

A Phase Transition in KNO_3 at Low Temperatures

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A hitherto undetected phase transformation in KNO_3 has been investigated by means of X-rays and measurements of electrical resistivity and dielectric constant as functions of temperature. Anomalous values of the electrical parameters accompany the cooling and reheating of samples through the transformation which occurs in the vicinity of -60°C . On cycling a sample through the transition temperature, a marked hysteresis is observed in these parameters, followed by a gradual return to the normal phase II state.

The physical properties of crystalline potassium nitrate have previously attracted considerable attention with the result that a large amount of data has been compiled on this interesting compound. Since there are, however, a number of aspects which remain unclear (*e.g.* details of structure and disorder properties), new fundamental information is actively sought.

Under the variation of temperature and pressure, the existence of seven modifications of KNO_3 has been established hitherto, and these have been designated¹ as phases I to VII, following the notation of Bridgman.² The transformations between the three modifications I, II, and III occurring between the melting point and room temperature at atmospheric pressure have been the subject of numerous investigations employing a wide variety of experimental methods. For a discussion of the electrical properties of phases I to III in relation to other characteristics, reference is made to an earlier publication by the present authors.³

Among the few investigations performed below room temperature, measurements of specific heat⁴ have indicated a lack of cooperative phenomena or other anomalous behaviour in this region. The experimental results described in the present paper, which include electrical properties between -95 and 25°C and some structural data within the range -180 to 20°C , show, however, the presence of well defined anomalies which are taken as evidence of a phase transformation.

EXPERIMENTAL

Polycrystalline samples of KNO_3 , suitable for the investigation of electrical properties, were formed by solidifying *p.a.* grade material (Merck) onto one face each of four clean silver plates of dimensions $20 \times 20 \times 1.0$ mm. (The surfaces of the plates were treated by honing with a fine stone in order to provide a matt finish promoting crystallization and adhesion of the salt.) The samples were cooled from the molten state to room temperature over a period of ~ 10 min, which was found to lead to the least mechanical failure of the crystals. The samples were then filed to a thickness of ~ 0.5 mm and a second electrode was applied in the form of conducting silver paint (Leitsilber 200, Degussa). Measurements of sample capacitance, obtained immediately after formation, showed a progressive fall in the value of dielectric constant, as the KNO_3 completed the process of transformation from the ferroelectric phase III to the room temperature phase II.⁵

The four samples were connected in parallel and mounted within the specially constructed cryostat depicted in Fig. 1, where they were allowed to achieve equilibrium at room temperature. The cryostat, which incorporates a 7 l liquid nitrogen Dewar flask, permits of gradual temperature changes in the range between room temperature and that of liquid nitrogen (-196°C) during experiments which may continue for several days with the use of a single charge of coolant.

The temperature of the sample was varied and controlled automatically by means of apparatus which has been described elsewhere;⁶ the sample temperature being de-

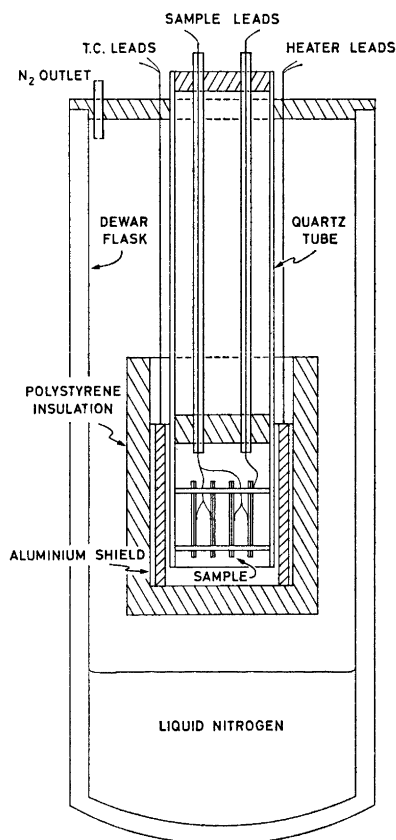


Fig. 1. Low temperature cryostat used for electrical measurements.

terminated by the use of a Chromel-Alumel thermocouple in conjunction with a calibrated set-point unit. The temperature of the sample was held constant for a period of 30 min prior to the recording of each set of observations.

Measurements of sample capacitance, dissipation and resistance were performed with the aid of an impedance bridge (General Radio, type 1650-A), which was operated at a frequency of 1 kHz.

The samples used for the electrical measurements were analyzed for impurity content by collecting Guinier photographic data at room temperature and by neutron activation analysis, the results being substantially as previously presented.³

X-Ray powder diffraction data for polycrystalline KNO_3 was obtained at various temperatures between -180 and 25°C using a General Electric diffractometer having a cryostat attachment ($\text{CuK}\alpha$ -radiation and diamond powder as internal standard).

RESULTS

Values of the dielectric constant ϵ and the quantity ρ_D obtained over the temperature cycle 2.5 to -95 to 25°C are shown as curves A and B, respectively, in Fig. 2. The values of ρ_D were calculated from expression

$$\rho_D = S/(\omega C_p D t)$$

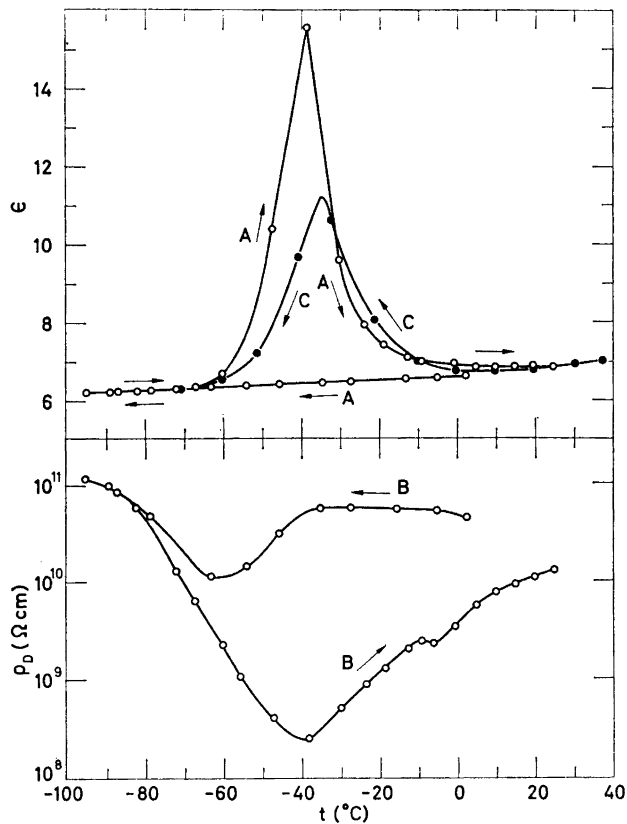


Fig. 2. Dielectric constant ϵ and the quantity ρ_D (see text) as functions of temperature.

where ω is the angular frequency, C_p the recorded parallel capacitance value, D the dissipation, t the sample thickness, and S the electrode area.

After completing these measurements, the sample was kept at room temperature for a period of 6 days, when the results shown as curve C (Fig. 2) were obtained on cooling. After an additional period of 20 days at room temperature, further measurements showed the sample to have regained its original characteristics as represented by the curve A.

The large values of dielectric constant and dissipation which were obtained on increasing the temperature (Fig. 2) suggested that the sample might exhibit a ferroelectric anomaly in this temperature range. In order to test this possibility, the voltage *versus* charge characteristic of the sample was examined at a frequency of 1 kHz utilizing an X-Y oscilloscope.

At the peak of the anomaly (-40 to -30°C), the oscilloscope trace was elliptical, without any detectable degree of asymmetry. On cooling the sample, the ellipse narrowed progressively and became a straight line at lower temperatures ($< -60^\circ\text{C}$).

The results were taken as an indication that the dissipation was of a predominantly resistive nature and a further experiment was therefore performed in order to obtain d.c. resistivity values for the temperature region. The results obtained, which are shown in Fig. 3 together with corresponding

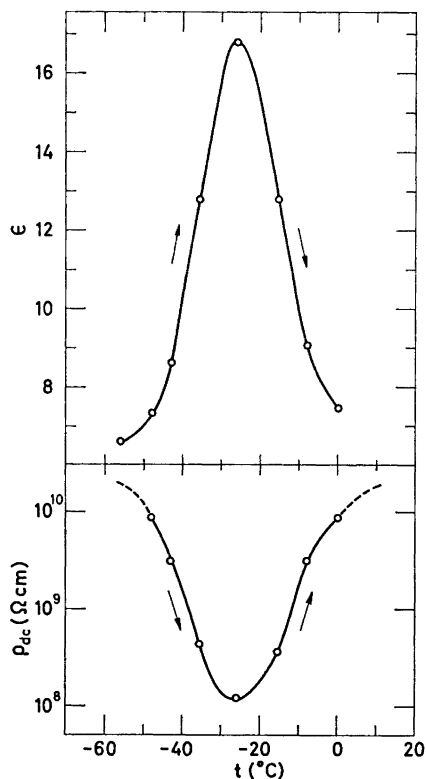


Fig. 3. Dielectric constant ϵ and d.c. resistivity $\rho_{d.c.}$ as functions of temperature.

values of dielectric constant, show that the anomalous values of dielectric constant are in fact associated with anomalously low resistivity values.

On a more rapid raising of the sample temperature ($1^{\circ}\text{C}/\text{min}$), comparatively high values of dielectric constant (in excess of the peaks shown in Figs. 2 and 3) were recorded at temperatures as high as 10°C . In these cases, the dielectric constant slowly regained its normal value. This process was apparently hastened by permitting laboratory air to enter the cryostat.

The results presented above relate to a particular set of four samples connected in parallel; those obtained for others showed no appreciable differences however.

The anomaly observed in the electrical measurements is clearly reflected in the results for the thermal expansion of the c -axis which are presented in Fig. 4, whereas the correlation is less marked in the case of the b -axis, and apparently absent for the a -axis.

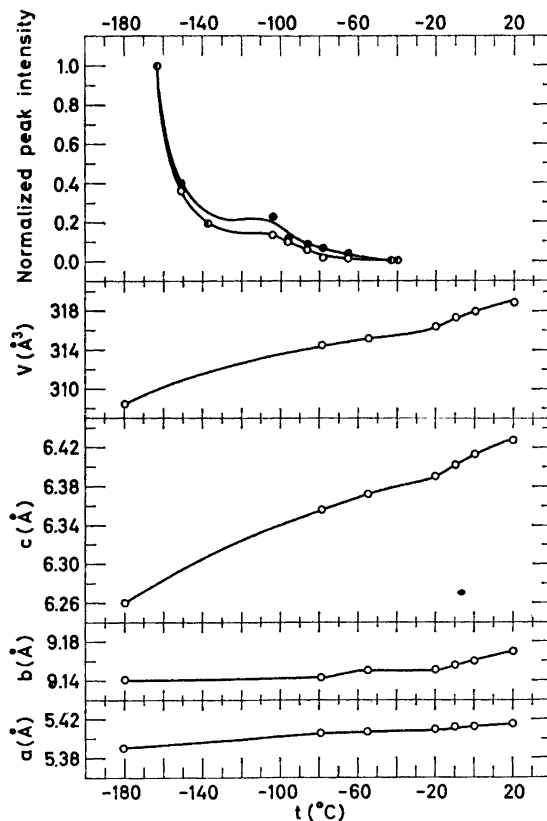


Fig. 4. Normalized peak intensity of two typical additional reflections and lattice parameters as functions of temperature.

The completion of the phase VIII \rightarrow II transition at $\sim -60^\circ\text{C}$ on heating, is confirmed by the observation of several additional temperature dependent reflections in the diffractogram; the normalized intensity for two of these additional peaks is shown in the upper part of Fig. 4. The evidence from X-ray powder data is insufficient to determine whether the low temperature phase VIII* belongs to a different space group from that of phase II. The difference in structure between the phase II and VIII which is thought to concern a minor adjustment of the nitrate group is now under further investigation using single crystal methods.

DISCUSSION

Recent determinations of the variations in resistivity³ and dielectric constant⁷ associated with phase transformations in KNO_3 have shown that these parameters are sensitive indicators of the structural state of a sample. Both quantities reflect the nature of the ionic bonding of the compound and are also affected by such macroscopic parameters as domain and polycrystalline structure.

In the present instance, the results show the occurrence of a solid-state transformation between the room temperature phase II and the low temperature phase VIII at approximately -60°C . That this transformation involves only a minor structural rearrangement is shown by the continuity of the value of the dielectric constant on decreasing the temperature through that of the transition (curve A, Fig. 2). This result is in accordance with the lack of anomaly in calorimetric measurements,⁴ since any marked changes in lattice energy or order-disorder state should be detectable on the specific heat curve unless the reaction were extremely sluggish.

The large peak in the value of the dielectric constant which occurs on increasing the sample temperature (Figs. 2 and 3), presumably results from the oscillation of ions within comparatively wide potential wells. This may be associated with a condition of disorder in the phase II, which, having the aragonite structure, is almost certainly antiferroelectric. No direct evidence of ferroelectricity has, however, been found. The gradual return of the dielectric constant of a sample to its normal value, after having been heated through the transition, in itself suggests the disappearance of disorder in the crystal.

The values for ρ_D measured with increasing temperature (Fig. 2) agree fairly well with those obtained for $\rho_{d.c.}$ (Fig. 3). The minima in ρ_D and $\rho_{d.c.}$ which accompany the dielectric anomaly indicate either a reduction in ionic potential barriers throughout the crystal, or the formation of paths of facile transport, perhaps lying along the boundaries of domains or polycrystals. Measurements on single crystals will be of interest in this respect.

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* The tentative designation of the low temperature phase by the numeral VIII is subject to a complete structural determination.

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