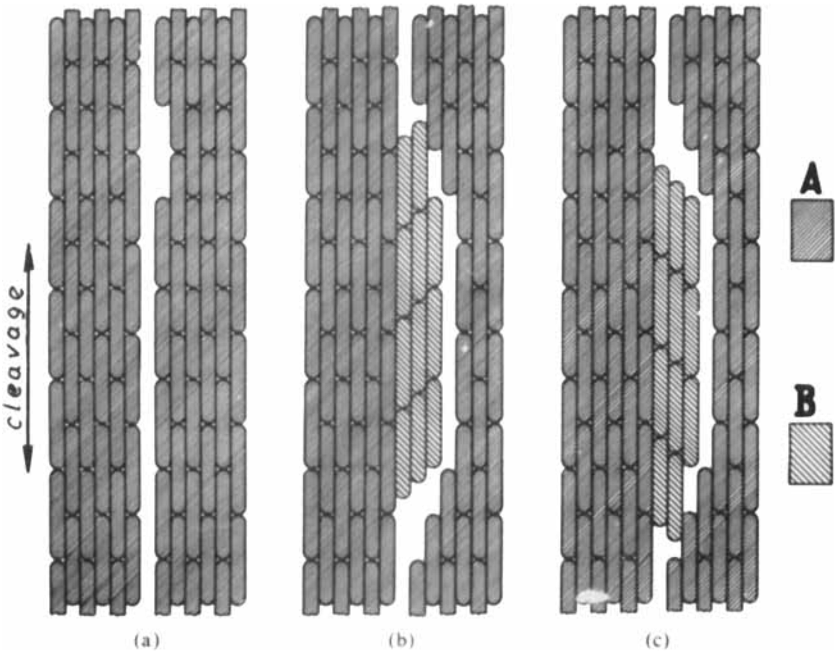

FIGURE 18 Nucleation in a layered crystal. (a) A lattice defect in the form of a thin crack in the original crystal *A* provides the substrate for the oriented growth of the new phase *B*. (b, c) An embryo which can grow in two definite equally probable orientations. The definite orientational relationship between the lattices is not an obstacle for the molecular rearrangement according to the *contact* mechanism described in Section 11.[12]

from a solid medium and are fully analogous to crystal growth from liquids and gasses. This growth manifests itself in two ways resulting in polymorphic transitions of *epitaxial* and *non-expitaxial* types. Reexamination of the literature (not only on molecular crystals) gives firm support to this solution to the problem.

The proposed "contact" mechanism of molecular rearrangement at interfaces simplifies the current state of the theory, is straightforward, and seems to fit the facts well.

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