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Polymorphic Transitions in Crystals: Kinetics

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The ideas expressed in the previous paper are further amplified and applied to the kinetics of polymorphic transitions. These ideas are then used to explain the behavior of real crystals observed under the microscope. Some experimental evidence obtained with molecular crystals is presented.

1 INTRODUCTION

The terms "mechanism" and "kinetics" are frequently used in the literature without an exact definition of their meaning. In order to avoid any ambiguity, we must first define their meanings in reference to the topic of polymorphic transitions in crystals. The mechanism is a physical process of rearrangement of the crystal structure at the *molecular* level, involving nucleation of a new phase and the manner of atomic-molecular rebuilding at the phase boundaries. The kinetics is the set of relationships between the *macroscopic* rate of a transition and all the parameters with which it varies.

Usually, experimental investigations of the kinetics of polymorphic transitions are undertaken with the objective of throwing light on the mechanism of the processes. In such studies the kinetics turn out to be complex, varied in its exhibitions, and insufficiently reproducible. This is one of the reasons why it is generally believed that there are many mechanisms, and that they are very complex. Experimental investigations have led us to the conclusion that there are no grounds for that belief, because the following two main peculiarities rather than plurality of the molecular mechanisms make the kinetics so complicated. Firstly, the rate of polymorphic transitions is not only a function of the mechanism and of temperature, but also of *concentration of certain lattice defects*, this concentration changing upon each successive polymorphic transition in the crystal. Secondly, the feedbacks

→ RATE OF TRANSITION → SECONDARY PHENOMENA—

are an important factor of the kinetics. This explains the observed inability to reproduce the kinetics quantitatively.

It is hardly possible to discover a mechanism of the phase transitions by way of kinetics investigations only; it is more appropriate to elucidate it using other methods, and then to investigate the kinetics. We have proposed a mechanism of polymorphic transitions in previous papers,[1–4] and we will now use this mechanism as a basis to consider the general principles of the kinetics. Emphasis will be placed on the simplest case, the movement of a flat interface through a monocrystal. This approach, in turn, makes it possible to verify the predictions of the mechanism, as well as to specify some of its details.

The change of the volume portion x of one phase is the value of interest in bulk kinetics. This portion is determined as a function of time τ by recording changes in a physical property or the intensity of a signal from one phase. We have analyzed several papers typical of studies of bulk kinetics. Powder or polycrystalline samples were used in such studies. The samples were placed in a thermostat where the polymorphic transition begins and proceeds. It was found by us that usually isothermal conditions were not attained in these works; the rate of the sample *warming up* in the thermostat was measured instead of the rate of transition.

The transition in a powder sample is controlled by the nucleation in the individual microcrystals. According to our data,[4] the actual temperature of the polymorphic transition is "pre-coded" in a single crystal. For the different particles of a powder sample, these temperatures will be different. That is why a powder changes to the other phase at no single temperature, but within a temperature range. The rate of the transition in the bulk, $dx/d\tau$, is proportional to the rate of passage through this range. If the $dx/d\tau$ measurements are begun too early (and this is usually the case), the illusion is created that the first-order reaction equation $dx/d\tau = K(1 - x)$ is satisfied, because the warming up of a sample in the thermostat is described by an equation of the same form: $dT/d\tau = K(T_{\text{th}} - T)$. The "reaction constants, K" found in this manner are then used to obtain the activation energy E_a of the transition from the Arrhenius equation $K = A \cdot \exp(-E_a/RT)$. The conclusions about the mechanism of the phase transition, based on that result, are evidently erroneous.

It should be noted that the first-order reaction equation adopted from chemical kinetics is not suited for use in the description of heterogeneous

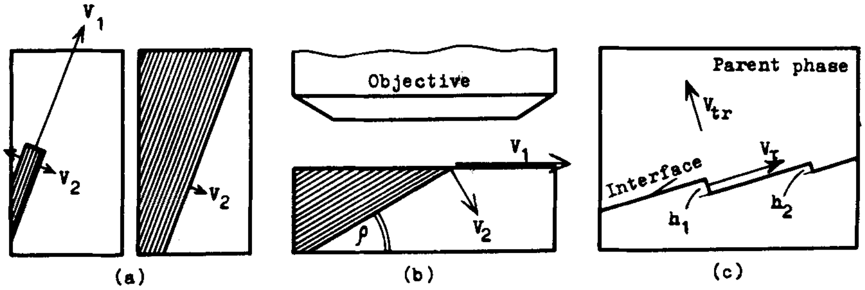

FIGURE 1 Some parameters of linear (interface) kinetics. The observed movement rate of the flat interface depends on: (a) Indices *(hkl)* of growing crystal face; $V_1 \gg V_2$. (b) Angle ρ between the plane of observation and growing face; $V_1 > V_2$. (c) Number and height *h* of ledges running along the interface plane per unit of time.

processes such as polymorphic transitions. The simplest example, when a flat intersecting interface moves through an elongated crystal (irrespective of the substance), confirms this. The bulk rate $dx/d\tau$ in this case evidently is not proportional to the remainder of the initial phase, in spite of the requirements of the equation. The necessary proportionality is absent also in the transitions in any powder sample for the reasons given in the previous work.[4]

The close inter-relation of the two problems, nucleation and interface movement, hinders the investigation of each one separately. For this reason, analysis of the problem using the "formal kinetics" formulae (as proposed first in Refs. 5 and 6) does not provide unambiguous conclusions. Other approaches seem to be more fruitful. Thus, experiments can be performed in which the two problems can be investigated separately. This is especially true for transparent samples since an optical microscope permits one to get the same information in a more reliable way.

In the *interface kinetics* method the velocity of normal interface movement V_{tr} is measured. The value of V_{tr} does not reproduce well even in the most idealized case such as the movement of a flat interface through a monocrystal. The main reasons for this poor reproducibility were mentioned above, and some others are shown in Figure 1. However, as will be seen below, valuable information can be obtained from *relative* changes in V_{tr} under different conditions.

2 A PROPOSED CONCEPTION OF INTERFACE KINETICS

The processes controlling the kinetics of polymorphic transitions will now be described. A proposal will be made which, firstly, is connected closely with our previous results and, secondly, enables us to explain simply and logically all the observed phenomena and relationships described in the next Section. The proposal is as follows.

The boundary between the two polymorphs is a natural flat crystal face of a daughter phase. The movement of this boundary, *i.e.*, the growth of this face, obeys the principle of layer by layer growth.[7,1] This growth is controlled by formation of two-dimensional nuclei. The flat shape of the moving interface denotes that $V_{tr} \ll V_r$ (Figure 1(c)), the normal velocity, V_{tr}, being limited by the rate of two-dimensional nucleation rather than by translocations of molecules while running the ledges during growth of the two-dimensional nuclei.

Two-dimensional nuclei can form only heterogeneously (as is the case with three-dimensional ones).[4] These nuclei are vacancy aggregations (VAs) in a parental crystal that act as heterogeneous sites; VAs are required for some steric freedom to be available for the molecules which build a two-dimensional nucleus on the contact interface (Mnyukh and Panfilova).[2] VAs have much smaller sizes in comparison with the microcavities that act as sites of three-dimensional nuclei. The VAs differ from each other in the number of vacancies that they consist of, in configuration, and in how closely they are located to the interface. For this reason they form a spectrum of the activation energy for two-dimensional nucleation.

When moving, the interface intersects the positions of the VAs. This motion thus creates a flow of the VAs onto the interface. The intensity of the flow is influenced by the VA migration. Not all VAs in this flow can be effective, but only those for which the nucleation barrier is surmountable at the given temperature. The portion of the VAs which has taken part in the nucleation goes onto the crystal surface together with the ledges.

Another important phenomenon of interface kinetics results from the fact that the interface movement is actually a process of crystallization in a medium. The entry of foreign particles into a new lattice in such processes is always less probable than that of its own molecules. In the case in question, these "foreign particles" are evidently not only contaminations, but also other defects of the parent lattice, including the VAs. The defects will be

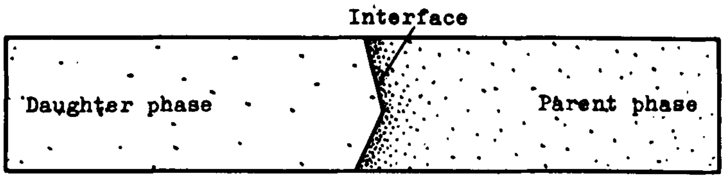

FIGURE 2 Accumulation of lattice defects in front of the interface moving through the crystal (schematic drawing). The phenomenon is similar to zone refining (recrystallization through melt); it plays a significant role in the kinetics of polymorphic transitions.

accumulated in front of the moving interface, forming a "cloud" (Figure 2). The consequences will be as follows:

a) V_{tr} enhancement at the expense of the intensification of VA flow to the interface;

b) intense coagulation of vacancies into VAs, and VAs into larger ones;

c) migration of the defects towards their lower concentration, i.e., away from the interface. Strains spreading from the interface will intensify this migration.

3 EXPERIMENTAL DATA AND THEIR EXPLANATION

Some phenomena described here have been reported (but not explained) earlier, and others are stated for the first time. In sum they present a substantiation of the foregoing conception of interface kinetics.

3.1 Crystal imperfection as a necessary condition for polymorphic transition

Earlier experiments were described[2] which are important to the topic of the present paper. They show that (1) in monocrystals of some medium quality the transition occurs spontaneously if sufficient overheating (undercooling) ΔT is applied relative to the equilibrium temperature T_0, (2) the transition in crystals of higher quality cannot occur without introducing an "artificial" defect by mechanical coercion with a needle, and (3) the transition in crystals of still higher quality is impossible under any conditions.

The reasons for the above behavior are as follows. The crystal of the first type contains at least one defect suitable for the three-dimensional nucleus to be formed. Besides, it includes defects required for two-dimensional nucleation, their concentration being sufficient for the interface movement. The crystal of the second type does not have even a single "natural" defect needed for the three-dimensional nucleation, but it contains quite a number of the defects needed for two-dimensional nucleation. As to crystals of the third type, conditions for movement of the interface are absent in them, because they do not contain a sufficient quantity of the defects needed for uninterrupted two-dimensional nucleation.

Two conclusions can now be formulated. Firstly, the *possibility of interface movement* ($V_{tr} \neq 0$) *is peculiar to non-ideal crystals only*, whereas in ideal or simply sufficiently defectless crystals $V_{tr} \equiv 0$. Secondly, the defects for two-dimensional nucleation are unlike those for three-dimensional nucleation, because a situation is possible when the former are present and the

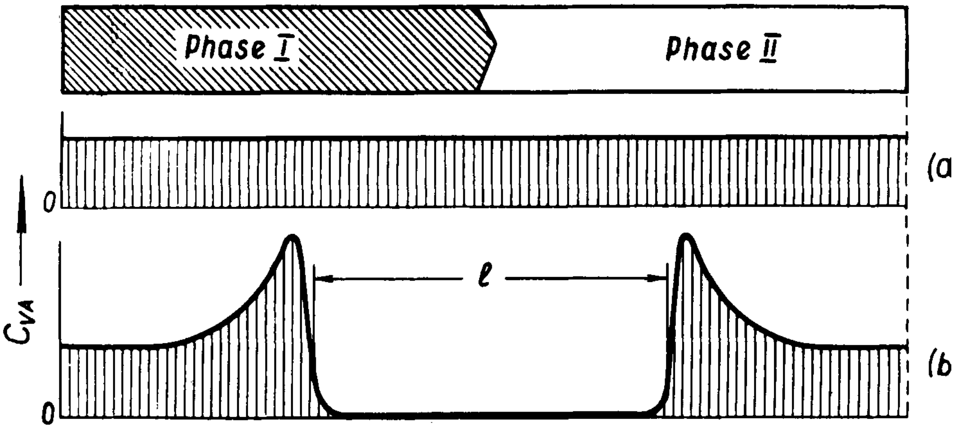

FIGURE 3 The suggested distribution of lattice defects (VAs) required for two-dimensional nucleation, after the interface has been moved many times back and forth within the limits of the crystal range l. (a) Uniform distribution of VAs before the transition. (b) After the absolute stabilization of the interface ($V_{tr} \neq f(T°)$). The negligible or zero concentration of the defects ($C_{VA} \cong 0$) in the l range is the result of "cleaning" from the defects. They are led away to the crystal surface and outside the l range.

latter are absent in a crystal. Although the defects of the two types play different roles during a polymorphic transition, we suppose all of them to be microcavities, their "structural" difference being only in their dimensions.

3.2 Experiments with a needle-shaped crystal: depletion of the reserve of lattice defects as a result of multiple cyclic transitions

One needle-shaped crystal of *p*-dichlorobenzene was observed for several weeks. After the polymorphic transition had been initiated, the interface was repeatedly moved back and forth many (more than 20) times without reaching the end faces of the crystal. As a result of the multiple transitions in the "working" part of the crystal from one phase into another and back, the velocity V_{tr} in each direction was lowered by ~ 3 orders without any deterioration of the appearance of the crystal (dimness, defects, etc.). Several additional cycles led to $V_{tr} \neq f(T)$, *i.e.*, to the situation when neither heating nor cooling were able to displace the interface. The interface remained fixed at room temperature (18–20°C) for some days though this temperature was rather far from the T_0 (30.8°C). After that break the experiments were resumed; it was found that the ability of the interface to move under the action of temperature has been restored, but only partially (much lower V_{tr} at the same ΔT_{tr}).

First of all, these experiments clearly demonstrate the nonreproducibility of V_{tr}. Their results can be explained as follows. The rapid drop in V_{tr} after a number of cyclic transitions is caused by a decrease in the number of VAs as they are expended on two-dimensional nucleation (they are led to the crystal surface). The value of V_{tr} drops to zero when the concentration of these defects, C_{VA}, falls below a required level. The resulting distribution of VAs in the sample may be represented as in Figure 3. A partial capability to move under the action of $\pm\Delta T$ is restored only after a long period of "rest" that is needed for the VAs to migrate from the regions outside the "working" part l.

3.3 Interface velocity as a function of the number of transitions

We should recall the experiments described earlier (Mnyukh *et al.* [8]). About 20 elongated *p*-dichlorobenzene single crystals have been used to measure V_{tr} as a function of the ordinal number n of transitions for different fixed ΔT. The $V_{tr} = f(n)$ dependence discussed here, and the $V_{tr} = f(\pm\Delta T)$ dependence to be discussed later, were obtained. A region 1 mm long was selected in the middle of a crystal (both end regions played a certain auxiliary role) and the time required for the interface to traverse this distance was measured. This was performed with two microscopes equipped with heating stages, one having a temperature $T_1 = T_0 + \Delta T$, and the other $T_2 = T_0 - \Delta T$. The crystal was transferred from the one stage to the other many times and every time V_{tr} was measured. Once one series of the measurements was finished, the next series was started with another ΔT value, and so on.

The $V_{tr} = f(n)$ curves are not reproducible quantitatively, but their character is reproduced (Figure 4). A new finding as compared with the results discussed in Section 3.2, is a *maximum* in the curves. This finding indicates that there are two competitive factors. The first which is responsible for the descending part of the curves was elucidated previously: it is expenditure of defects on two-dimensional nucleation. The second, most probably, is the formation of an additional quantity of VAs owing to the coagulation of vacancies in front of the interface, where the density of the defects is high (Section 2 and Figure 2). Migration of VAs and vacancies from the periphery is responsible for the ability of the crystal to display anew the maximum after the "rest."

3.4 Stabilization of immovable interface

Let the interface move at a velocity $V_{tr,1}$ during overheating (undercooling) ΔT. If we stop the motion for a time $\Delta\tau$ (by means of a suitable temperature change) and then restore the initial ΔT value, it is always found that $V_{tr,2}$ (new velocity) $< V_{tr,1}$. The longer the time $\Delta\tau$ the lower the $V_{tr,2}$.

In Figure 5 (a–c) the reasons for the tendency toward interface stabilization are shown. Accumulation of the defects in front of the moving interface

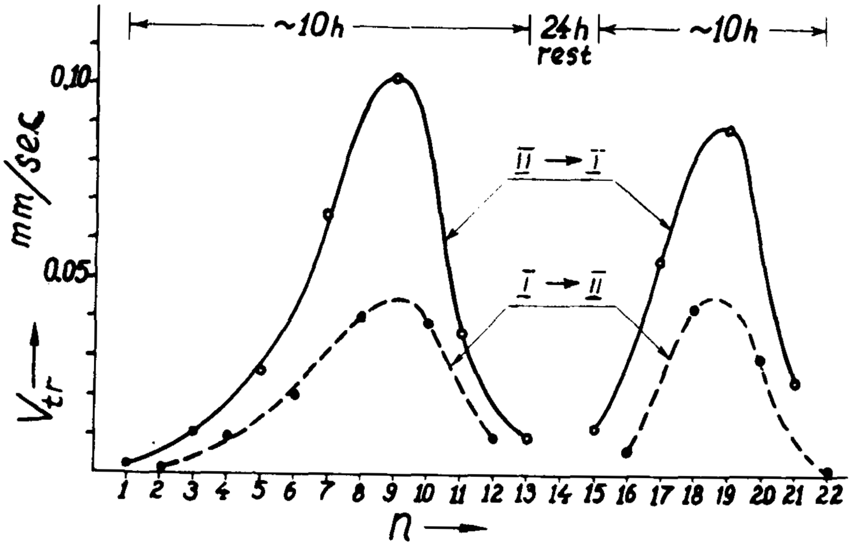

FIGURE 4 Linear (i.e. interface) velocity of polymorphic transition, V_{tr}, in a *p*-dichlorobenzene crystal vs the number of transitions, *n*.[8] Two phenomena are revealed: the existence of a maximum and the restoration of a capability to exhibit it again after a long "rest." The maxima are found for both directions of transition.

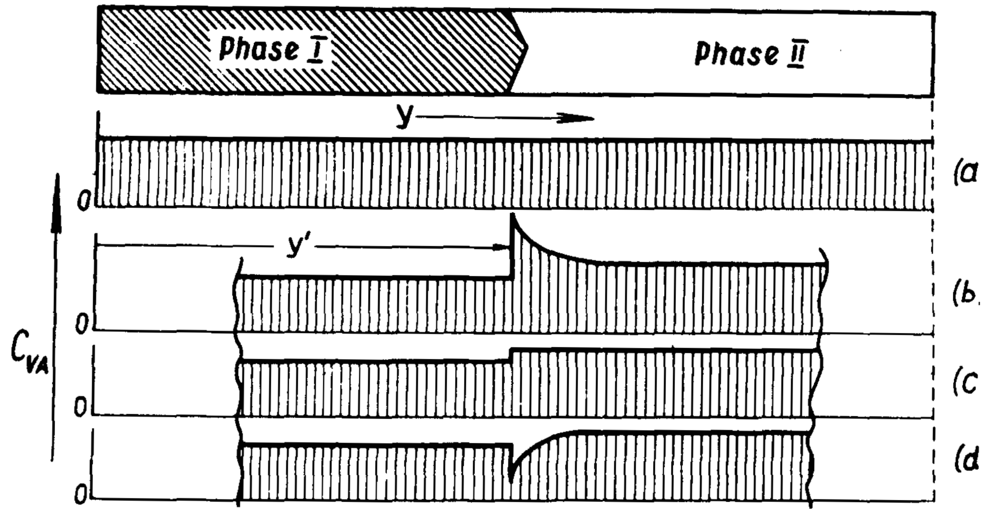

FIGURE 5 Concentration distribution of the VA type defects in a crystal. (a) The initial, $C_{VA} = f(y) = \text{const}$. (b) C_{VA} in the course of uniform motion of the interface which is in the y' position at the given moment (corresponds to Figure 2). (c) C_{VA} in the case of long stopping of the interface in the position y'. (d) C_{VA} after the interface has resumed its motion and goes ahead.

raises the intensity of the VA flow to the interface, which increases the V_{tr}. If a stop occurs, a migration of the defects begins toward their lower concentration, i.e., away from the interface. As the "cloud" of the defects disperses, the resumed movement proceeds with a lower velocity.

3.5 Chang's effect[9]

An interface, if stopped for a prolonged period of time at a particular place, is retarded spontaneously at the same place in the backward motion provided that the motion proceeds immediately after the direct run.

While moving, the interface consumes a definite number of VAs per unit length, getting them from the "cloud" accumulated in front. A prolonged stop, however, allows the "cloud" to disappear. When the movement is resumed the needed amount of VAs subtracts from the uniform C_{VA} distribution (Figure 5d). During the backward run the interface retards its movement exactly at this "hole" in the concentration distribution.

3.6 Acceleration of the transition under the influence of another interface

Using the effect described in subsection 3.4 one can provide the experimental conditions under which isothermal growth of a daughter crystal D_1 is retarded or stopped, and the transition proceeds at the expense of growth of D_2 from another site (Figure 6a). It was found that approach of D_2 to D_1 greatly accelerates growth of the latter. The character of the dependence of V_{tr} on the distance l for D_1 is shown in Figure 6b.

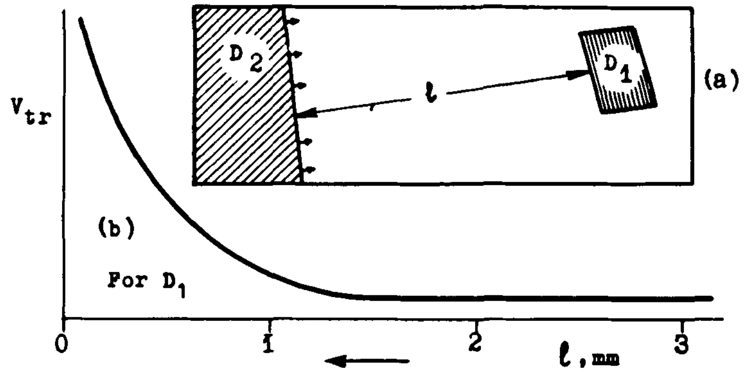

FIGURE 6 Excitation and progressive acceleration of the growth rate V_{tr} for the daughter crystal D_1 under the action of the other interface (D_2) as the latter is drawn nearer. The distances l correspond to those observed in reality in *p*-dichlorobenzene.

Transport of VAs to D_1 where these defects are needed for two-dimensional nucleation is the cause of this effect. The increase of the D_1 growth velocity at large values of the distance can be attributed to the flow of the VAs which become mobile under the action of the strains spreading from D_2. Further increase of this velocity is caused by the "cloud" of VAs moving in front of the interface of D_2.

3.7 Cyclic reiteration of the initial stage of the transition

Experiments were performed in which the beginning of the transition (*ie.*, formation of the small daughter crystal D) was excited many times, at one and the same point, by heating, and every time was returned to the initial phase by cooling. It turned out that achievement of the same size of the daughter crystal D in each succeeding cycle required much more time than in the previous cycle. The T_{tr} had to be raised to insure the previous growth velocity V_{tr}. These temperatures are listed in Table I together with temperatures T_n at which the nucleus formed. It is to be noted that an increase of T_{tr} by 1 – 2°C makes V_{tr} rise several times. The causes of the temperature compensation will be shown in Section 5.

TABLE I

The temperatures providing one and the same growth velocity of the daughter crystal during cyclic reiteration of the initial stage of the polymorphic transition (low- to high-temperature transition of *p*-dichlorobenzene, T_0 = 30.8°C).

No. of cycle	1	2	3	4	5	6	7
T_n	43	43.5	42	42.5	41.5	43	43.5
T_{tr}	45	47	47.5	48	48	49	50

Our theory (Section 2) readily explains this behavior. As each succeeding cycle takes place, the crystal area where D reiteratively appears and disappears is "cleaned" of the lattice defects needed for the two-dimensional nucleation. Both the defects which are used for the two-dimensional nucleation and those which are pushed away by the interfaces turn out to be outside the maximum outline of D. The upward part of the curve $V_{tr} = f(n)$, present in Figure 4, is here absent because the distance that the interface travels is too short to form the "cloud" where new VAs would be created due to coagulation of the vacancies.

3.8 Dependence of interface velocity on temperature

The $V_{tr} = f(\pm \Delta T)$ curve shown in Figure 7 was plotted for *p*-dichlorobenzene by the data described in Section 3.3. Each experimental point in the curve 1 is the result of twofold averaging, first on all the transitions in each crystal, and then on different crystals. The curves 2 and 3 are the data of Lemanceau and Clement[10] and Danilov and Ovsienko[11].

Three peculiarities can be seen. (1) The curve is a tangent to the X-axis at T_0, and this evidently is a general peculiarity of polymorphic transitions. (A more detailed investigation of V_{tr} in the neighbourhood of T_0 shows that the precise tangentiality is absent, see point 3.9). (2) The left-hand part of the curve reveals a maximum analogous to that found in the case of crystallization of melted material. In both processes there are two factors acting in opposite directions with $|-\Delta T_{tr}|$ increasing. The first, which can be called

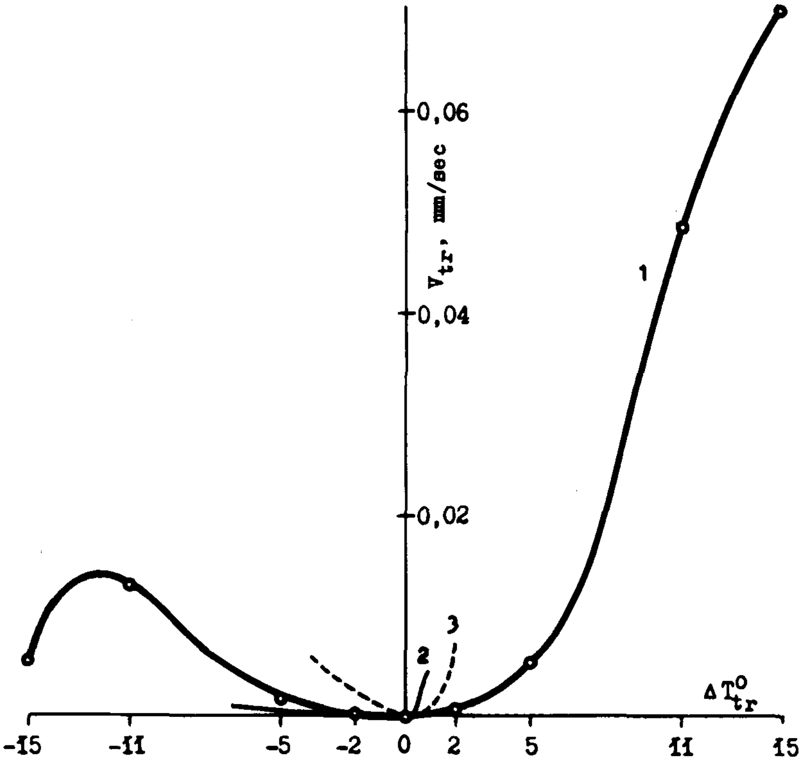

FIGURE 7 Plots of linear velocity of transition vs ΔT_{tr} for *p*-dichlorobenzene.[8] $\Delta T_{tr} = T_{tr} - T_0$, where $T_0 = 30.8$°C. 1—The present author's work; each experimental point is the result of a twofold averaging of measurement data. 2—Lemanceau and Clement.[10] 3—Danilov and Ovsienko.[11]

the "factor of the moving force," gives rise to a V_{tr} increase; the second, which can be called the "factor of the absolute temperature" gives rise to a V_{tr} decrease. The factors themselves, however, are not the same in the two cases. (3) As to the right-hand part of the curve, the two factors act in one and the same direction. One would think only acceleration of the V_{tr} rise will take place with rising $+\Delta T_{tr}$, but this is not the case. Certain deceleration of the V_{tr} rise is observed at large $+\Delta T_{tr}$ values. The cause of this phenomenon will be explained in Section 5.

3.9 Interface movement hysteresis

Temperature lags (overheating or undercooling) in the beginning of a polymorphic transition, $\Delta T_n \neq 0$, were shown by the author[4] as being inevitable because of an energy barrier for nucleation of the new phase. But if this barrier has been overcome (a nucleus has been formed), even then some value of $\Delta T_{tr} \neq 0$, though smaller than ΔT_n, was found to be necessary for the interface movement to occur. When investigating a polymorphic transition in a substance, we always measured T_0 as precisely as possible. To do this, an interface was moved back and forth by means of small temperature deviations from the temperature at which the interface remained immovable. It was found in all the cases that V_{tr} did not approach zero asymptotically when $\Delta T \rightarrow 0$; there is a *temperature range* (sometimes some tenths or hundredths of a degree) where the interface is insensitive to temperature variations (Figure 8). Irrespective of the direction of the temperature change, the interface begins to move at the end of the range, i.e., *hysteresis* of the interface motion takes place. This phenomenon is in accordance with our conception that two-dimensional nucleation is the parameter controlling the interface kinetics, because the formation of two-dimensional nuclei is very naturally associated with the overcoming of some barrier.

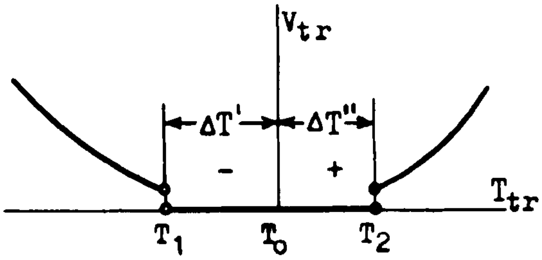

FIGURE 8 Temperature range between $T_1 = T_0 - \Delta T'$ and $T_2 = T_0 + \Delta T''$, in which an interface is immovable and insensitive to temperature variations (i.e. $V_{tr} \equiv 0$). Actual ΔT_{tr} can be larger than the threshold values $\Delta T'$ and $\Delta T''$.

4 ON ACTIVATION ENERGY OF POLYMORPHIC TRANSITIONS

The entire set of data leads us to another interpretation of the activation energy of transition, E_a, than the one that is generally understood at present. Usually E_a is taken to be equal to the barrier height between the atomic (molecular) lattice arrangements of the polymorphs; the rate of phase transitions is controlled by this E_a value. Such an interpretation of the activation energy reflects a still widespread approach to polymorphic transitions as if they represent some kind of homogeneous reaction, or lattice transformation by uniform deformation. However, such an interpretation leads practically to $E_a = \infty$, because polymorphic transitions are impossible in perfect crystals.

One should keep in mind, firstly, that the polymorphic transition actually occurs by nucleus formation and subsequent interface movements, and, secondly, the details of how this really happens. With such an understanding we must infer that there is no single inherent value of E_a for a given polymorphic transition in the given substance. Each transition can be defined with *several* different E_a's according to the process stages:

E'_a. Activation energy for the formation of a three-dimensional nucleus initiating an embryo of the new phase in a given crystal. The E'_a depends on the structure of the lattice defect at which the nucleus arises. Inasmuch as all the nucleation temperatures that are "pre-coded" in the corresponding defects are different, one should infer that E'_a is not a constant, and can take various values. These values form a spectrum where E'_a cannot be smaller than some threshold $E'_{a,\mathrm{min}}$ corresponding to the threshold delay of nucleation temperature $\Delta T_{n,\mathrm{min}}$. The opposite end of the spectrum has no such confinement.

E''_a. Activation energy for the formation of two-dimensional nuclei on a smooth interface. E''_a is not a constant either, but a spectrum caused by structural differences in the defects acting as sites of two-dimensional nuclei. (Perhaps, disposition of the defect against the interface is also of importance.) The theory stated in Section 2 can explain all the facts only if such a spectrum exists.

E'''_a and E''''_a. Other two activation energies can be suggested, the former for formation of a one-dimensional step at a two-dimensional step, and the latter for molecular translocations from the parental phase to a daughter phase while moving the one-dimensional step. In general, $E'_a > E''_a > E'''_a > E''''_a$.

Dependence of the rate of polymorphic transitions on these activation energies is indirect, complicated, and quite different for different conditions. It should be emphasized that the existence of these activation energies is inseparably linked to the existence of corresponding lattice defects.

The rate of a transition is controlled by two factors: the *number* of the appropriate defects in the crystal (existence, the number, distribution through the volume), and the *quality* of the defects. The above-mentioned set of activation energies characterizes only the quality of the defects present in a given crystal. As a rule, the rate of the transition is first of all influenced by E'_a and E''_a. Thus, the transition in a fine powder will be controlled solely by E'_a values in the crystal particles. In the other case, when a flat interface moves along a crystal, E''_a comes into operation instead of E'_a. However, E''_a acts only as one of the parameters controlling the interface velocity of the transition. The significance of the E''_a spectrum will be evident from the next section.

5 INTERRELATION OF THE PARAMETERS CONTROLLING THE INTERFACE KINETICS

Now we can summarize the parameters controlling interface kinetics, as well as their interrelations. This is done with the help of the scheme (Figure 9). It is actually self-explanatory if one keeps in mind the material discussed in the previous sections. As the present author hopes, the scheme provide a program for thinking about the problem under discussion in terms of the new approach proposed in Section 2. Although the scheme in Figure 9 is simplified (only main relations are shown) and represents the simplest case of the kinetics, it allows the complexity of the kinetics to be estimated.

6 THE TYPES OF KINETICS BASED ON GENERATION OF LATTICE DEFECTS

For the interface in a molecular crystal to be of a macroscopically flat shape specific conditions are required such as small ΔT_{tr} and high quality of the single crystal. Otherwise, one observes a nondescript shape for the interface which leaves behind a turbid region with a great number of grains; X-ray patterns show that the single crystal becomes polycrystalline. From the fact that the united interface converts the single crystal into a polycrystal the only thing that can be deduced is that the interface *generates* the lattice defects which act as sites for three-dimensional nucleation in front of it. The strains originating from the interface are the obvious cause of such kinetics. Not having time for the relaxation, they give rise to deterioration of the adjacent lattice.

Thus the kinetics in question is based on the principle: ... interface movement → strains → generation of crystallization sites in front of the

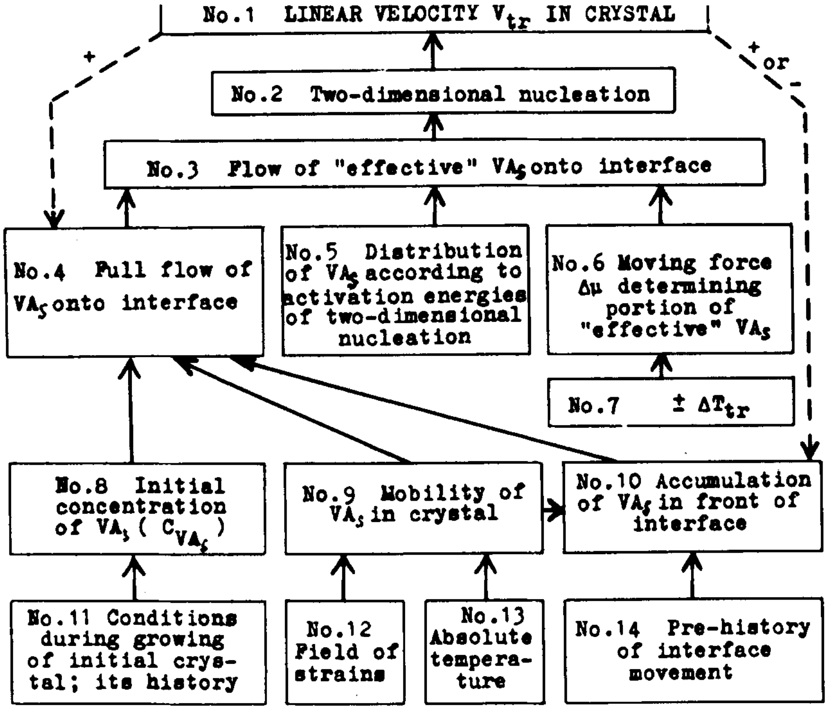

FIGURE 9 Parameters controlling the linear (interface) kinetics of polymorphic transitions, as well as relations between these parameters. The arrows are directed from the controlling parameters to those being controlled.

If the VAs were motionless the full VA flow to the interface (No. 4) would be controlled by the starting concentration of the VAs (No. 8) and by interface movement velocity (No. 1). The dependence of No. 4 on No. 1 is a positive feedback (dotted arrow). Migration of the VAs (No. 9), stimulated by a strane relaxation, also influences the VA flow. The accumulation of the VAs in front of the interface (No. 10) depends on the mobility of the VAs (No. 9) and on V_{tr} (No. 1). Accumulation of VAs in front of the interface (No. 10) is the principal parameter controlling the intensity of the VA flow onto the interface (No. 4) and, finally, controlling the value of V_{tr} (No. 1) as well. It is seen that there is a tangle of relationships and feedbacks. For this reason it is impossible to predict and reproduce V_{tr}.

The scheme elucidates the causes of the effect of temperature. The effect is two-fold. The $\pm\Delta T$ deviations from T_0 (No. 7) determine $\Delta\mu$, the difference between the specific free energies of the two polymorphs, which is a "driving force" for the polymorphic transition (No. 6). In turn, $\Delta\mu$ determines the part of VA flow, which is effective, i.e., suitable for the two-dimensional nucleation. Besides, independent of the position of T_0, V_{tr} is greatly affected by absolute temperature (No. 13) which determines the mobility of VAs (No. 9). The reduction of VA mobility induced by lowering the temperature diminishes the ability of the VAs to be accumulated in front of the interface (No. 10) as well as the ability of vacancies to coagulate into new VAs (not shown in the scheme); as a result, V_{tr} falls.

The maximum in the $V_{tr} = f(\Delta T_{tr})$ curve at the temperatures lower than T_0 (Figure 7) is caused by the action of both temperature parameters (No. 7 and No. 13) in opposite directions. On the other hand, the two parameters act in the same direction for V_{tr} growth upon raising the temperature from T_0. The combination of parameters No. 7 ($\pm\Delta T_{tr}$) and No. 8 (initial concentration of VAs) is responsible for the deceleration of V_{tr} growth velocity at large $+\Delta T_{tr}$ values. The significance of the former consists in determining the effective portion (No. 6) of the total number of VAs which, according to the latter, is confined. At large overheating $+\Delta T_{tr}$, when the proportion of effective VAs is comparable with unity, further temperature rise would not produce much in enhancement of the V_{tr} because of the depletion of the VA reserve.

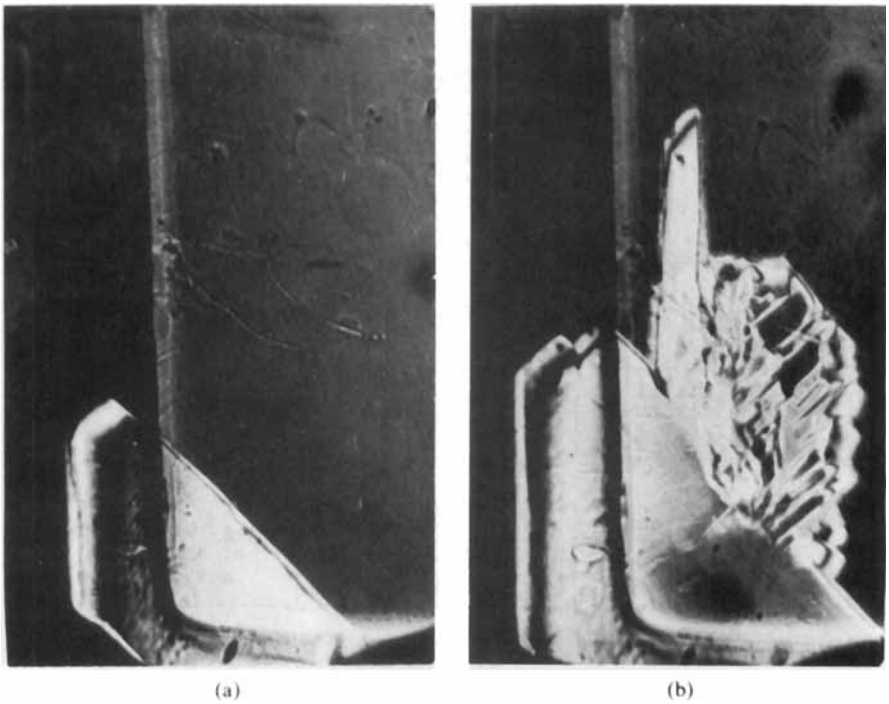

FIGURE 10 Conversion from the kinetics based on consumption of available defects (a) to the other (b) based on generation of new defects in the field of strains spreading from the interface. The conversion manifests itself as an "explosion" on the flat interface.

interface → growth of crystals from these sites (*i.e.*, interface movement) → ... and so on. This type of kinetics is based on a *positive feedback.* In principle the velocity of the interface movement can be very high in these cases, but not higher than the propagation of an elastic wave.

Since the interface is capable of generating the sites for three-dimensional nucleation (these are microcavities), it would be logical to expect the existence of intermediate kinetics based on the generation of smaller defects such as VAs. We believe that we have observed a case of this kind (Figure 10). The photographs show a slow movement of the flat interface to be followed by a local "explosion" at which the velocity of the transition increases by one order of magnitude. Two different types of kinetics were found to be recorded in Figure 10(b). The conversion from one type to the other is very sharp, this feature being characteristic of the processes which become unsteady under the action of positive feedbacks.

A *rhythmical* polymorphic transition found, in particular, in thin elongated plates of hexachloroethane[12] is an example of the kinetics that involves a *negative feedback*. A normal motion of the interface at sufficiently large ΔT_{tr} is interrupted from time to time by stops, sharp lines remaining at these places after the interface goes ahead. The directions of both the interface and tracks of its stops coincide with the cleavage of the initial crystal. The effect resembles rhythmical crystallization of a melt material. However, the cause of the negative feedback is different. Rhythmical stops occur evidently as a result of temporary disturbance of the proper contact between the two polymorphs when the strains reach the ultimate strength of the plate and are released by means of displacement deformation along the cleavage. The rhythmical polymorphic transition is absent if (a) ΔT_{tr} is small and thus there is sufficient time for strain relaxation, and (b) crystal samples have a large cross section and so, the strains do not exceed the ultimate strength of the crystals.

CONCLUSION

Thus, it is shown in this work that the kinetics of polymorphic transitions is a complex, multiparameter, and irreproducible phenomenon which makes sense only for sufficiently imperfect crystals and depends rather on the history of the sample and on feedbacks than on the nature of the sample. This conclusion, however, does not contradict the opinion of the author that there is only one general molecular mechanism of polymorphic transitions.

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