

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⁽⁸⁾).

CELL CONSTANTS OF KNO₃-I AND KNO₃-III

Cell constants of KNO₃-I have already been determined at 152°C and 1 bar by TAHVONEN⁽²⁾ and those of KNO₃-III at 120°C and 1 bar by BARTH⁽⁴⁾ where in the latter case the KNO₃ 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 KNO₃, 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 2θ /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 KNO₃-I taken at $t = 137^\circ\text{C}$ and $P = 1$ bar, and Fig. 6 is a pattern of KNO₃-III taken at $t = 103^\circ\text{C}$ and $P = 3600 \pm 500$ bars. The radiation is MoK α 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⁽⁴⁾ 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 KNO₃ polymorphs

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

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

† Obtained metastably.

‡ Hexagonal constants calculated from a and α given by FINBAK and HASSEL⁽³⁾.