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TRANSITION RATES OF 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 KNO_3 phase diagram.

Most transitions show rate curves that taper off near the completion of the process, but metastable persistance 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 KNO_3-I and 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 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 KNO_3-I $\rightleftharpoons$ KNO_3-II and KNO_3-II $\rightleftharpoons$ KNO_3-III rates because of the similarity of these phases in structure to those of calcite and aragonite. EDWARDS[1] found that KNO_3-II had the aragonite structure and TAHVONEN[2] determined KNO_3-I to be calcite-type but with disorder present in the NO_3^- groups. FINBAK and HASSEL[3] also described KNO_3-III as calcite-type but later BARTH[4] proposed a smaller cell ($Z = 1$) for the structure. The disorder of the NO_3^- ion in KNO_3-I and the uni-directional order of the NO_3 ion in 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 $CaCO_3$-I, $CaCO_3$-II, KNO_3-I, and KNO_3-III; therefore the normal calcite-type pseudo-cell (hexagonal, $Z = 6$) has been retained in this study.

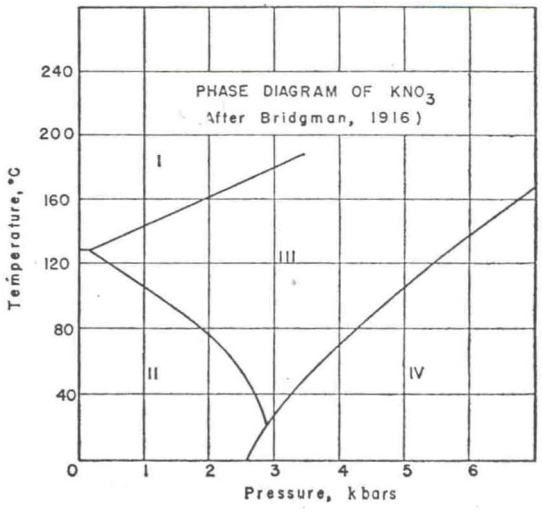

FIG. 1. Phase diagram of KNO_3 (after BRIDGMAN[6]).

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