

# TRANSITION RATES OF $\text{KNO}_3$ HIGH-PRESSURE POLYMORPHS\*

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**Abstract**—A beryllium pressure vessel mounted in an X-ray goniometer and modified for heating to 300°C has permitted the direct recording of transition rates across all of the equilibrium boundaries of the  $\text{KNO}_3$  phase diagram.

Most transitions show rate curves that taper off near the completion of the process, but metastable persistence of phase III occurs in the phase II field and becomes greater at high pressures and low temperatures along the negative II-III phase boundary.

Several diffraction patterns of the transitions I-II and III-II revealed preferred orientation of grains in the resulting aragonite-type phase.

Cell parameters of  $\text{KNO}_3$ -I and  $\text{KNO}_3$ -III (both modified calcite-type structures) taken in their stability fields show a marked reduction in the *c*-axis length going from phase I to phase III with increasing pressure at constant temperature.

## INTRODUCTION

THE  $\text{KNO}_3$  phase diagram, Fig. 1, reveals two hexagonal (I and III) and two orthorhombic (II and IV) phases, all lying in a pressure and temperature region allowing easy study of the rates across any of the phase boundaries. From the present study something can be said about the rates across all boundaries, but more effort was put into a study of the  $\text{KNO}_3$ -I  $\rightleftharpoons$   $\text{KNO}_3$ -II and  $\text{KNO}_3$ -II  $\rightleftharpoons$   $\text{KNO}_3$ -III rates because of the similarity of these phases in structure to those of calcite and aragonite. EDWARDS<sup>(1)</sup> found that  $\text{KNO}_3$ -II had the aragonite structure and TAHVONEN<sup>(2)</sup> determined  $\text{KNO}_3$ -I to be calcite-type but with disorder present in the  $\text{NO}_3^-$  groups. FINBAK and HASSEL<sup>(3)</sup> also described  $\text{KNO}_3$ -III as calcite-type but later BARTH<sup>(4)</sup> proposed a smaller cell ( $Z = 1$ ) for the structure. The disorder of the  $\text{NO}_3^-$  ion in  $\text{KNO}_3$ -I and the uni-directional order of the  $\text{NO}_3$  ion in  $\text{KNO}_3$ -III, both resulting in a loss of the 113 and other lines of the normal calcite-type pseudo-cell,† might justify halving the *c*-axis of

this large cell, but the structural arrangement of the cations and ionic groups are nearly identical in  $\text{CaCO}_3$ -I,  $\text{CaCO}_3$ -II,  $\text{KNO}_3$ -I, and  $\text{KNO}_3$ -III; therefore the normal calcite-type pseudo-cell (hexagonal,  $Z = 6$ ) has been retained in this study.

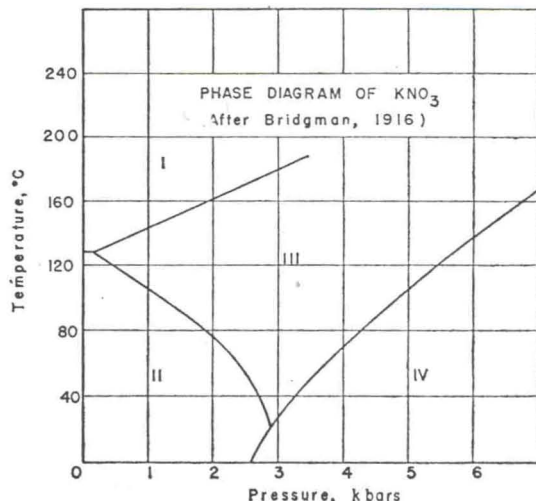


FIG. 1. Phase diagram of  $\text{KNO}_3$  (after BRIDGMAN<sup>(6)</sup>).

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† The true unit cell of calcite is a rhombohedron with  $Z = 2$  formula weights per cell.

The rates were measured in a beryllium cylinder mounted on a Norelco X-ray goniometer, a detailed description of which has already been presented (DAVIS and ADAMS<sup>(5)</sup>). The vessel was modified for heating to 300°C by winding the cylinder with No. 22 (B. & S. gauge) Ni-chrome-V wire. The heating coil was separated from the vessel wall by a thin layer of Alundum cement; another layer of this cement was applied over the furnace to act as thermal insulation against heat loss to the atmosphere. The temperature was measured by means of a Chromel-alumel thermocouple placed in a hole directly beneath the lower piston. Temperatures were determined from readings on a Leeds-Northrup portable potentiometer with which one scale division corresponded to 0.02 mV.

Previously (DAVIS and ADAMS<sup>(5)</sup>) the  $\text{KNO}_3$  was mixed with starch in an attempt to obtain better pressure distribution throughout the sample. However, since this might also affect the rate, only pure  $\text{KNO}_3$  was used in the present study. The sample material was pressed into pellets  $4.6 \times 1$  mm and placed at the bottom of the cylinder bore under a similar pellet of beryllium metal.

The transition rates were measured by fixing the goniometer at the  $2\theta$  value expected for a high-pressure or high-temperature line while the chart recorder is operating, then applying the pressure or temperature to start the transition. There was some difficulty experienced in boosting the temperature over the phase boundary and then being able to stop it from rising further. Since some creep of the temperature was unavoidable, an accurate record of the variation of the temperature on the sample during the progress of a transition has been included with the rate curves.

## RESULTS

### $\text{KNO}_3\text{-II} \rightleftharpoons \text{KNO}_3\text{-IV}$

Forward and reverse transitions for this rate have already been described (DAVIS and ADAMS<sup>(5)</sup>). The conclusions concerning these rates are summarized as follows:

(1) The rate curve is assymetrical. In two experiments the forward change required 14–30 min for completion and the reverse change only seconds.

(2) The forward change appears to take place in steps, whereas the reverse apparently does not (possibly because of the rapidity of the rate the steps were not seen).

(3) Except for the step intervals one of the rate curves approached first-order kinetics, but it is apparent that factors, such as nucleation, strain energy, and grain growth, may affect the order of the rate.

### $\text{KNO}_3\text{-III} \rightleftharpoons \text{KNO}_3\text{-IV}$

Phase III is the high-temperature phase (see Fig. 1) and therefore the forward rate, as written in the above heading, occurs with lowering temperature. As the temperature is raised the IV–III change takes place quite slowly. At a pressure of 3000 bars and a temperature rising from 50 to 85°C, only about 20 per cent conversion took place in 15 min. Upon raising the temperature to 105°C the reaction went to completion in 10 min. It is assumed that much of the change took place in the several minutes required to raise the temperature to the 105°C value.

For the reverse (III–IV) rate no transformation had taken place after 17 min at 3000 bars and 29°C. At this pressure the temperature was not low enough to permit the formation of phase IV again. When the pressure was suddenly dropped to zero, phase II appeared leaving about 10 or 20 per cent of phase III remaining.

### $\text{KNO}_3\text{-I} \rightleftharpoons \text{KNO}_3\text{-II}$

Examination of the phase diagram, Fig. 1, shows that the stability fields of phases I, II, and III meet at a triple-point at 113 bars and 128.3°C.\* The only place possible to measure the rate of the  $\text{KNO}_3\text{-I} \rightleftharpoons \text{KNO}_3\text{-II}$  transition is near this point, and it has been very difficult to obtain records not showing the appearance of phase III. It is fortunate that the strong peak of phase III lies less than one degree ( $2\theta$ ) from the strong peak of phase I; otherwise accurate recording of the appearance of these two phases simultaneously and in closely following intervals would have been difficult. The up-temperature transformation often went to completion without the appearance of phase III. For example, at

\* As measured by BRIDGMAN.<sup>(6)</sup>



$P = 1$  bar the temperature was very slowly raised from  $124^\circ\text{C}$ . The transition began at  $127^\circ\text{C}$  and was essentially complete in  $2\frac{1}{2}$  min. No phase III was observed. Figure 2 shows the rate curve and the slight temperature shift during the transition. In one experiment, in which the piston was left out of the vessel,\* the II-I transformation went to completion in about one minute. In another experiment, in which approximately 500 bars had been applied

phase I peak occurred here. Phase III grew to a maximum, leveled off, and then rapidly died out as phase II appeared.

Figure 4 shows rate curves during which phase III appeared both at the beginning and at the end of the experiment. At the start, about  $125^\circ\text{C}$ , phases I and III both grew simultaneously at the expense of phase II, and shortly thereafter phase III disappeared. Why phase I did not grow more when phase III disappeared is not

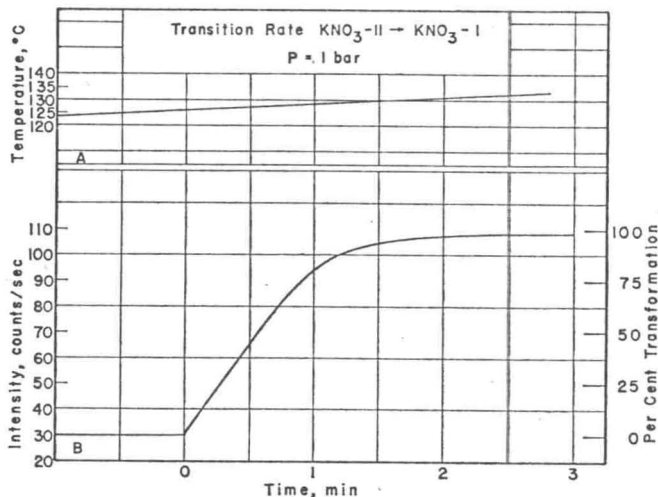


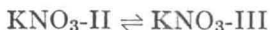
FIG. 2. Transition rate  $\text{KNO}_3\text{-II} \rightarrow \text{KNO}_3\text{-I}$  at 1 bar; (a) variation of temperature during the rate, and (b) rate curve representing growth of the strong 014 peak with time.  $\text{MoK}\alpha$  radiation.

to the sample, the transition commenced at  $t = 115^\circ\text{C}$  and took about  $3\frac{1}{2}$  min to run to completion.

It was not possible in any of the runs to record the I-II rate without the appearance of phase III. An example of the rate curves recorded when phase III appeared is found in Fig. 3. At a temperature slightly less than  $125^\circ\text{C}$  the peak representing phase I dropped off suddenly, leveled off, and then grew some again. At  $120^\circ\text{C}$  it dropped off again, this time permanently, while another peak, representing phase III began to grow. Actually the growth of phase III might have begun earlier, as indicated by the dashed line of Fig. 3, since a drop in intensity of the

understood. This is strange when it is seen that phase III grew an additional amount at the time when phase I was diminished at the end of the experiment.

The appearance of phase III, as shown in Figs. 3 and 4, illustrates the well-known phenomenon that in a chemical or polymorphic transition the phase that first appears, as the  $P$ - $t$  environment is changed, may not be the one which is most stable in that environment. The appearance of phase III at the end of the experiments mentioned took place at temperatures below that of the established phase boundary; at these temperatures phase III considered to be metastable.



At a pressure of 500 bars the transition II-III took place in less than 2 min and began at

\* To avoid applying even a few bars pressure on the sample.

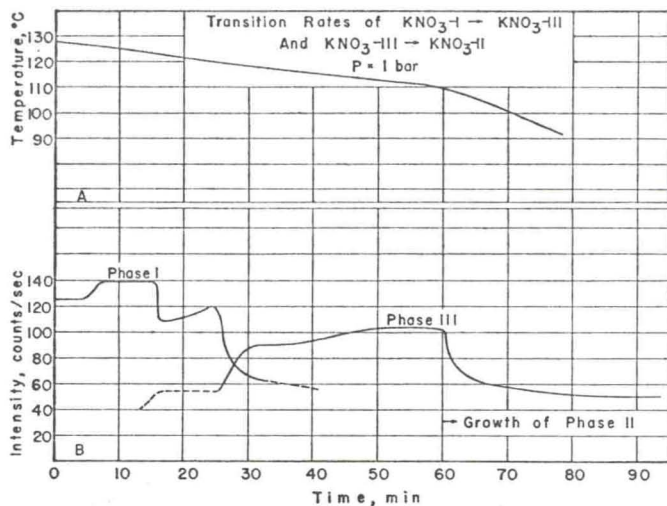


FIG. 3. Transition rate of  $\text{KNO}_3\text{-I} \rightarrow \text{KNO}_3\text{-III}$  and of  $\text{KNO}_3\text{-III} \rightarrow \text{KNO}_3\text{-II}$  at 1 bar; (a) variation of temperature during the rates, and (b) rate curves representing growth and diminution of the strong 014 peaks of phases I and III.  $\text{MoK}\alpha$  radiation.

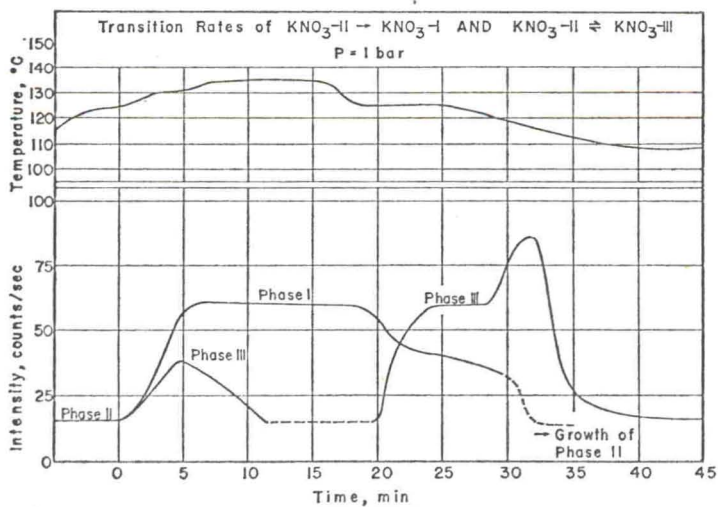


FIG. 4. Transition rate of  $\text{KNO}_3\text{-II} \rightarrow \text{KNO}_3\text{-I}$  and of  $\text{KNO}_3\text{-II} \rightleftharpoons \text{KNO}_3\text{-III}$  at 1 bar; (a) variation of temperature during the rates, and (b) rate curves representing growth and diminution of the strong 014 peaks of phases I and III.  $\text{MoK}\alpha$  radiation.

$t = 118^\circ\text{C}$ . As the temperature was increased slowly to  $130^\circ\text{C}$  the III-I transition took place. The temperature maximum of  $143^\circ\text{C}$  was attained after which the temperature was lowered slowly. At  $128\text{--}130^\circ\text{C}$  the reverse transition I-III took place and immediately (at about  $t = 120^\circ\text{C}$ ) the transition III-II began, but slowly. At this pressure the III-II transition went to completion in approximately 13 min.

Essentially the same transition sequence was observed at a pressure of 1500 bars. Here the initiation of the II-III transition took place at  $113^\circ\text{C}$ , the III-I transition at  $145^\circ\text{C}$ , the I-III transition again at  $145^\circ\text{C}$ , and the III-II transition somewhere near  $115^\circ\text{C}$ . This latter point was not accurately determined because the transition III-II proceeded so slowly that after  $\frac{1}{2}$  hr only a small amount of phase II had appeared. After 10 hr there was still about 10 per cent of phase III remaining. During the 10 hr period, however, the pressure had dropped to about 500 bars due to leaks in the pressure system; had the pressure remained constant during this time, less of the transformation might have taken place.

Other similar experiments performed support the conclusion that the metastability of phase III is prolonged at low temperatures when pressure is increased and that the duration of the persistence of phase III increases with lowering temperature and increasing pressure along the negative slope of the II-III phase boundary. Because of the effect of lower temperatures in the phase II field as pressure is increased this phenomenon is not wholly unexpected. The separation of the effects of pressure and temperature on the kinetics of this transition cannot be made with certainty. The rate IV-III (with the phase boundary  $dt/dP$  positive) was also sluggish at 3000 bars and  $100^\circ\text{C}$ , but since the rate here is between different phases a comparison cannot be made.

One transition across the II-III boundary was studied at constant temperature. At  $t = 93^\circ\text{C}$  the pressure was abruptly raised to 3000 bars. The transition II-III took place within  $1\frac{1}{2}$  min. Upon release of the pressure to zero (nominal) the reverse transition III-II went to completion in 7 min. It is interesting to note the lack, in this experiment, of the persistence of phase III that was seen under similar  $P$ - $t$  conditions but with pressure constant and temperature variable.

#### GRAIN ORIENTATION RESULTING FROM TRANSFORMATION

Preferred orientation of grains in the powder pellet was very striking during the rate study of  $\text{KNO}_3\text{-II} \rightleftharpoons \text{KNO}_3\text{-III}$ . With the forward rate, the pattern of phase III was quite consistent from experiment to experiment but after completing the reverse process the resulting aragonite-type phase II yielded an anomalous pattern. In two cases the 111 (relative intensity  $I/I_0 = 100$ , normally) and 021 ( $I/I_0 = 56$ , normally) peaks were completely missing. The 221 ( $I/I_0 = 41$ , normally) and 041 ( $I/I_0 = 20$  normally) peaks were very weak. On the other hand, the unresolved lines 040 and 220 showed an intensity of 90-100 whereas usually each line should show  $I/I_0$  less than 10. Line 211 was also unusually strong.

These results might indicate an orientation of the crystals with the 010 and 110 cleavages, or both, normal to the direction of applied load, thus indicating the lack of true hydrostatic stress conditions within the pressure vessel.

A similar orientation effect was noticed upon completion of the rate  $\text{KNO}_3\text{-I} \rightarrow \text{KNO}_3\text{-II}$ . In this case, however, the strong lines were either 130, 112, or 022, or some combination of these (all are unresolved with molybdenum radiation).

Such orientation phenomena indicate that the transition of a calcite-type structure (i.e., I and III) to the aragonite-type structure (II) is not of the "single-crystal" variety, but is one involving complete breakdown of crystal units and reconstruction of those of the new phase, a concept wholly in harmony with the accepted nature of the calcite-aragonite transition.

#### ORDER OF TRANSITION

All of the rate curves of the study are non-linear; that is, the curves show a marked tail-off near completion of the transition.

Using a general rate theory (with the variables defined to conform to solid-state transitions) modified by PEsSEN,<sup>(7)</sup> it can be concluded that the rate of transformation at any instant, for most of these transitions, is equal to a constant times the quantity of reactant phase remaining raised to a power between 1 and 2 (i.e., the transition order lies between 1 and 2).

It is suspected that such tail-off is the result of



the elimination of the rate-accelerating processes of strain and nucleation toward the end of the transition. A more detailed treatment of rate theory as applied to polymorphic transitions has been presented elsewhere (DAVIS<sup>(8)</sup>).

#### CELL CONSTANTS OF KNO<sub>3</sub>-I AND KNO<sub>3</sub>-III

Cell constants of KNO<sub>3</sub>-I have already been determined at 152°C and 1 bar by TAHVONEN<sup>(2)</sup> and those of KNO<sub>3</sub>-III at 120°C and 1 bar by BARTH<sup>(4)</sup> where in the latter case the KNO<sub>3</sub> compound was obtained in a metastable condition. The present data are justified in that the constants for phase I were obtained at conditions closer to those of the I-II boundary, and that those of phase III were obtained within the stability field of this phase. Table 1 summarizes the cell data for all known polymorphs of KNO<sub>3</sub>, and includes the new data of this paper.

The 110 lines of both phases I and III were accurately obtained with slow scanning ( $\frac{1}{4}$ -deg/min) with a resulting 1-deg  $2\theta$ /in. chart scale. A diamond powder internal standard was used to correct for sample-height change and the pressure on the sample was estimated from vessel-calibration curves. For phase I the temperature was 133°C

and the pressure atmospheric. For phase III,  $t = 133^\circ\text{C}$  and  $P = 2500 \pm 500$  bars. Excellent patterns obtained at slightly different  $P$ - $t$  conditions provided the complete diffraction data, and the spacings were corrected to the pressures and temperatures mentioned above. Figure 5 is an X-ray diffraction pattern of KNO<sub>3</sub>-I taken at  $t = 137^\circ\text{C}$  and  $P = 1$  bar, and Fig. 6 is a pattern of KNO<sub>3</sub>-III taken at  $t = 103^\circ\text{C}$  and  $P = 3600 \pm 500$  bars. The radiation is MoK $\alpha$  with an applied power of 40 kV and 20 mA.

Final cell-constant data were obtained from a least-squares program designed for the IBM 7090 computer by W. E. Sharp of this institution. The observed and calculated spacings are summarized in Table 2. The constants are those of the calcite-type hexagonal pseudo-cell ( $Z = 6$ ); they allow convenient comparison with dimensions of other calcite-type cells found in the nitrates and carbonates. It should be pointed out that the primitive cells of phases I and III are actually rhombohedrons with  $Z = 2$  and  $Z = 1$  respectively.

Although BARTH<sup>(4)</sup> was able to obtain the phase III structure metastably at 120°C and room pressure, the cell constants resulting from his data

Table 1. Cell constants of the KNO<sub>3</sub> polymorphs

Phase	Source	$P$ (bars)	$t$ (°C)	Cell constants Å		$Z$	space group
I	TAHVONEN <sup>(2)</sup>	1	152	$a_0 = 5.396$	$c_0 = 19.410$	6	$H^*$
I	DAVIS and ADAMS (This paper)	1	133	$a = 7.181$	$\alpha = 44^\circ 8.5'$	2	$R\bar{3}2/m$
				$a_0 = 5.42_3$	$c_0 = 19.33_3$	6	$H^*$
II	EDWARDS <sup>(1)</sup>	1	25	$a_0 = 5.44$	$b_0 = 9.19$		
III	BARTH <sup>(4)</sup>	1	120†	$c_0 = 6.46$		4	$Pm\bar{c}n$
III	DAVIS and ADAMS (This paper)	2500	133	$a_0 = 5.431$	$c_0 = 18.222$	6	$H^*$
				$a = 4.365$	$\alpha = 76^\circ 53'$	1	$R3m$
				$a_0 = 5.44_0$	$c_0 = 17.51_6$	6	$H^*$
III	FINBAK and HASSEL <sup>(3)‡</sup>	1	115†	$a_0 = 5.44_2$	$c_0 = 18.26_5$	6	$H^*$
				$a = 6.849$	$\alpha = 46^\circ 48'$	2	$R\bar{3}2/m$
IV	JAMIESON <sup>(9)</sup>	5000	25	$a_0 = 16.12$	$b_0 = 10.12$		
				$c_0 = 7.75$		18	?
IV	DAVIS and ADAMS <sup>(5)</sup>	3000	25	$a_0 = 11.04_8$	$b_0 = 8.36_7$		
				$c_0 = 7.40_2$		10	$Pmn2_1?$

\* Hexagonal pseudo-cell (when ordered, space group =  $R\bar{3}c$ ).

† Obtained metastably.

‡ Hexagonal constants calculated from  $a$  and  $\alpha$  given by FINBAK and HASSEL.<sup>(3)</sup>

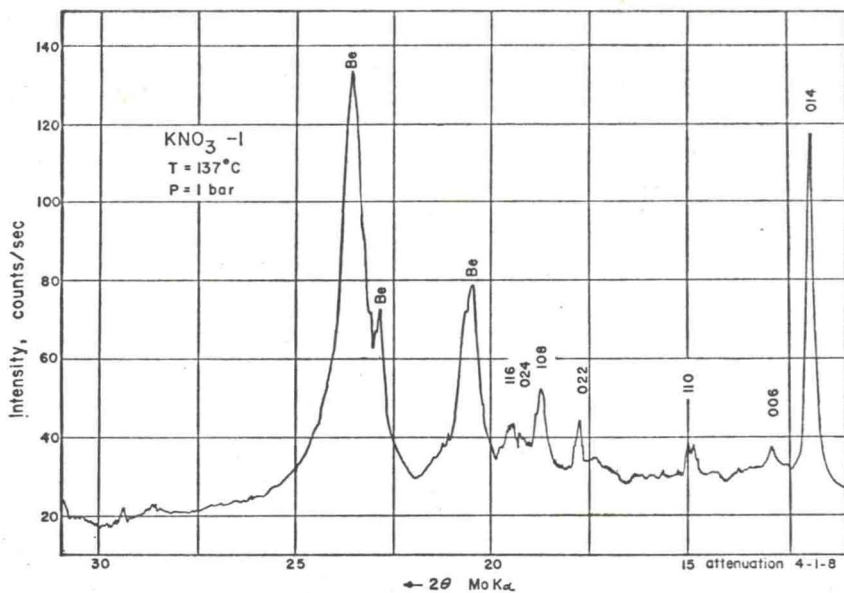


FIG. 5. X-ray diffraction pattern of  $\text{KNO}_3$ -I at  $137^\circ\text{C}$  and 1 bar. Indices based on hexagonal pseudo-cell (calcite-type). Diffraction peaks from beryllium vessel walls labeled Be. MoK $\alpha$  radiation.

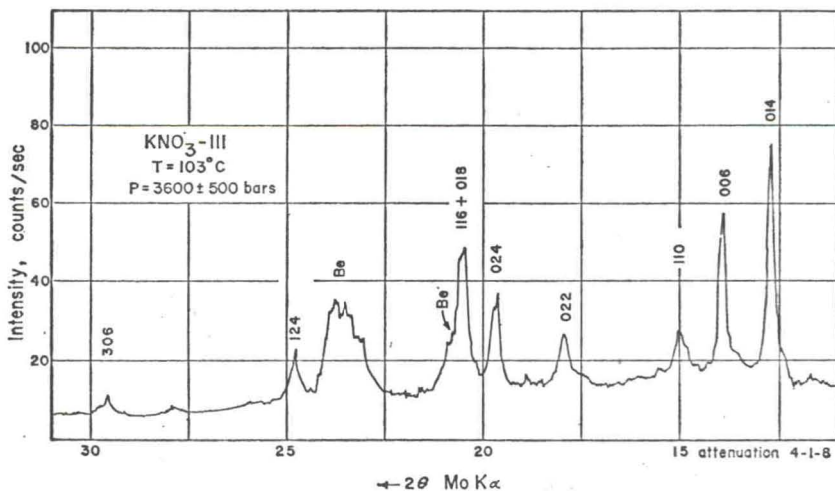


FIG. 6. X-ray diffraction pattern of  $\text{KNO}_3$ -III at  $103^\circ\text{C}$  and  $3600 \pm 500$  bars. Indices based on hexagonal pseudo-cell (calcite-type). Diffraction peaks from beryllium vessel walls labeled Be. MoK $\alpha$  radiation.

Table 2. X-ray diffraction data

KNO <sub>3</sub> -I			
hkl	<i>d</i> <sub>calc</sub> (Å)	<i>d</i> <sub>obs</sub> (Å)	<i>I</i> / <i>I</i> <sub>0</sub> *
014	3.37	3.39	100
006	3.22	3.13	5
110	2.71	2.71	9
022	2.28	2.28	13
108	2.15	2.16	22
024	2.112	2.111	7
116	2.075	2.074	10

Cell constants:  $a_0 = 5.42_3$  Å,  $c_0 = 19.33_3$  Å.  
Temperature 133°C, Pressure 1 bar.

KNO <sub>3</sub> -III			
hkl	<i>d</i> <sub>calc</sub> (Å)	<i>d</i> <sub>obs</sub> (Å)	<i>I</i> / <i>I</i> <sub>0</sub> *
102	4.15	4.10	3
014	3.21	3.20	100
006	2.92	2.92	65
110	2.72	2.73	16
022	2.27	2.28	19
024	2.074	2.074	37
108	1.986	2.015	58
116	1.990		
124	1.650	1.652	16
306	1.383	1.389	8

Cell constants:  $a_0 = 5.44_0$  Å,  $c_0 = 17.51_6$  Å.  
Temperature 133°C, Pressure 2500 ± 500 bars.

\* Relative peak heights.

would not be expected to represent either the same absolute dimensions or same axial ratio that the cell would have at other temperatures and pressures. The data of this paper show that there is a relatively large compression parallel to the *c*-axis of phase III in going from atmospheric pressure (Barth's data) to 2500 bars (our data). The large compression along the *c*-axis as compared to that along the *a*-axis is expected in light of previous high-pressure work with KNO<sub>3</sub> and CaCO<sub>3</sub> (DAVIS<sup>(8)</sup>).

The pressure existing at the equilibrium boundary I-III at 133°C is 500 bars. When the specific volumes of each phase are corrected to this point we have for phase I,  $v = 0.48_7$  cm<sup>3</sup>/g, and for phase III,  $v = 0.45_1$  cm<sup>3</sup>/g, giving a  $\Delta v$  of 0.03<sub>6</sub> cm<sup>3</sup>/g.

#### SUMMARY

Observations on transition rates across the boundaries of the KNO<sub>3</sub> phase diagram have been obtained using a beryllium pressure vessel wired for heating to moderate temperatures. The rates are

determined by continuous scan by X-radiation passing through the walls of the vessel.

Most of the curves obtained show decreasing rates near completion of the transition, resulting in transition orders lying between 1 and 2. However, changes studied near the triple-point I-II-III were complicated by the metastable appearance of phase III, both with increasing temperature and decreasing temperature across the point. The persistence of phase III in the phase II field becomes greater with lowering temperature and increasing pressure.

The I-II and III-II transitions often result in preferred orientation of the aragonite-type phase (II) with the 010 or 110 cleavages, or both, lying normal to the direction of applied load.

It is suspected that the elimination of such rate-modifying factors as nucleation and strain may be responsible for the tail-off observed in nearly all of the transition curves measured.

KNO<sub>3</sub>-I at  $t = 133^\circ\text{C}$  and  $P = 1$  bar has cell constants  $a_0 = 5.42_3$  Å,  $c_0 = 19.33_3$  Å ( $Z = 6$ ) using the hexagonal pseudo-cell of calcite. Constants for KNO<sub>3</sub>-III at  $t = 133^\circ\text{C}$  and  $P = 2500 \pm 500$  bars are  $a_0 = 5.44_0$  Å,  $c_0 = 17.51_6$  Å ( $Z = 6$ ) referred to the same cell. The specific volume decrement,  $\Delta v$ , at the transition boundary ( $t = 133^\circ\text{C}$   $P = 500$  bars) is 0.03<sub>6</sub> cm<sup>3</sup>/g.

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