On the Electrical Properties of $RbNO_3$ and $CsNO_3$

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The resistivity and dielectric constant at 1 kHz have been determined over wide ranges of temperature for polycrystalline samples of $RbNO_3$ and $CsNO_3$, and the four-terminal d.c. resistivity of zone melted single crystals of the compounds obtained as functions of temperature.

Anomalous electrical characteristics found below room temperature are discussed in relation to possible phase transitions at -45 and $-35°C$ in $RbNO_3$ and $CsNO_3$, respectively. The results obtained above room temperature are considered in relation to known polymorphic transformations in the solid state.

Four solid phases have been identified for $RbNO_3$ (m.p. 310°C[1]); experimental values of the transformation temperatures being 160, 218, and 281°C on heating at atmospheric pressure.[1-3] The most convenient designations of these phases, in order of decreasing temperature, are I, II, III, and IV, although one should note that this numbering is not found uniformly throughout the literature.

X-Ray investigations of $RbNO_3$ have shown that phase I is cubic,[4] while the trigonal[5] (or possibly tetragonal[4]) phase II was earlier supposed on purely optical evidence to have extended to the melting point.[6] The cubic phase III[4,7-9] has recently been deduced to contain random orientations of the nitrate groups.[10] On decreasing the temperature, phase III is succeeded by a further trigonal phase, IV; the relationship between the two being illustrated by the fact that the hexagonal c-axis of the phase IV structure becomes a cube diagonal of phase III.[4] Determinations of structure and unit cell dimensions of phase IV show a considerable variation in results.[4,11,12]

A recent neutron diffraction investigation[13] indicated that phase IV $RbNO_3$ is isostructural with phase II $CsNO_3$. Results for the latter were consistent with the presence of a threefold screw axis in the c-direction and the space group $P3_1$ or its enantiomorph $P3_2$.

The existence of a single high pressure phase in the temperature range from ambient to 170°C has been reported, the transition to phase IV being sluggish at the lower temperatures.[14]

A small birefringence, and a degree of anisotropy of refractive index amounting to $<1\%$ of the value of 1.51 in the c-axis direction, are consistent with a multiplicity of ordered nitrate group orientations in phase IV.[15]

Investigations of the UV spectra of $RbNO_3$ confirmed the previously quoted values of the transition temperatures.[16-17] Interpretation of the results, which are thought to

be influenced by the value of the nearest neighbour cation separation from the nitrate group, is hindered by the lack of well established structural and expansion parameters.

No electrical measurements appear to ¦have been performed on single crystals or at reduced temperatures. The conductivity of compressed powder samples has been measured above room temperature, the results showing clearly the course of the transformations.[4] Measurements of dielectric constant at 1 MHz show a rather sharp increase in value at 50°C,[18] and it has been suggested that $RbNO_3$ is ferroelectric in phases II and IV.[19]

Consistent with the variations in structural symmetry observed between $LiNO_3$, $NaNO_3$, and KNO_3 (whose electrical and other properties have been discussed previously by the present authors [20–24]), $CsNO_3$ differs from $RbNO_3$ in having only two phases so far identified in the temperature range from ambient to the melting point (405.5°C [25]). The transition temperature has been determined by means of DTA to be 151.5,[25] 153.8,[26] and 154.0°C.[27]

The high temperature phase I of $CsNO_3$ was shown optically to have a cubic structure,[6] and upon reconsideration of the results of X-ray investigations [8,28,29] this phase was deduced [10] to have the same disorder properties as phase III $RbNO_3$. Phase II $CsNO_3$ is trigonal and isostructural with phase IV $RbNO_3$.[13,29,30] The existence of one additional structural form at high pressures has been reported.[14]

The only electrical investigations of $CsNO_3$ appear to be a measurement of dielectric constant at 1 MHz from room temperature to 160°C,[18] and of conductivity in phase I from ~ 215°C to the melting point.[31] Substantial spontaneous polarization of crystals at room temperature was found by means of the resulting pyroelectric properties, and similar results were also obtained for phase IV $RbNO_3$.[30]

EXPERIMENTAL

Single crystals of $RbNO_3$ and $CsNO_3$ were grown by means of zone melting equipment described previously.[22] The starting materials employed were supplied by E. Merck ($RbNO_3$) and Fluka ($CsNO_3$). The impurity contents of these, and of the zone refined samples, as determined by the method of atomic absorption, were as follows (all values are in ppm, those for the purified single crystals being in parentheses):
$RbNO_3$: Cl 20, SO_4 100, N 30, Pb 3, Cu 3, Fe 3, Zn 3, Al 10, Ca 50 (4.1), Mg 5 (1.5), Li 0.4 (0.15), Na 100 (160), K 1000 (120), Cs 50, Ba (2.5). $CsNO_3$: Li 6.2 (1.0), Na 33 (7.1), K 7.6 (4.4), Mg 8.6 (2.2), Ca 27 (13), Ba < 1 (< 2), Ag < 2 < 1), Al 26 (7.1), Pb 11 (8.9), Cu 2.1 (1.8), Fe 7.6 (7.1).
The four-terminal resistivities of the single crystals were determined as functions of temperature with the use of suitable temperature control equipment [32] and an electrometer bridge circuit employing balanced dynamic capacitor detectors.[33]
The investigation of dielectric properties as functions of temperature at 1 kHz was performed on polycrystalline samples obtained by cooling the melt between parallel silver plates, using temperature control and measuring equipment described previously.[21,23]

RESULTS

Consistent with the mode of obtaining and presenting results employed in the earlier papers in this series,[20–23] values of dielectric constant ϵ and resistivity ϱ_D for polycrystalline $RbNO_3$ and $CsNO_3$ are shown in Figs. 1 and 2,

respectively, for decreasing and increasing values of temperature. Values of the same parameters obtained above room temperature are shown in Figs. 3 and 4.
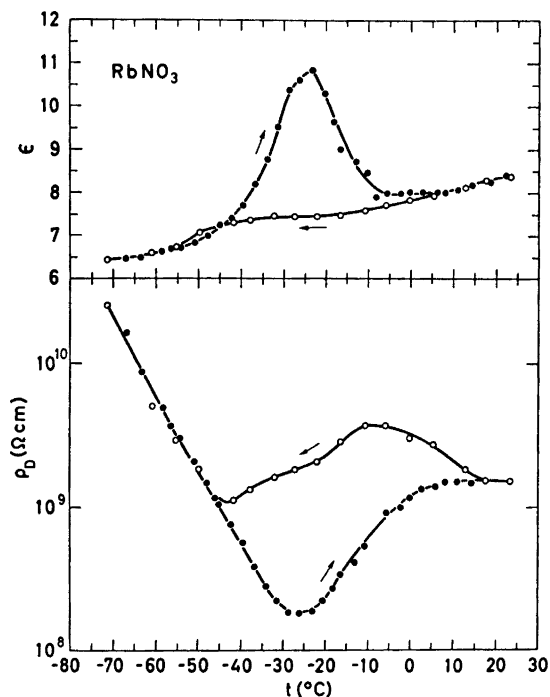

Fig. 1. Dielectric constant ϵ and resistivity ρ_D for RbNO$_3$ as functions of temperature. Open circles denote values obtained with decreasing temperature, filled circles with increasing temperature.

The low temperature curves for the two compounds show a general similarity of form for a given parameter, and are anomalous in a number of respects. On decreasing the temperature, a discontinuity in the slope of ϵ is seen at temperatures of $-45°C$ for RbNO$_3$, and $-35°C$ for CsNO$_3$. The anomalous peaks are followed by reductions to plateaus in both cases. The corresponding values of ρ_D show anomalous reductions in value with falling temperature until the temperatures of the peaks in ϵ are reached. Below these temperatures, normal increases in ρ_D are observed, rising to limits defined by the measuring apparatus.

On heating the samples from $-70°C$, hysteresis effects are evident for both parameters, values close to the original ones being regained only at room temperature. The amount of the hysteresis in ϵ is $> 30 \%$ of the base value in both compounds.
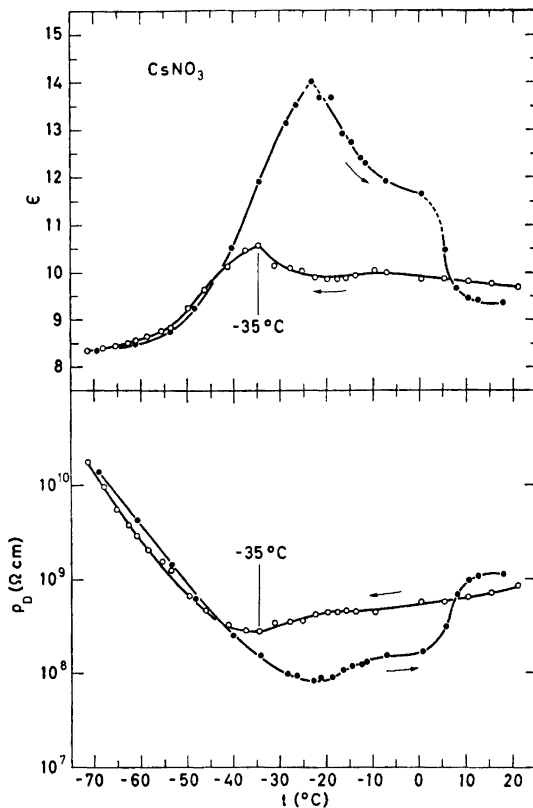
Fig. 2. Dielectric constant ϵ and resistivity ρ_D for $CsNO_3$ as functions of temperature. Open circles denote values obtained with decreasing temperature, filled circles with increasing temperature.

Above room temperature, the polymorphic transformations between the phases IV and III, and between III and II, in $RbNO_3$ (Fig. 3) are marked by step-like increments in parameter values. The transition temperatures were observed to be as follows: $168 \pm 4°C$ for IV→III, $161 \pm 2°C$ for III→IV (completed), $222 \pm 2°C$ for III→II, and $218 \pm 2°C$ for II→III.

Incremental changes in ϵ of more than an order of magnitude occur at the phase IV→III transition, and 2.5 orders at III→II. Even larger increments are observed on cooling. Similarly, increments of > 2 orders are observed in the corresponding values of ρ_D.

The effects of the phase III⇌II transition recorded for $CsNO_3$ (Fig. 4) are of a different nature from those seen in $RbNO_3$. On heating the sample, ϵ rises to a peak at 152°C which is superimposed on an overall increase of the exponential type, while more continuous variations are seen in the values of ρ_D. Hysteresis is evident between heating and cooling curves.
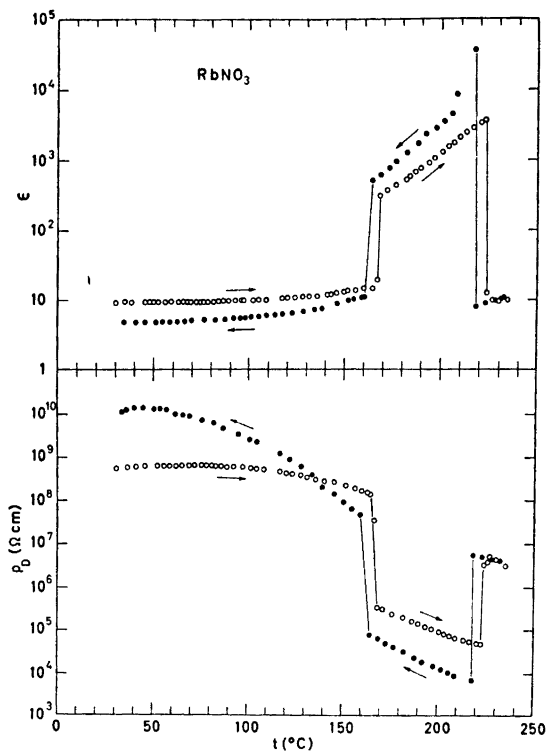
Fig. 3. Dielectric constant ϵ and resistivity ϱ_D for $RbNO_3$ as functions of temperature. Open circles denote values obtained with decreasing temperature, filled circles with increasing temperature.

The four-terminal d.c. resistivity of $RbNO_3$ from room temperature to 297°C is shown in Fig. 5, where the results are plotted as a function of the reciprocal absolute temperature in order to facilitate the calculation of energy parameter values. All three of the known solid state transitions are detected in this temperature range. The transition temperatures obtained on heating are: 161 ± 1.5°C for IV→III, 219 ± 1.5°C for III→II, and 281 ± 1.5°C for II→I. Characteristic energy gaps W for the phases, deduced according to the expression

$$\varrho = \varrho_0 \exp\ (W/2kT)$$

are as follows: ~ 2.0 eV (IV), 1.6_1 eV (III), 1.5_5 eV (II), and ~ 1.5 eV (I). Increments in the values of ϱ at the transitions are: IV→III 3 orders of magnitude, III→II 2 orders, and II→I 0.2 orders. The upper limit of resistivity was determined by the measuring equipment.

The corresponding results for $CsNO_3$ are shown in Fig. 6, where it is seen that the curve comprises two linear sections with characteristic energy parameters W of 1.9_4 and 2.1_4 eV for phases I and II, respectively.
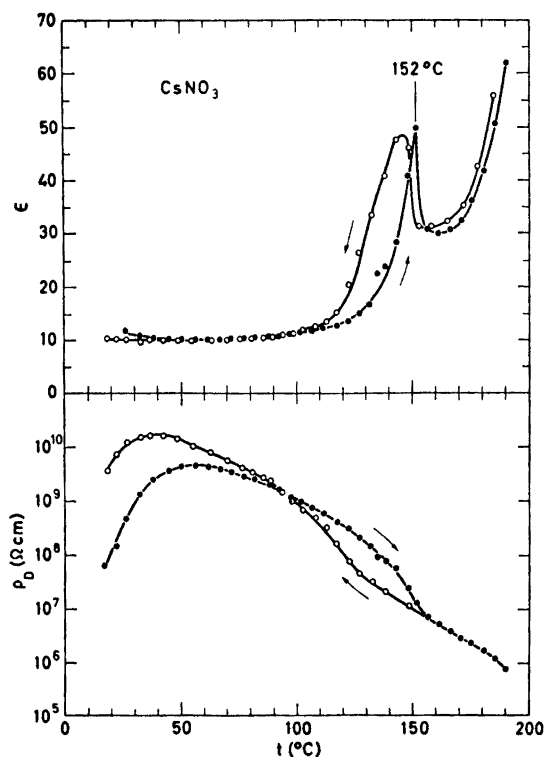
Fig. 4. Dielectric constant ε and resistivity ϱ_D for $CsNO_3$ as functions of temperature Open circles denote values obtained with decreasing temperature, filled circles with increasing temperature.

The linear sections are connected by a transitional curve extending over the temperature interval 127 to 150°C; the effective increment between the two sections being approximately an order of magnitude in the value of ϱ.

DISCUSSION

The data presented here for $RbNO_3$ and $CsNO_3$ appear to be the first obtained below room temperature for these compounds. The results were referred to briefly in an earlier communication [34] where, in common with those for other univalent nitrates, they were taken to be indicative of solid state transitions; characteristic temperatures of the effects being − 45 and − 35°C for $RbNO_3$ and $CsNO_3$, respectively. Adopting the tentative designations V and III for the low temperature phases in $RbNO_3$ and $CsNO_3$, respectively, one notes the following properties which these transitions have in common.
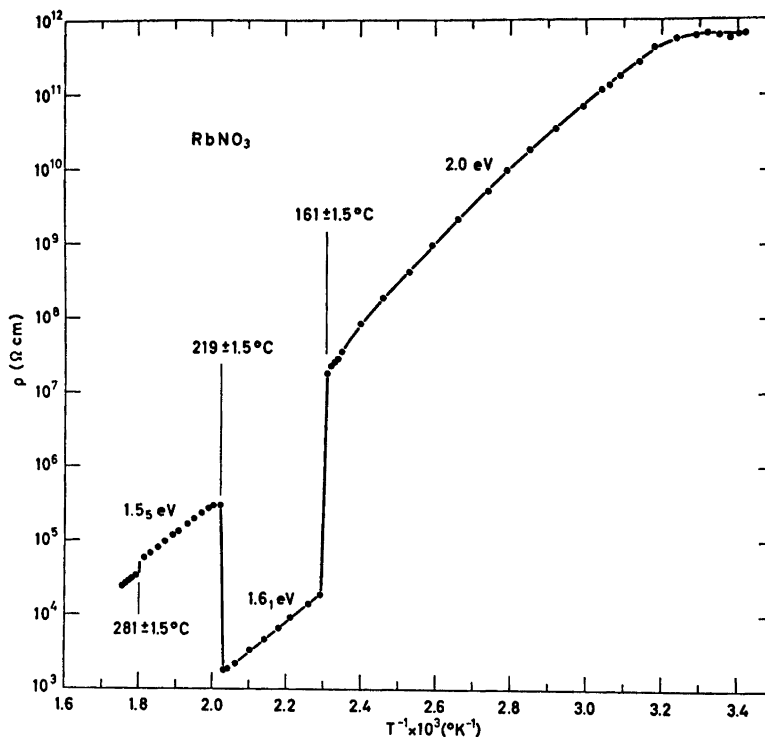
Fig. 5. Four-terminal d.c. resistivity ϱ for zone refined single crystal of RbNO$_3$ with increasing temperature, as function of inverse absolute temperature T. Current parallel to c-axis of phase IV.

On cooling, the low temperature phases show values of ϵ which are indicative of a normal reduction of polarizability. Although the origin of this polarizability cannot be positively identified, it is probably directly associated with the nitrate group. The values of ϱ_D below the transitions have a more usual form of temperature dependence than in the room temperature phases. On raising the temperature, ϵ shows a degree of hysteresis associated with the transition which implies the presence of substantial disorder, and which is difficult to account for in terms of impurities or mechanical strain in the sample.

In this connection, it is worth noting that the observed phenomena do not have any features which might indicate a relationship with the defect relaxation effects observed by Breckenridge,[35–37] and others [38],[39] in alkali halides and other crystalline compounds. Comparatively small contributions to ϵ are, for example, to be expected in such cases.

In the light also of results obtained in investigations parallel to the present one, on NaNO$_3$ [21] and KNO$_3$,[23] it was suggested [34] that only minor structural rearrangements are involved in the low temperature anomalies in RbNO$_3$
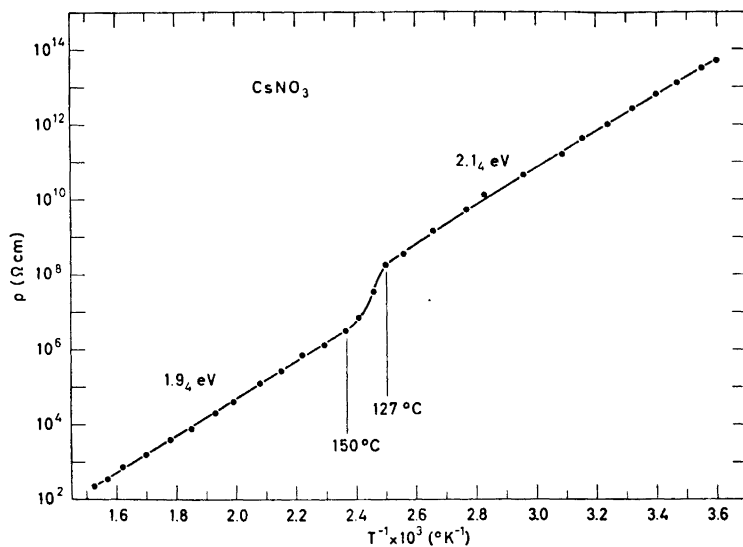
Fig. 6. Four-terminal d.c. resistivity ϱ for zone refined single crystal of CsNO$_3$ with increasing temperature, as function of inverse absolute temperature T.

and CsNO$_3$. A degree of confirmation of this has since been supplied by Owen and Kennard [40] who noted an absence of DTA anomalies in the temperature range -90 to $26°C$, albeit at far greater rates of temperature change than employed in the present work. A negative calorimetric result does not exclude the possibility of a transition between a state in which a structural unit of the lattice merely oscillates, and one in which it frequently jumps between alternative allowed orientations which are not inherently distinguishable. This limitation of the calorimetric technique has been discussed, for example, by Darmon and Brot [41] in relation to the finding of such effects in benzene by the use of NMR.[42] Owen and Kennard [40] reported an absence of evidence of structural change in CsNO$_3$, as a result of neutron diffraction experiments at $-195°C$ and room temperature. No details of resolution were given for the investigation.

The present dielectric anomalies in RbNO$_3$ and CsNO$_3$ indicate that further information on lattice dynamics at the relevant temperatures would be of considerable interest. Effects which might be sought are the incidence of jumping between equivalent or nearly equivalent states of the nitrate group, changes in polarizability, *etc.*

By analogy with the variation in unit cell dimensions of KNO$_3$ at reduced temperatures,[23] it is to be expected that the anomalous electrical properties CsNO$_3$ in the region of $-35°C$ are associated with a discontinuity in the coefficient of thermal expansion rather than in unit cell volume. In this connection, the reported [43,44] continuity of EPR data, obtained with the use of VO^{2+} ions as added observers in KNO$_3$ and CsNO$_3$, through the temperatures concerned is of interest. The change between isotropic and anisotropic spectra

at low temperatures ($-196°C$ in KNO_3 and $-110°C$ in $CsNO_3$) due to increased hindrance to the rotation of VO^{2+}, appears to be mainly a volume effect, and consistent therefore with the present findings.

The values of ϵ obtained above room temperature for $RbNO_3$ (Fig. 3) show clearly the effects of the known polymorphic transformations in the region. There is no confirmation of the increase in this parameter at $50°C$ reported by Meinnel and Clinet,[18] possibly owing to the difference in measuring frequencies. The high values of ϵ (2×10^2 to 2×10^4) obtained for phase III imply that lattice dipoles are relatively easily distorted or rotated in this phase; or that exceptionally large amplitudes result from the presence of positional or rotational disorder in the lattice. Furthermore, the steep inclination of the ϵ curve in phase III demonstrates its transitional nature in lying between two phases of more normal ϵ values. Calorimetric data [1] shows phase III to have a steeply increasing value of specific heat with temperature, consistent with a progressively increasing degree of disorder. The corresponding temperature variation of ϱ_D is consistent with this interpretation, which supports the suggestion by Strømme [10] that there is orientational disorder of the nitrate ions in this phase.

The dielectric constant of $CsNO_3$ above room temperature (Fig. 4) shows an increase which is premonitory to the phase II→I transformation. This transformation appears to be of a different type from those recorded in $RbNO_3$ above room temperature. In accordance with the supposed similarity between phase I $CsNO_3$ and phase III $RbNO_3$,[10] values of ϵ for the former are seen to increase extremely rapidly, but comparison of the values of ϵ and ϱ_D for the two phases nevertheless indicates that there is considerable dissimilarity between them. The comparatively minor effect upon ϱ_D of the transformation in $CsNO_3$ suggests that the increase in polarizability is not accompanied by a general reduction in lattice barriers as in phase III $RbNO_3$.

The four-terminal d.c. resistivity values for $RbNO_3$ (Fig. 5) confirm the three known solid state transition temperatures on heating. Except perhaps at the lowest temperatures, the conductivity recorded is most probably of an intrinsic nature. The d.c. values of ϱ for phase III are similar to those obtained using a.c. (Fig. 3), showing the latter to be due to reduced lattice barriers rather than increased dielectric loss consequent on relaxation effects.

The values of four-terminal d.c. resistivity of a single crystal of $CsNO_3$ (Fig. 6) are devoid of extrinsic effects, consistent with the greater purity of the sample compared with those investigated by Bizouard et al.,[31] whose data exhibit a departure from linearity within the phase I region. The value 1.9_4 eV for the conductivity energy parameter in phase I may be compared with that of 2.0_4 eV which is obtained from the data presented by Bizouard et al.[31] Similarly, the transition temperature of $150°C$ is in good agreement with those obtained calorimetrically.[25-27] The degree of linearity of the single crystal resistivity curve in phases I and II emphasizes that, apart from a premonitory variation over the temperature interval 127 to $150°C$, the phases possess a high degree of stability.

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