

Solid State Transitions in Univalent Nitrates Below Room Temperature

J. H. FERMOR and A. KJEKSHUS

Kjemisk Institutt A, Universitetet i Oslo, Blindern, Oslo 3, Norway

The performance of electrical measurements on the anhydrous, univalent nitrates, *i.e.* LiNO_3 , NaNO_3 , KNO_3 , RbNO_3 , CsNO_3 , AgNO_3 , TlNO_3 , and NH_4NO_3 , shows that they all exhibit solid state transitions below room temperature. Of these compounds, KNO_3 and NaNO_3 have been investigated earlier by the present authors,^{1,2} and are included here for the sake of completeness.

Values of dielectric constant ϵ and the parameter ρ_D (a form of resistivity; *cf.* Ref. 2) have been obtained at 1 kHz over the temperature cycle — room temperature to -70°C to room temperature, for several samples of each compound, using

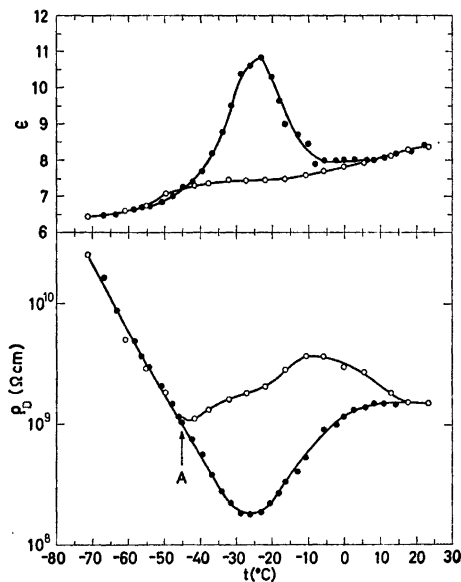


Fig. 1. Dielectric constant ϵ and resistivity ρ_D for RbNO_3 as functions of temperature. Open circles denote values obtained with decreasing temperature, filled circles those with increasing temperature.

the method described earlier.¹ As in the previous work, samples were formed by cooling the molten *p.a.* grade compounds between plane electrode assemblies of silver.

The occurrence of phase transitions in the compounds is demonstrated by an anomalous dependence of ϵ and ρ_D on temperature. These characteristics show some variation in form from compound to compound, but are sufficiently alike to imply that the transitions are of a similar nature.

A typical example of the results obtained, are those for RbNO_3 , which are shown in Fig. 1, where ρ_D and ϵ are plotted as functions of temperature. The diagram shows that on decreasing the sample temperature, ρ_D rises to a maximum at $\sim -8^\circ\text{C}$, followed by a sharp minimum at -45°C , and then increases regularly over the remainder of the temperature range. On increasing the temperature, the almost linear portion of the ρ_D -curve extends beyond -45°C to form a minimum at $\sim -25^\circ\text{C}$. The value at this minimum is approximately one decade below that at room temperature. On further increase of temperature, a broad maximum is found at $\sim 10^\circ\text{C}$.

The corresponding values of ϵ are also anomalous in that a slight irregularity in its rate of fall with decreasing temperature at $\sim -45^\circ\text{C}$ coincides with the commencement of a marked hysteresis on raising the temperature. The curve develops a maximum at $\sim -25^\circ\text{C}$ which is 1.5 times the value obtained on cooling.

These results are taken as evidence of a phase transformation, the hysteresis suggesting the existence of disorder in the room temperature phase on heating. Similar results have been obtained for the other compounds of this study, and, consistent with the interpretation given in connection with the results obtained for NaNO_3 and KNO_3 , it is suggested that the temperature at the point marked *A* in Fig. 1 is characteristic of the course of the transformation. The various temperatures t_A for the compounds are listed in Table 1, together with the room temperature values for ρ_D and ϵ .

There is a degree of systematic dependence of t_A upon such parameters as the radius and mass of the cation, and in both of these correlations t_A has a minimum value with potassium nitrate.

In the case of NH_4NO_3 , the value of t_A is the same as that found for the phase

Table 1. Transition temperatures t_A , for the univalent nitrates, together with room temperature values of resistivity ρ_D and dielectric constant ϵ .

Compound	t_A^a (°C)	ρ_D (Ω cm)	ϵ	ϵ_s^b
LiNO ₃	-10	$\sim 10^7$	~ 15	2.5
NaNO ₃	-30	3.0×10^9	9.9	2.1
KNO ₃	-60	2.0×10^{10}	7.0	2.0
RbNO ₃	-45	1.5×10^9	8.4	2.3
CsNO ₃	-35	1.0×10^9	9.0	2.5
TlNO ₃	-35	3.0×10^9	13.0	3.3
AgNO ₃	-35	1.1×10^9	8.2	3.1
NH ₄ NO ₃	-32	1.3×10^9	7.0	2.4

^a The probable error limits in these figures are $\pm 5^\circ\text{C}$.

^b The values of n used in deriving ϵ_s are taken from Landolt-Börnstein.³

IV \rightarrow V transition temperature as a result of measurements of dielectric constant and differential thermal analysis by Kamiyoshi and Yamakami.⁴ This transition has furthermore been established optically,⁵ and by means of X-ray diffraction.^{6,7}

Electrical conduction in these compounds is ionic in nature and probably extrinsic in most of the samples examined. Thus, in view of the possibility of polarization potentials developing at the electrodes in the present two terminal method of investigation, the values of ϵ given in Table 1 are liable to be somewhat higher than the true figures, as also are the values of ρ_D . (Additional inaccuracies arise in determining the sample geometries.) The values of ϵ for NH₄NO₃ given by Kamiyoshi and Yamakami⁴ are, on the other hand, almost certainly too low, owing to their use of powdered samples. Their value $\epsilon = 2.3$ at room temperature is, for example, no more than may be expected for the electronic contribution alone, as calculated from the refractive index n using the expression $\epsilon = n^2$, where ϵ is the dielectric constant at optical frequencies. This quantity is given in Table 1 for the various compounds. The difference between ϵ and ϵ_s arises as a result of the additional contributions to the polarizability provided by atomic, ionic, and dipole orientational sources, of which the latter is the most highly temperature dependent.

X-Ray data obtained in the present study, suggest that the transitions involve only minor structural rearrangements,

which, in view of the pronounced effect on the electrical characteristics, appear to concern dipole polarizability and the distribution of potential within the crystal lattice.

A fuller discussion of the electrical properties of these compounds will appear in forthcoming publications.

Acknowledgements. This work was made possible by the kind provision of laboratory facilities by Professor H. Haraldsen and the financial support of *Norges almenvitenskapelige forskningsråd*.

1. Fermor, J. H. and Kjekshus, A. *Acta Chem. Scand.* **22** (1968) 836.
2. Fermor, J. H. and Kjekshus, A. *Acta Chem. Scand.* **22** (1968) 1628.
3. Landolt-Börnstein, *Eigenschaften der Materie in ihren Aggregatzuständen, 8. Teil. Optische Konstanten II*, Springer, Berlin-Göttingen-Heidelberg 1962.
4. Kamiyoshi, K. and Yamakami, T. *Sci. Rep. Tohoku Univ. First Series* **11** (1959) 418.
5. Hendricks, S. B., Deming, W. E. and Jefferson, M. E. *Z. Krist. Mineral. Petrogr.* **85** (1933) 143.
6. Hendricks, S. B., Posnjak, E. and Kracek, F. C. *J. Am. Chem. Soc.* **54** (1932) 2766.
7. Brown, R. N. and McLaren, A. C. *Proc. Roy. Soc. (London)* **A 166** (1962) 329.
8. McLaren, A. C. *Rev. Pure Appl. Chem.* **12** (1962) 54.

Received July 12, 1968.