

MEMORY EFFECT IN SINGLE-CRYSTAL TRANSFORMATIONS OF ARAGONITE-TYPE TO CALCITE-TYPE POTASSIUM NITRATE

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ABSTRACT

An X-ray and optical study of over 30 single-crystal transformations of $\text{KNO}_3(\text{II}) \rightleftharpoons \text{KNO}_3(\text{I})$ involving the aragonite-type (II) and disordered calcite-type (I) structures, has resulted in the following observations: (a) at slow heating rates small crystals transform with preservation of the single-crystal condition, including minute internal and external detail, (b) the 110 plane of the calcite-type crystal parallels the 010 plane of the original aragonite-type crystal, (c) the c -axes of the two structures are not parallel but differ by an angle of 26 degrees, both axes lying in the plane normal to the [110] (I) and [010] (II) directions common to the two structures, and (d) a pronounced incubation period exists for the transformation for all specimens studied; this period averages 4.1 minutes for all specimens.

The structural relationships given above are completely reversible and independent of crystal shape, size, or perfection, indicating a memory effect that must be structurally controlled. Ideally, the c -axis of phase II parallels rows of closest potassium atom spacing of the phase I structure as viewed along the [110] projection, and the 001 plane of phase II departs by only 4 degrees from the $1.I \cdot 10$ plane of phase I, a fact verified by the single-crystal experiments.

The volume change for the transformation at the phase boundary is only 0.71 percent whereas that for the calcite-aragonite transformation of CaCO_3 is 6.4 percent at 375°C and 1 atm. Single crystals involved in the latter transformation polygonize to the point that similar transition data are inconclusive.

INTRODUCTION

The calcite $\rightleftharpoons$ aragonite transformation is known to be reconstructive (Buerger, 1961, p. 16); that is, bonds cannot merely be stretched to achieve the new atomic configuration but atoms are completely detached (except for certain polyhedra) from one another in the reactant phase and recombined into the product phase. Such transformations require large activation energies and ordinarily result in considerable break-up of grains. Recent work (Davis, 1964, p. 490) brought forth the possibility that all known phases of KNO_3^1 may have structural analogs in the CaCO_3 phase diagram, with the reservation that the calcite-type form of KNO_3 (phase I) probably contains NO_3^- groups in a state of rotational disorder (Tahvonen, 1947).

Because of the isostructuralism between KNO_3 and CaCO_3 and also be-

¹ Recently, Rapoport and Kennedy (1965) discovered three new polymorphs of KNO_3 . No corresponding regions in the CaCO_3 phase diagram have yet been observed.

cause of the easy accessibility of the transformation boundary between phase II and I of KNO_3 (aragonite and calcite types, respectively), the characteristics of the calcite-aragonite transformation can be studied with a simple X-ray diffraction heating furnace.

The irreversible transformation of aragonite to calcite at 400°C for single crystals was studied by Dasgupta (1964), and he concluded that the [100] directions of the two phases were mutually parallel and [110] of aragonite paralleled [010] of calcite. Dasgupta also pointed out that the preferred orientation of the polygonized grains of calcite after the transformation indicated a parallelism of the c -axes for the two phases.

Brown, Fyfe, and Turner (1962) observed various replacement orientations of natural calcite upon aragonite in the glaucophane schists of California. These authors observed three orientations in which the c -axis of calcite was contained in the 100 plane of aragonite and one orientation with the c -axis contained in the 010 plane. Although these examples may not be solid state transformations, but replacement by solution, one might expect some definite structural relationship to exist between the two polymorphs.

Direct observation of single-crystal transformations involving no polygonization but showing a memory effect are rare, but a good example of such a study is that of Kitaigorodskiy, *et al.* (1965) who observed and photographed single crystal transformations in α - β p -dichlorobenzene. Oddly, there was no crystallographic control of the orientation of the new (β) phase but whatever the orientation for each experiment, a reversal of the completed forward transformation resulted in the same crystallographic orientation for the final α -phase that existed prior to initiation of the process. Kitaigorodskiy, *et al.* explain the memory effect to be the result of preservation of a "seed" nucleus of reactant phase at a defect site in the crystal.

EXPERIMENTAL METHOD

The single crystals were heated at room pressure in a Tempres X-ray diffraction furnace in which the final temperature set by a Helipot was approached as slowly as desired by adjustment of a power Variac. The emf of a pair of platinum vs. platinum-10% rhodium thermocouples was "bucked" by a voltage divider to control the heating rate, and the temperature of the sample was determined by chromel-alumel thermocouples in contact with the platinum sample tray. Temperature readings are considered accurate to within $\pm 1^\circ$.

The furnace-sample holder assembly was converted into a one-circle goniometer by construction of a small rod-shaped spindle that fitted inside the ceramic tube that ordinarily supports the platinum sample tray. Three holes of different sizes were drilled into the spindle and a wire for

rotation of the spindle was added through the furnace window. Rotation measurements of the single crystals are accurate to within $\pm 2^\circ$. The furnace is equipped with screws for rocking the sample a few degrees in, and normal to, the plane of the goniometer reflecting circle, and these adjustments permitted accurate orientation of the single crystal reflecting surface.

More than thirty single crystals of various sizes were ground down on emery paper to dimensions that were within the limits of the sample holder and spindle. The KNO_3 single crystals were obtained from dry reagent supplies, and also grown directly from a cooled saturated aqueous solution. The latter type contained numerous fluid inclusions (to be discussed later) but also displayed crystal faces much more completely than the dry reagent crystals.

When the crystal was reduced to appropriate size the ground surface was rubbed against moist cloth or toweling to remove the deformed surface layer. The grinding also permitted us to obtain a sufficiently large reflecting surface of the crystallographic direction desired. The sample, in the shape of a disk, plate, or prism, was then placed on the sample tray and oriented by means of the rocking screws until a strong reflection was obtained from the ground surface. The furnace door was closed and as the temperature was raised slight adjustments of the rocking screws were made to maintain perfect orientation. The temperature was raised at a rate between 0.3 and 0.5°C/min, most variations within this range being due to unavoidable changes in furnace characteristics and air currents in the vicinity of the furnace. A few experiments were made for which this heating rate was considerably larger, but here only reflection data, and not physical transformation characteristics, were desired. The maximum temperature reached in any of the experiments was less than 140°C and usually less than 135°C. The $\text{KNO}_3\text{-I} \rightleftharpoons \text{KNO}_3\text{-II}$ transformation temperature is 127.5°C as established from careful powder runs made in this laboratory.

The crystals contained many inclusions and were often twinned. In view of this condition a general class notation has been used to indicate the perfection of the crystal. The crystals have been assigned to four classes: class A crystals are visually perfect, are not twinned, contain no inclusions, and show no strain under polarized light; class B crystals contain a few liquid or air inclusions but are not twinned; classes C and D pertain to crystals with progressively more inclusions and class D crystals are obviously twinned and/or strained.

OBSERVED CRYSTALLOGRAPHIC RELATIONSHIPS

Observations with the flat stage. Table 1 presents the transformation data for 22 of the KNO_3 single crystals studied for the forward reaction $\text{II} \rightarrow \text{I}$.

All listed in the table were heated in the Tempres stage on the platinum sample tray. Many other runs with KNO_3 and CaCO_3 single crystals were made only to obtain specific orientation data, or for photographic purposes, and are not included in the table.

In each case the diffraction patterns for the initial aragonite-type phase consisted of only one peak (a necessary condition for an untwinned single crystal). The Bragg angles were checked on the first 15–20 peaks to make certain of the single crystal condition. Many crystals were examined optically for the same purpose. When the transformation took place the rate was recorded by either oscillating about, or by setting the goniometer exactly at the center of, the phase II peak. In the latter case the setting was made just before the transformation was reached so that shift of the peak from thermal expansion would be insignificant. The temperature-time curve was recorded either automatically with a recording potentiometer or by manual plotting on the diffraction chart. When the high temperature phase (I) appeared the Bragg angles were then checked to determine which, if any, diffraction peaks were present.

As can be seen from Table 1 the only initial surface of phase II that yielded strong reflections for the resulting phase I was the 020 (II)¹ surface. In all crystals of this orientation studied the resulting phase I reflection was consistently 110 (I).² That these two planes are mutually parallel for this transformation is established with certainty from the consistent results of this study as well as from similar observations on calcite and aragonite by Dasgupta (1964).

Experiments involving initial 200 (II) reflections (9 and 10) and those involving 110 (II) reflections (4 and 16) demonstrate, on the other hand, that no plane in the prism zone of the calcite-type phase (I) becomes oriented parallel to either of these two planes of phase II. This was unexpected in view of the previously reported parallelism of the *c*-axes for the two structures, which, if operative in the KNO_3 polymorphs should yield a strong 300 (I) reflection from an initial 110 (II) reflection. Slow scanning (1/4 deg/min) with the goniometer revealed only a very weak reflection in this region and it is not certain even if this comes from the calcite-type phase. By comparing the observed absolute intensities in Table 1 for the 020 (II) and 110 (I) reflection with the calculated relative intensities of the 110 (I) and 300 (I) reflections for calcite, the latter reflection should have an absolute reflection intensity in the 6×10^5

¹ When necessary, to avoid confusion, the phase pertaining to a given reflection will be given in parentheses following the Miller indices.

² The indices for calcite-type KNO_3 , as used here, are the Miller indices for the hexagonal cell with $c/a \cong 3.6$ and $Z=6$.

TABLE 1. INTENSITY DATA FOR SINGLE CRYSTAL TRANSFORMATIONS OF $\text{KNO}_3(\text{II}) \rightarrow \text{KNO}_3(\text{I})$

No.	Dimensions, mm			Per- fection	T_i °C	t_{90} min	dT/dt °/min	P min	Initial Phase II Reflection		Resulting Phase I Reflections $I, 10^3$ counts/sec				
	L	W	H						hkl	$I, 10^3$ counts/sec	114	006	110	other	
1	11	7	1.5	A—	129	—	—	1.5	020	190	9	0	300	—	
2	8	3	1	A—	130	2.0	0.397	2.5	020	2500	0	0	1120	—	
3	8	6	2	A—	135	1.5	0.435	7.5	020	1600	40	0	1300	—	
4	10	8	2	C	131±2	10?	0.532	3.5?	020	1800	—	—	—	—	
5	10	4	2	B—	133	2.5	0.422	5.5	110	600	90	0	300	—	
6	10	8	2	D	132	4-6	0.376	4.5	111	10	3.5	0	960	—	
7	9	5	2	D	132	6.2	0.300	4.5	002	900	170	0	20	—	
8	7	3	2	A	131	5.0	0.431	3.5	002	1100	11	0	0	—	
9	8	3	2	B	134	1.0	0.269	6.5	200	1300	130	0	0	—	
19	7	3	3	B—	131	1.3	0.300	3.5	200	350	5	0	30	300=2	
11	9	3	1.5	B	—	—	—	—	(in [010] zone $\phi=45^\circ$ no initial I)	200	0	0	18	003=0.5	
13	6	3	2	B—	131	2.6	0.435	3.5	102	1050	0	0	0	—	
14	4	2	1	C	131	6.2	0.368	3.5	200	1000	19	1.5	7	024=4.5	
15	10	2	2	B—	—	2.0	0.3	—	102	250	3.5	1.5	0	116=8.5	
16	10	2	2	B—	131	4.0	0.3	3.5	020	1100	0	0	950	—	
19	4	3	2	A—	—	—	—	—	110	3250	56	0	8.5	—	
20	3	2	1	B	—	—	—	—	002	650	6	2	0	—	
22	1	1	1	C	—	—	—	—	202	3000	150	0	0	—	
25	5	2	1	A—	131±2	—	—	—	(in [010] zone $\phi=30^\circ$ no initial I)	—	0	0	0	—	
26	4	3	2	A—	132	4.4	2.5	4.5	040	1800	75	0	1150	—	
27	4	4	2	C	130	3.2	2.5	2.5	002	2100	50	20	0	11·10=750	
28	4	4	3	B—	131	4.4	2.5	3.5	002	1400	5	<1	<1	11·10=20	
									002	900	43	0	0	11·10=50	

Explanation of Symbols: L = (length always parallel to the c -axis), W = width, H = height, t_{90} = time for 90 percent transformation, T = temperature, °C, T_1 = temperature for the first appearance of phase I peak, $P = T_1 - T_x$ where T_x is 127.5°C, I = absolute intensity.

counts/second range. We thus observe only 1/300 of the expected intensity.

Note that several surfaces have yielded very weak $1\bar{1}4$ (I) reflections, even for cases where the orientation is such as to yield a completely dominating phase I peak of considerably different index. This condition is believed to be caused by one or a combination of three possible factors: (1) slight distortion of the structure to form a mosaic of blocks of differing orientation, (2) the presence of small grains of highly variable orientation developing on the surface of the single crystal, and (3) twinning of the structure. Examination of the table shows that nearly all crystals of phase I show $1\bar{1}4$ reflections in their patterns, although they are in most cases very weak compared to either the phase II reflection or the dominating phase I reflection. Factor (2) is considered relatively unimportant as visual observation of several crystals during the transformation with the furnace door slightly open showed a perfectly smooth crystal surface. Optical examination of the larger crystals, however, indicates that factor (1) is a major cause (to be discussed in a later section) and for this reason the use of the term "single crystal" for phase I may be inappropriate. Nevertheless, it is obvious that upon reversal of the transformation the resulting phase II is still a single crystal by all physical appearances, and for the smaller crystals optical examination shows excellent continuity of extinction. The term "single crystal" is therefore used throughout with the understanding that some mosaic structure may be present in the larger crystals.

With direct evidence, therefore, that the c -axes of the two crystals were not parallel, but that the 010 (II) and 110 (I) directions were, other orientations of the initial reflecting surface were studied, especially in the [010] (II) zone. An attempt was also made to cut a crystal parallel to the (111) face but the cut was slightly misaligned. Nevertheless, the cut was close enough so that the surface gave a weak 111 reflection (no. 6, Table 1) and the test was made. The resulting phase II pattern showed a moderate $1\bar{1}4$ (I) reflection which pointed to the possibility that one set of planes of this form was oriented somewhere in this region.

Several crystals were cut and aligned to give reflections in the [010] (II) zone; ϕ -angles¹ for these reflections are 30, 45, and 50 degrees, the latter being coincident with 202 (II) reflection plane. None of these tests showed intensities for either 006 (I) or $1\bar{1}4$ (I) sufficiently strong to pinpoint the location of the c -axis in this zone.

Observations with the spindle stage. Thus to obtain a unique solution to the

¹ ϕ is here defined as the angle between the c -axis and the normal to a section or reflection surface within a given crystal structure.

problem a sample spindle was constructed that could be rotated about 60 degrees around the goniometer axis, thus permitting one to locate one of the phase I reflections appearing in the $[010]$ (II) zone; possible phase I reflections expected in this zone are $\bar{1}14$, $\bar{1}18$, $11\cdot10$, 006 , etc. Because of the ease with which the stronger $\bar{1}14$ reflection could be located this peak was selected for most of the experiments. All were mounted with $[010]$ (II) parallel to the goniometer axis. Table 2 summarizes the data for the spindle experiments and shows conclusively that the two c -axes depart considerably in the transformation of the two structures. All other positions of ϕ up to 30 degrees in the 60-degree arc of the spindle movement yielded zero to very weak intensities for $\bar{1}14$. The average of the angles γ between $[001]$ (II) and $[\bar{1}14]$ (I), is seen to be 17.5 degrees. The angle

TABLE 2. SUMMARY OF X-RAY DATA OBTAINED FROM SPINDLE OF HEATING STAGE

No.	Dimensions, mm			Perfection Class	I_{002} (II)	$I_{\bar{1}14}$ (I)	γ deg.
	L	W	H		10^3 counts/sec	10^3 counts/sec	
99	5	3	3	B	500	250	21
100	3	1	1	B+	200	310	17
101	3	1	1	B	112	50	19
102	3	3	3	A-	1,100	600	13
						Average	17.5

between the c -axis and $[\bar{1}14]$ of KNO_3 (I) is 45.8 degrees giving an angle for the deviation of the two c -axes of 28.3 degrees. It is difficult to assign limits of uncertainty to this figure; however, the maximum observed variation in γ here is 8 degrees and could possibly represent a real variation in tilt of the mosaic blocks of the phase.

Structural relationships, Figure 1-A, is a projection along $[010]$ of the aragonite-type structure with atom positions based on measured cell constants at $125 \pm 1^\circ\text{C}$: $a = 5.42_6$, $b = 9.19_6$, and $c = 6.55_0$ Å (orthorhombic, $Pmcn$, $Z = 4$). In Fig. 1-B a projection of KNO_3 -I is made along the $[110]$ direction using an orthorhombic pseudo-cell with constants $A = \sqrt{3} a$, $B = 2a$, and $C = c$, where at $134 \pm 1^\circ\text{C}$ $a = 5.42_6$, and $c = 19.36_2$ Å (hexagonal, $R\bar{3}c$, $Z = 6$). Doubling the B dimension of the orthorhombic pseudo-cell allowed a more direct comparison of cell content and atom position with that of the phase II structure.

With the observed γ -angle of about 17.5 degrees from the spindle experiments, one can predict from Figure 1 which, if any, reflection of phase I should result from a section cut parallel to 001 (II). In Figure 1-B

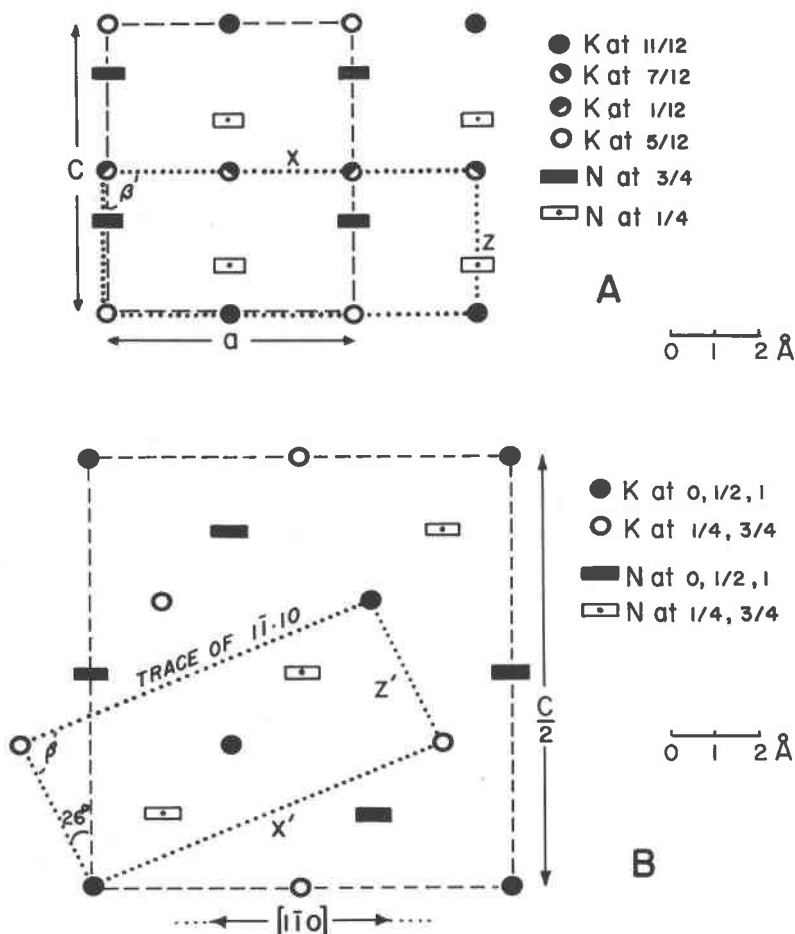


FIG. 1. A: Projection of the aragonite (II) structure onto the side pinacoid 010. The a and c dimensions of the true unit cell are given by the dashed lines. A reference cell with dimensions x , y , and z , $Z=3$ is outlined by the dotted line. The NO_3 -units are not specified as to orientation.

B: Projection of the calcite (I) structure along $[110]$. The vertical dimension is equal to $1/2$ the length of the c -axis of the X-ray pseudocell ($Z=6$) and the horizontal dimension is equivalent to the long diagonal of this cell. The dimension in the direction of the projection is twice the length of the a -axis of the pseudocell. The reference cell given by the dotted lines is obtained from the phase II reference cell by distortion of β and appropriate expansions and contraction of the edges x , y , and z (see text).

we can see that the trace of planes containing the closest spacing of K atoms in projection departs from the c -axis by 26 degrees; if it is assumed that this trace also represents the c -axis direction for phase II prior to

transformation then one would expect a strong $1\bar{1}.10$ reflection from a surface cut only 4 degrees from 001 (II). Of course, the sense of rotation about [010] in the transformation is arbitrary.

Experiments 26 through 28 represent the final test of the model obtained thus far; three crystals were cut as close to the basal 001 pinacoid as possible and the crystal was scanned at the high temperatures for the desired reflection. Experiment 26 yielded such a strong $1\bar{1}.10$ reflection that fortuitous alignment of the cut surface is indicated. The other two experiments also show strong $1\bar{1}.10$ reflections, even stronger than the $1\bar{1}4$ reflections, although considerably weaker than experiment 26. In view of the fact that the $1\bar{1}.10$ plane has a relative intensity of about 1 ($1\bar{1}4=100$) for calcite structures, these intensity relations are quite convincing of the correctness of the model.

We can thus conclude that during the transformation $\text{KNO}_3\text{-II} \rightarrow \text{KNO}_3\text{-I}$ the c -axis of phase I departs from that of phase II by a theoretical value of 26 degrees, or observed value of 28 degrees, and that the [010] direction of phase II is coincident with the [010] direction of phase I. Also, in view of the relationships given above the 100 plane of phase II becomes the $1\bar{1}2$ plane of phase I, the latter plane containing potassium atoms in a distorted close-packed arrangement.¹ The crystallographic relationships between the two phases are shown by means of the stereographic projection of Figure 2.

The transformation can be described best in relation to the "reference" cell (but not repeat unit) shown by the dotted lines in Figure 1, A and B. In Figure 1-A the dotted lines outline a cell containing 3 KNO_3 , with β -angle of 90 degrees and with cell edges x, y , and z . The transformation to β', x', y' , and z' is accomplished by distortion of β from 90 to 86 degrees, by expansion of z by 5.8 percent, by expansion of x by 4.0 percent, and by contraction of y by 10.9 percent.² Projection of the resulting reference cell is given by the dotted lines of Figure 1-B. Note that the z dimension (normal to the plane of the figure) for the phase I structure is not equal to B , only $3/4 B$. Both reference cells have $Z=3$ and assuming movement of the atoms and NO_3^- groups are not great it should theoretically be possible to propose movements paths of least energy for the atoms and groups of the cell. However, these cells are not unit cells. In fact, there are two kinds of "reference" cells of identical volume in Figure 1-B, each of which is repeatable only along directions of the x - z diagonals. Therefore, such a model cannot be obtained without examination of comparable atom positions over space containing at least two, perhaps more,

¹ The average spacing of the K atoms in the $1\bar{1}2$ plane of phase II is 4.77 Å; in the $1\bar{1}4$ (cleavage) plane of phase I the average spacing is 4.96 Å.

² This does not imply actual physical changes by these amounts.

such cells. A projection of several cells for each phase in the z and y directions shows that the movement plan is complex and cannot at present be explained in terms of simple translation components.

PHYSICAL CHANGES ACCOMPANYING THE TRANSFORMATION

This transformation is accompanied by three important physical processes that warrant further mention here. They are (1) a consistent

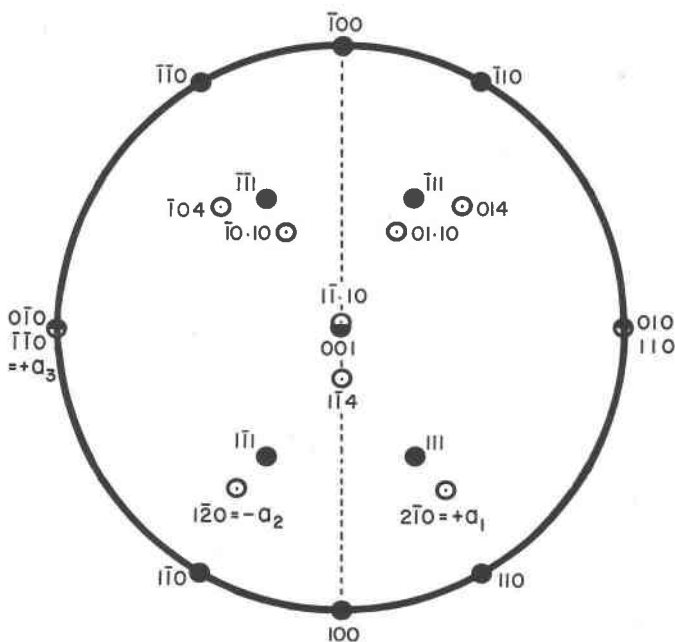


FIG. 2. Stereographic projection of the poles to crystal planes in the phase II and phase I structures as they are related in the transformation. Solid circles are for phase II and open circles are for phase I. Upper hemisphere.

and reproducible memory effect (with the crystallographic relationship discussed above), (2) a remarkable resistance to polygonization, and (3) a pronounced incubation period with resulting sigmoidal transition curve.

In perhaps 20 out of the 22 experiments recorded in Table 1 special efforts were made to record data for the reverse transformation, that is, $\text{KNO}_3\text{-I} \rightarrow \text{KNO}_3\text{-II}$ taking place with lowering temperature. In these experiments an X-ray diffraction pattern was obtained after the reverse transformation had taken place and in all but one or two cases the reflection initially obtained for the forward transformation was also pres-

ent after the reverse change, although reduced in intensity by as much as 50 percent. In several patterns very weak reflections from other diffracting planes appeared but were completely dominated by the major one. Thus the transformation takes place with the so-called "memory effect." Unlike the experiments of Kitaigorodskiy, *et al* (1965, p. 466), these transformations show crystallographic control. The same orientation of phase I results from any given crystal of phase II, and in the reverse transformation the phase II structure develops in the precise orientation with respect to crystal morphology as existed prior to the heating. In Kitaigorodskiy's experiments the β -phase of *P*-dichlorobenzene could develop with any apparently arbitrary orientation within the host crystal, even though the reverse $\beta \rightarrow \alpha$ transformation also resulted in the original α -orientation (even after many reversals of transformation for the same crystal). They concluded that storage of a metastable seed nucleus within the stable transformed material accounted for this phenomenon.

It is apparent that the degree of preservation of the single crystal depends on its size and shape. For prismatic crystals whose average dimension was less than about 2 mm the crystal could be heated and cooled through the transformation several times with very little internal or external damage, but larger, or more equant, crystals gradually broke up into domains showing some optical discontinuity under crossed nicols. Figure 3 presents photographs of several single crystals showing these characteristics.¹ The prismatic crystal shown in A-D of Figure 3 is approximately $4 \times 1 \times 1/2$ mm in dimension, elongated parallel to the *c*-axis, and showing prismatic and pinacoidal crystal faces. In the center of the crystal is a long needle-shaped inclusion approximately half-filled with trapped solution from which the crystal was grown. A number of smaller inclusions are also present but are nearly invisible due to trapped solution. The photograph was taken under crossed nicols and shows uniform extinction throughout. The second photograph was taken after one cycle through the transformation and shows two interesting features; (1) the development of two domains of slightly different orientation, and (2) ejection of the fluid from the inclusions. Other than these effects there appears to be no distortion or break-up of the crystal and minor surface and internal features are completely unchanged. Figure 3-C is the same crystal after three cycles (six passes over the transition boundary), and it now shows better extinction than that of photograph B which means that the two tilted blocks have been restored to an orientation consistent with

¹ The SSC and SC series crystals described in Figures 3 and 4 do not correspond to the experiments listed in Table 1, but represent different runs entirely.

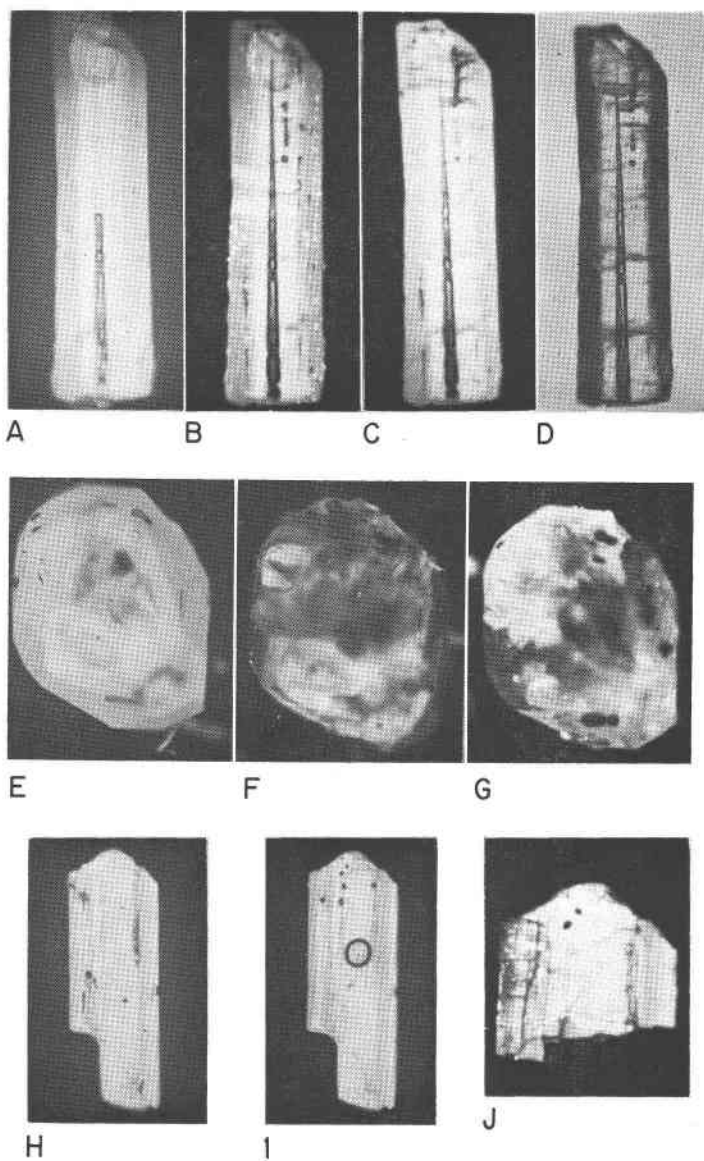


FIG. 3. **A.** SSC-1 Before transformation. Crossed polarizers, $\times 20$. c -axis vertical, $[010]$ normal to diagram. **B.** SSC-1 After one cycle. Note two domains of slightly differing orientation, and evacuated spine cavity. Crossed polarizers, $\times 20$. **C.** SSC-1 After three cycles. Note excellent uniformity of extinction with crossed polarizers. $\times 20$. **D.** SSC-1 After three cycles. Same as Fig. 3 but with polarizers not crossed. **E.** SSC-2 Before transformation. Crossed nicols, $\times 20$, c -axis position unknown. **F.** SSC-2 After one cycle. Note clouding by inclusion of air bubbles. Crossed polarizers, $\times 20$. **G.** SSC-2 After three cycles. Much of the air has been ejected and more large fluid inclusions have been evacuated. **H.** SSC-3 Before transformation. Crossed polarizers, $\times 20$. c -axis vertical, $[010]$ normal to diagram. **I.** SSC-3 After one cycle. Numerous cavities have been evacuated of fluid. Large dark circle is air bubble in immersion oil. Crossed polarizers, $\times 20$. **J.** SSC-3 After three cycles. Only upper $1/4$ of crystal preserved. Note refilling of some cavities. Crossed polarizers, $\times 40$.

the rest of the crystal. However, one notices that microfractures have begun to develop normal to the c -axis which may be the result of the greater expansion coefficient parallel to c than parallel to a , or as a result of expansion differences during the transformation. These microfractures are not as readily visible in polarized light as they are in plain light (D, Fig. 3). They have been observed in most of the larger crystals, and always have the same orientation relative to the crystal c -axis (phase II).

The effect of the same treatment on an equant crystal is shown in E-G, Figure 3. The crystal is approximately $2 \times 2\frac{1}{2} \times 2$ mm and also shows several inclusions (some containing only air) and crystal faces. Photograph E is before any heating, F after one cycle, and G after three cycles, all under crossed nicols. The inclusions containing fluid have been evacuated and fractures containing numerous air pockets give the crystal a cloudy appearance.

Photographs H-J, Figure 3, show a small crystal with numerous fluid inclusions; before transformation they are barely visible but in I, after one cycle, 6 out of 8 inclusions in the upper $\frac{1}{4}$ of the crystal have been evacuated, and two are still filled. Also, an unfilled inclusion near the left-center of the crystal (H) has been filled in with solution (I). After three cycles (J) four of the six inclusions evacuated after the first cycle had been refilled! This phenomenon has been observed with several other crystals and demonstrates the interesting fact that fluid can be stored, ejected, and moved around within the structural framework of the crystal during a polymorphic transformation. The fluid seems to be stored along domain boundaries, cracks, and large defect sites, and not necessarily in other cavities.

Photographs A and B, Figure 4, show a large crystal ($3\frac{1}{2}$ mm across) before and after one cycle with more detail on the microfractures and inclusions. The crystal outlines and faces remain unchanged but unevenly distributed microfractures have formed approximately normal to the crystal c -axis. The dark appearance of the microfractures results from included air. Photograph E, Figure 4, is a view of the minute structure of a large crystal after one cycle. The photograph shows domains of slightly differing orientation, each domain bounded by microfractures normal to the c -axis (right to left in E). Some of these tilted domains may be responsible for much of the weak $11\bar{4}$ reflection intensity observed in almost all X-ray diffraction patterns of transformed crystals.

DISCUSSION

Such minor distortion of the KNO_3 crystals appears inconsistent with the reconstructive nature of the transformation. Both the volume change to the activated state and the volume change for the transformation must

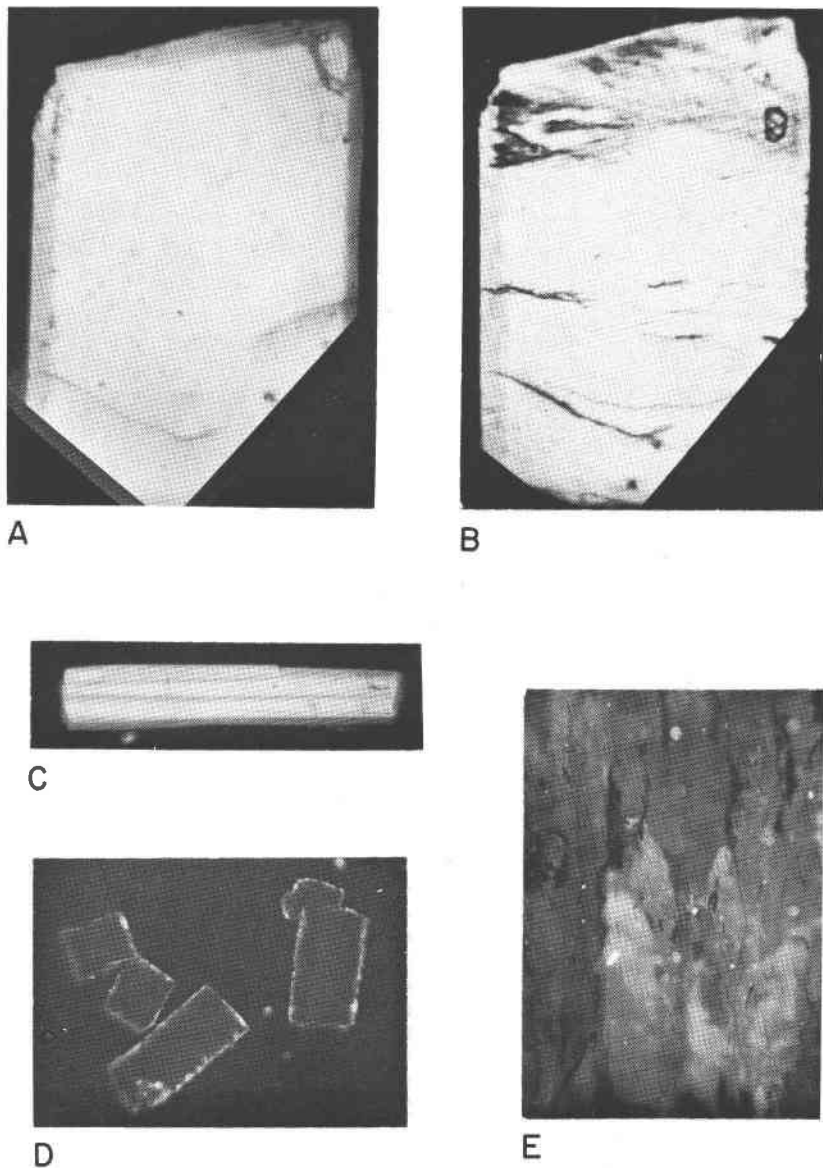


FIG. 4. A. SC-2 Before transformation. Note large fluid-filled cavity in upper right corner. Crossed polarizers, $\times 17$. c -axis vertical and $[010]$ normal to diagram. B. SC-2 After one cycle. Note evacuated cavity and fractures. Crossed polarizers, $\times 17$. C. Aragonite needle before transformation. Crossed polarizers, $\times 15$. c -axis parallel to needle axis. D. Same needle as in Fig. 3 but polygonized and broken into segments. Heated to 400°C $1\frac{1}{2}$ hours. Crossed polarizers, $\times 15$. E. Mosaic structure in SC 3 after one cycle (No. 3 of Table 1), crossed polarizers, $\times 20$. c -axis left to right.

be small to explain such conditions. The cell constants given previously for phases II and I of KNO_3 yield a volume change of $0.0035 \text{ cm}^3/\text{gm}$, or 0.71 percent of the initial volume. By comparison with the CaCO_3 polymorphs, we find that using the thermal expansion coefficients for aragonite given by Kozu and Kani (1934) and those for calcite given by Austin, *et al* (1940) the volume change at 375°C for the aragonite $\rightarrow$ calcite transformation is $0.0223 \text{ cm}^3/\text{gm}$, or 6.4 percent of the initial volume. We thus have the required Δv 's for the transformations but we know nothing of the activation volume; to obtain the latter one must also obtain the activation energy and certain thermodynamic quantities pertaining to the activated state that cannot be measured directly.

Photographs C and D, Figure 4, show photographs under crossed nicols of one of the aragonite samples heated to observe the physical effects of the irreversible transformation to calcite. The crystal turned milky and under crossed nicols was seen to be composed of innumerable tiny grains of calcite. Regardless of the value of activation volume for this transformation, a change of volume for the two phases that is a factor of 10 greater than that for the corresponding KNO_3 transformation accounts for the extreme polygonization. Experimental determination of the Δv of transformation for calcite $\rightleftharpoons$ aragonite at high temperatures is needed inasmuch as the Δv calculated above for this transformation is not an equilibrium value and is thus not strictly comparable to the equilibrium value measured for KNO_3 . However, it is known that the volume change for calcite $\rightleftharpoons$ aragonite at the phase boundary at 25°C is *not* significantly different from $6\frac{1}{2}$ percent, and should this condition be the same at higher temperatures then rather important differences in the two transformation types must be assumed to exist.

In the experiments with aragonite a check on the $1\bar{1}\cdot 10$ reflection showed that this reflection was seven times stronger than that expected for the powder pattern. All other peaks of the pattern were present, although intensities varied somewhat from the powder pattern expected. The parallelism of $[010]$ (II) and $[110]$ (I) determined by Dasgupta (1964) agrees with conclusions reached here, but the parallelism of both c -axis does not. Possibly the aragonite specimens in his experiments did not all convert to calcite at 400°C in the three-hour time allotted. The appearance of preferred orientation of crystallites in Dasgupta's rotation photographs may be due in part to incomplete conversion of the initial single crystal. Davis and Adams (1965, Fig. 2-B) show that at least some kinds of aragonite are only 70 percent transformed to calcite in three hours. Brown, Fyfe, and Turner (1962, p. 573) observed no such parallelism of c -axes in aragonite replaced hydrothermally by calcite whereas their orientation IV comes close to that observed in the results for KNO_3 reported here.

In view of the conclusions made above concerning the structural relationships of the two phases during the transformation, the usual concept, of rotation of the anion groups 30 degrees and displacement from $\frac{1}{3}$ of the distance between the cation layers to $\frac{1}{2}$ of this distance as has been done for aragonite and calcite, is no longer appropriate. For KNO_3 , at least, the structural relations observed require a 26-degree rotation of the NO_3 groups about an axis lying *in* the plane of the group, as well as cation and anion translations of an unknown nature.

OBSERVATIONS ON TRANSFORMATION RATES

A large number of runs made with powdered KNO_3 gave a transformation temperature of 127.5°C, both with increasing and decreasing tem-

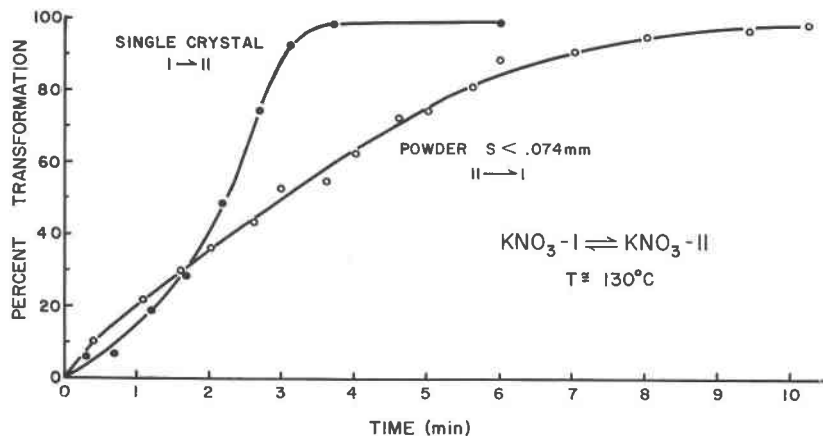


FIG. 5. Percent transformation vs. time for a single crystal (solid circles) and for a powder specimen of KNO_3 at 130°C. The single crystal involves the forward direction and the powder sample the reverse direction in the transformation.

perature. Bridgman (1916) measured a transition temperature, also for powdered material, of 128.3°C. With the single crystals, the transformation does not appear (within measurement) to begin until several minutes after the 127.5°C point is reached. This fact can be seen from the column labeled P, Table 1. The average of all such delays (P), relative to the powder transformation temperature, is 4.1 minutes. This delay is part of the so-called incubation period¹ and it strongly suggests that the number of nuclei formed for the transformation is small,² and that the

¹ Time interval in which the dominant process is the formation of one or more stable product nuclei.

² That the number of nuclei is less than 5 for crystals about 1 mm long (perfection B-C) has been verified by high temperature optical studies in this laboratory. The mosaic structure in phase I, and the crystallographic relationships deduced by the X-ray study have also been observed by this means.

transformation rate is controlled primarily by the growth rate of the new phase. An example of a rate curve for a single crystal transformation is compared with one for a powder specimen in Figure 5. Here the incubation period is small, about two minutes, after which transformation is rapid and nearly complete in $3\frac{1}{2}$ minutes. The incubation period is correlated with the time interval between $t=0$ and that point at which the new phase is detected by X-ray. Experience in this laboratory has shown that large unstrained crystals undergo transformation with an incubation period, whereas strained or small grains (as in powders obtained from grinding in a mortar) yield rate curves following a power law with no significant incubation period.

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