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ON THE MECHANISM OF THE POLYMORPHIC TRANSITION FROM THE CRYSTALLINE STATE TO THE ROTATION-CRYSTALLINE STATE

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The rotation-crystalline state of matter (r.c.s.), called in the foreign literature the rotational form or plastic crystals, is, along with the liquid-crystalline state, one of the two known mesomorphic states occupying, in their structure, properties, and temperature range of existence, a position between a crystal and a liquid. It has been the object of a number of studies (see, for example, ([1])), which, however, have not touched upon the question of the mechanism of the process of transformation of a crystal into the r.c.s. (c $\rightarrow$ r.c.s.). It is known that the r.c.s. is characterized by preservation of the crystalline lattice of the molecular centers and by the loss by the molecules of long-range orientational order as a result of thermal rotation. This structural feature gave Ya. I. Frenkel ([2]) grounds for calling such a phase transition orientational melting. Unfortunately, this figurative term did not help prevent the spread of the incorrect notion of such a transition as the onset, upon reaching a certain temperature, of rotation of the molecules around the same mean positions that they occupied in the lattice. The sharp changes in the symmetry of the lattice, the space network of the molecular centers and the mode of packing of the molecules, as well as the considerable jump in density, which usually occur in this process, testify against such a mechanism.

The question of the mechanism of the c $\rightarrow$ r.c.s. transition arises in connection with the results, reported in a number of previous publications ([3-10]), of a study of c $\rightarrow$ c transformations, in which it was shown that the c $\rightarrow$ c transformation occurs at interfaces that are planar crystallographic faces of the daughter crystal growing in arbitrary orientation within the matrix. It was also found that the growth of these faces has a layered mechanism, extremely reminiscent of the corresponding mechanism of crystal growth from the liquid and gas phases. The conclusion was drawn that at the boundary between solid phases there is no intermediate layer of excited molecules of gas-like or liquid-like type, whose

existence is assumed by many authors (see [11]).

The objects of the present investigation were hexachloroethane (phase-equilibrium temperature $T_{0,\alpha\beta} = 71.6^\circ$) and CBr_4 ($T_0 = 46.9^\circ$). Its aim was to determine whether the mechanism of c → r.c.s. transformations belongs to the same type as that of c → c transformations, or whether it possesses some fundamentally different features. Before the investigation was begun, both answers seemed equally probable, although it was obvious that the transition is not reduced simply to replacement of the vibrational state of the molecules in the lattice by a rotational one. While some features, for example the transformation of the single-crystalline matrix into a system of arbitrarily oriented grains of the r.c. phase ([7]), seemed to indicate a commonality of mechanisms, others indicated differences. The latter were reduced, basically, to two points, as followed from our own preliminary observations and indirect data in the literature. First, even when very favorable conditions were created for the growth of a single crystal of the r.c. phase from a low-temperature single-crystalline matrix on the heating stage of a microscope (high quality of the matrix crystal, closeness to T_0, and temperature stability), it was not possible to obtain the regular forms of phase-boundary interfaces characteristic of crystallographic faces, whereas under such conditions ···

the same conditions, in the case of c→c transitions, growth faces were invariably observed. Secondly—and this is especially important—the impression was created that c→r.c.s. transitions always occur at the temperature of thermodynamic phase equilibrium, T_0, without any temperature lags ΔT ($\Delta T = T_t - T_0$, where T_t is the actual transition temperature).

To clarify the mechanism of the polymorphic transformation, the question of the presence or absence of ΔT is of fundamental importance. In the literature this question has never been considered specifically, apart from isolated indications by various authors of the existence of hysteresis in particular cases of polymorphic transformations. Our data indicate that $\Delta T \neq 0$ always in transformations of the c→c type.* This is explained by the fact that such a transition is, in essence, crystallization and begins with the formation of a crystal nucleus of the daughter phase in the matrix medium. The reasons requiring supercooling for the formation of crystallization centers in liquid and gaseous media fully explain the necessity of ΔT in c→c transformations. The only specific feature is that the sign of ΔT may be either positive or negative; i.e., depending on the direction of the process, either supercooling or overheating is required. Not only the formation of nuclei, but also the existence of crystal growth faces inside a solid matrix is possible only under conditions of some overheating or supercooling of it. Otherwise, the phase boundary will follow the isotherm $T = T_0$, which separates regions of the specimen with $T > T_0$ and $T < T_0$. The shape of the isotherm will be determined by the temperature field, which depends on the heating conditions.

c→r.c.s. transitions occupy an intermediate position between c→c transitions and melting (c→l), for which, as is known, $\Delta T = 0$. There are no grounds

for the a priori assertion that this process of transition to a considerably less ordered state is also a variety of crystallization. Therefore, the question of the existence of ΔT in c→r.c.s. transitions could be answered only by experiment. Our preliminary data [7] indicated that ΔT in CBr_4 either is identically zero or is very small. The same followed indirectly from the data of other authors. Thus, from work [12] it is seen that the c→r.c.s. transition in cyclohexanol always occurs at one and the same temperature $T = -8.3^\circ$, coinciding with T_0, whereas the r.c. phase can be supercooled to -60°. Here it is appropriate to draw an analogy with melting, for which $\Delta T = 0$, and solidification, for which the supercooling may reach tens of degrees. Considering the data of another work [13], we note that the temperatures of the beginning and end of the c→r.c.s. transition in CBr_4 practically coincide with T_0.

To determine whether ΔT differs from zero in c→r.c.s. transitions, we performed measurements of this quantity in CBr_4 and C_2Cl_6. From the study of c→c transformations it is known [4] that higher values of ΔT are obtained on more perfect and smaller crystals, since defects of the matrix crystal serve as crystallization centers. Such perfect crystals of size 0.5-1 mm were grown in sufficient quantity and used for measuring ΔT. Each CBr_4 crystal was placed in a miniature cuvette with glycerin and slowly heated so that a temperature of 46.0° was reached in approximately 20-30 min. The heating rate was then greatly reduced, passing through the interval from 46.0° to T_t also in 20-30 min. At the moment the transformation began, the temperature was read from the mercury thermometer of the Boëtius heating stage. The accuracy of the temperature reading was ±0.05°. Systematic error in the values $\Delta T = T_t - T_0$ was eliminated by measuring T_0 with the aid of the same thermometer. For this purpose, the onset of the transformation was induced in the crystal, and by small temperature oscillations of ever decreasing amplitude–

* Phase transformations of the first order are meant.

Table 1

Delays ΔT of the polymorphic transition to (β-phase) → r. c. s. (χ-phase) in CBr_4. $\Delta T = T_p - T_0$, where T_p is the actual transition temperature, and $T_0 = 46.9^\circ$ is the temperature of thermodynamic equilibrium of phases α and β

Crystal no.*	T_p, °Ck → r. c. s.	ΔT, °Ck → r. c. s.	T_p, °C(k →) r. c. s. → k	ΔT, °C(k →) r. c. s. → k
1	47.1	0.2	45.9	1.0
2	47.15	0.25	46.4	0.5
3	47.45	0.55	–	–
4	47.1	0.2	46.0	0.9
5	47.0	0.1	44.6	2.3
6	47.1	0.2	46.1	0.8
7	47.0	0.1	45.2	1.7
8	47.0	0.1	45.4	1.5

Crystal no.*	T_p, °Ck → r. c. s.	ΔT, °Ck → r. c. s.	T_p, °C(k →) r. c. s. → k	ΔT, °C(k →) r. c. s. → k
9	46.9	0.0	46.1	0.8
	$\overline{T}_p = 47.20$	$\overline{\Delta T} = 0.19$	$\overline{T}_p = 45.71$	$\overline{\Delta T} = 1.19$

Crystal no.*	T_p, °Cr. c. s. → k	ΔT, °Cr. c. s. → k	T_p, °C(r. c. s. → →) k → r. c. s.	ΔT, °C(r. c. s. → →) k → r. c. s.	ΔT, °C(r. c. s. → k → →) r. c. s. → k
10	29.0	17.9	47.0	0.1	–
11	31.1	15.8	46.9	0.0	–
12	29.9	17.0	46.9	0.0	4.1
13	29.8	17.1	46.9	0.0	4.5
14	29.9	17.0	46.9	0.0	2.0
15	31.9	15.0	46.9	0.0	4.9
16	30.9	16.0	46.9	0.0	14.0
17	29.9	17.0	46.9	0.0	9.2
18	31.7	15.2	46.9	0.0	11.1
19	30.7	16.2	47.0	0.1	13.0
	$\overline{T}_p =$ 30.40	$\overline{\Delta T} =$ 16.50	$\overline{T}_p =$ 46.92	$\overline{\Delta T} = 0.02$	$\overline{\Delta T} = 7.85$

* Crystals 1-9 were obtained from solutions in ethyl alcohol, chloroform, acetone, or their mixtures, had good faceting and were transparent; crystals 10-19 were obtained from the melt on the microscope stage, consisted of several r. c. blocks, and had no faceting.

small displacements of the phase boundary in both directions; the limiting temperature was taken as T_0. After measuring $\Delta T_{\text{k}\to\text{r.c.s.}}$, the transformation was carried to completion, and then the temperature was slowly lowered and $\Delta T_{\text{r.c.s.}\to\text{k}}$ was measured. We note that in the latter case the matrix is already the r. c. phase in the form of a system of disoriented blocks occupying the habit of the initial β-single crystal. In such a matrix the number of defects–potential crystallization centers of the other solid phase–inevitably increases greatly in comparison with the original one. When comparing $\Delta T_{\text{k}\to\text{r.c.s.}}$ with $\Delta T_{\text{r.c.s.}\to\text{k}}$, this difference in the quality of the matrices had to be taken into account. In order to equalize the initial conditions somewhat, measurements of $\Delta T_{\text{r.c.s.}\to\text{k}}$ were also performed on matrix CBr_4 crystals grown from a drop of melt on the heating stage of the microscope. Good single crystals could not be obtained, but the best crystals selected for the measurements consisted of a small number of transparent blocks and undoubtedly had fewer defects than those obtained by the polymorphic transformation of the initial β-matrix.

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

The results of measurements of ΔT on CBr_4 crystals are partly given in Table 1. These data, as well as the corresponding measurements on hexachloroethane crystals, make it possible to conclude that the phase transitions k $\rightarrow$ r. c. s. occur with a delay, although it is small. According to measurements on 28 C_2Cl_6 crystals,* the delays of the transformations k $\rightarrow$ r. c. s. averaged

* C_2Cl_6 crystals were precipitated from a solution in toluene at a temperature of 50-54°, at which the β-form arises; at room temperature the γ-form precipitates from the solution ($T_{0,\beta\gamma} = 43.6°$).

Fig. 1. Polymorphic transformation $\beta \rightarrow \alpha$ in CBr_4: growth of faceted crystals of the rotational-crystalline α-phase (in the lower part of the photographs) in the medium of a single-crystalline β-matrix. 100×. **a, b**—two stages in the growth of a "cluster" of α-crystals; **c**—partially faceted blocks of the α-phase; in the upper left corner a face of the matrix crystal is visible; **d**—another "cluster" of α-crystals.

Fig. 2. Polymorphic transformation $\beta \rightarrow \alpha$ in C_2Cl_6. A less perfect picture than in the case of CBr_4 (Fig. 1), but the features of a face of an α-crystal are distinctly visible; in the upper and lower right corners a face of the matrix crystal is visible. 100×

$\Delta T_{\text{c}\rightarrow\text{r.c.s.}} = 0.52°$, fluctuating within 0.1-1.3°. In all cases $|\Delta T_{\text{c}\rightarrow\text{r.c.s.}}| < |\Delta T_{\text{r.c.s.}\rightarrow\text{l}}|$, but this inequality is confirmed with particular obviousness if the quality of the matrices is somewhat equalized by obtaining the r.c.s. matrix from a melt of CBr_4. Of 20 experiments, in each of which $\Delta T_{\text{c}\rightarrow\text{r.c.s.}}$ was compared for one "good" and one "bad" crystal, in 19 cases it turned out that $|\Delta T_{\text{c}\rightarrow\text{r.c.s.}}|^{\text{good}} > |\Delta T_{\text{c}\rightarrow\text{r.c.s.}}|^{\text{bad}}$. This not only once again confirms that $\Delta T_{\text{c}\rightarrow\text{r.c.s.}} \neq 0$ (both crystals of a pair were heated identically), but also testifies to the formation of nuclei of r.c. phase crystals on defects of the matrix lattice. At the same time it was shown that the visual assessment of the quality of the matrix crystal by transparency, absence of visible defects, and perfection of faces was entirely permissible.

Thus, all the data indicate the absence of any fundamental differences between the mechanisms of the c $\rightarrow$ c and c $\rightarrow$ r.c.s. transitions. In both cases the polymorphic transformation may be regarded as reconstructive in the sense proposed in (7). In both cases the symmetry and type of packing of the molecules change, the density and entropy change discontinuously, the process proceeds at the phase boundary, centers of crystallization arise on defects of the matrix lattice,

and there is no crystallographic dependence of the orientations of the lattices of the matrix and daughter crystals. The differences observed, as is now clear, are not fundamental. The small value of $\Delta T_{\text{c}\to\text{r.c.s.}}$ is explained phenomenologically by the intermediate position that the r.c.s. occupies between the crystalline and liquid states, and in essence by the ease with which crystallization centers of the r.c. phase arise, which follows from the structural features of the r.c.s.

The difficulties in obtaining faceted crystals of the r.c. form from the solid phase by polymorphic transformation are due to a number of reasons: the lattice potential energy is lower than in the crystalline state (this also explains the difficulties in growing perfect crystals from the melt), simultaneous emergence of a large number of centers, the need for very fine regulation of the temperature because of the smallness of $\Delta T_{\text{c}\to\text{r.c.s.}}$, and, finally, the large ($\sim 3\%$) jump in density, causing the appearance of strong stresses and damage to the matrix already at the initial stage of growth. In order to remove any doubts about the commonality of the mechanisms of the c $\to$ c and c $\to$ r.c.s. transitions, it seemed to us very important to find faceted r.c.s. crystals growing inside a crystalline matrix. Although the difficulties listed greatly reduce the probability of obtaining a clear picture, refinement of the experimental conditions and enlargement of the scope of the experiment made it possible to obtain the necessary microphotographs. In Fig. 1*a* and *b* one can see a druse of faceted r.c. single crystals in a β-matrix of CBr_4. An analogous case is presented in Fig. 1*c*. The presence of faceting in individual growing r.c. blocks and Fig. 1*b* leaves no doubt. The detection of corresponding growth faces in C_2Cl_6 was not as successful, but in this case as well it turns out that fragments in a generally formless phase boundary in a number of cases possess faceting (Fig. 2).

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Note: Figure translations are in progress. See original paper for figures.