

A Dependence of Transition Properties of the Univalent Nitrates upon Structural Entities

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Low temperature dielectric transitions occurring in LiNO_3 , NaNO_3 , KNO_3 , RbNO_3 , CsNO_3 , AgNO_3 , TlNO_3 , and NH_4NO_3 are shown to have characteristic temperatures which depend on the degree of packing of ions in the crystal lattice. The same factor is also shown to influence the melting points of the compounds. As an example of transformations at intermediate temperatures, observed values of dielectric constant in KNO_3 at 1 kHz are considered in relation to the phase II to I transition at ~ 402 K. The range of existence of phase III_m (m=metastable) appears to be connected with a region of increased dielectric constant in phase II.

Changes in the physical properties of univalent nitrates with temperature form a rather extensive topic; much of the literature dealing with the structural and order-disorder transformations occurring above room temperature. The present work is concerned primarily with the low temperature, and melting transitions, since these are found to have features in common. Between these temperature extremes, the phase II to I transformation in KNO_3 is taken as an example of a first order structural transition.

TRANSFORMATIONS BELOW ROOM TEMPERATURE

As reported earlier,¹ dielectric transitions occur below room temperature in LiNO_3 (263 K), NaNO_3 (243 K), KNO_3 (213 K), RbNO_3 (228 K), CsNO_3 (238 K), AgNO_3 (238 K), TlNO_3 (238 K), and NH_4NO_3 (241 K); the temperatures in parentheses being characteristic of the transitions on cooling in each case. In general, the transitions are detected by a peak in the dielectric constant ϵ on cooling, with a discontinuity in slope at the maximum value. On heating, there is a considerably larger and more rounded maximum at a somewhat higher temperature. Corresponding minima are found in the a.c. resistivities. In the case of KNO_3 , a determination of unit cell dimensions showed there to be an anomalous variation in cell volume in the region of the transition.² That lattice expansion can have an important bearing on dielectric transitions has been shown on

theoretical grounds by Simpson³ for cases where there is a change in the freedom of orientation of electric dipoles.

The transitions in the univalent nitrates appear to involve only small changes in energy, since no corresponding anomalies are noted in the specific heat curves of NaNO_3 and KNO_3 ,⁴ or by means of differential thermal analysis in RbNO_3 and CsNO_3 .⁵ In TlNO_3 , on the other hand, a discontinuity in slope has been noted⁶ in previously published specific heat data.

The dielectric anomalies are in themselves insufficient to enable the nature of the transitions to be determined in detail, but some progress in interpretation may be made, pending the use of supplementary experimental techniques. The values of the electrical parameters obtained below room temperature for LiNO_3 ,⁷ NaNO_3 ,⁸ KNO_3 ,² RbNO_3 ,⁹ CsNO_3 ,⁹ AgNO_3 ,⁶ TlNO_3 ,⁶ and NH_4NO_3 ⁶ suggest that the anomalies reflect considerable alterations in lattice forces. The form of the curves does not, for example, appear to be consistent with an impurity relaxation effect, or to result from the reorientation of dipoles constituted by interstitial ions closely associated with vacancies in the corresponding sublattice. These phenomena would be expected to result in more symmetrical maxima and minima, smaller variations in ϵ , and an absence of hysteresis, as may be seen for example in Ref. 10.

Although the exclusion of water from the nitrate samples was given a high priority, at the cost of obtaining non-standard values of dielectric parameters, the complete absence of water is unlikely. The dielectric transitions do not reflect a freezing and remelting of solutions of the salts, however, the eutectic temperatures being in most cases much higher. If additional impurities were included in solution, thus reducing the operative eutectic temperatures, the anomalous increases in dielectric constant on heating which were found for KNO_3 ($\Delta\epsilon=9.2$), RbNO_3 ($\Delta\epsilon=2.5$), CsNO_3 ($\Delta\epsilon=4.0$), and AgNO_3 ($\Delta\epsilon=2.8$) would indicate extremely high impurity contents, and therefore this cannot be regarded as a reasonable explanation of the anomalies.

The dielectric anomalies may, however, reflect structural or order-disorder transformations; and it is natural to suppose that the nitrate groups play an important role by reason of internal changes, modifications in ordering, or a combination of such effects. A noticeable feature of the transitions is that on heating the samples, an increasing value of ϵ is continued into the region of the normal room temperature phase to form a maximum. Such high values of ϵ as those recorded, in combination with low a.c. resistivities, can be most simply accounted for by the rotation of electric dipoles through restricted angles, by large ionic displacements, or a combination of the two. Dipoles could, for example, arise from distortions from planarity of the nitrate groups, and the transitions involve the ordering of these dipoles. The symmetrical out of plane mode of oscillation of the group, of frequency $\nu_2 \approx 830 \text{ cm}^{-1}$,¹¹ is largely restricted to the ground state within the temperature range of the anomalies (210 to 265 K), and this favours a locking of distorted groups into an ordered structure.

The possibility that the dielectric transitions reflect structural order-disorder transformations is supported by the similarity of the experimental data with those obtained by Guillien¹² for the lambda transitions in ammonium halides at comparable temperatures. The first of these transformations was

discovered calorimetrically by Simon¹³ in NH_4Cl , and the results of a large number of investigations including those using neutron diffraction^{14,15} show that whereas the orientations of the NH_4^+ tetrahedra are ordered in the low temperature phases, at room temperature they are randomly distributed between two alternative orientations. Some aspects of the order-disorder process itself are still uncertain, however, in spite of the large number of studies on the subject. By analogy, it may be suggested as a possibility that the low temperature dielectric transitions in the univalent nitrates correspond to the onset of orientational disorder of the nitrate group. Only very small amounts of energy are involved in reorientations between equivalent positions at low frequencies. If the nitrate group is regarded as planar, as claimed by Walsh¹⁶ on quantum mechanical grounds, the most probable reorientations are those through angles of 120° about the threefold axis of the group. These reorientations would be consistent with the suggestion by Schroeder *et al.*,¹⁷ on the basis of infrared measurements, that the barrier opposing reorientation is surmounted at room temperature in several nitrates.

An additional possibility which cannot be definitely excluded at present, however, is that small departures from planarity of the nitrate groups are involved in the transitions. In this case, additional crystallographic parameters are introduced in the structural model, with corresponding possibilities for disordering. Whichever form the disorder takes, it is interesting to consider the variation of the transition temperature T_a within the family of compounds. It is reasonable to suppose that anion-cation and anion-anion interactions influence this parameter, and therefore the lattice volume V_l associated with each anion is selected as an independent variable. Thus V_l is the unit cell volume per formula unit less that of the cation. The latter is assumed to be spherical, and of radius r_c appropriate to sixfold coordination.

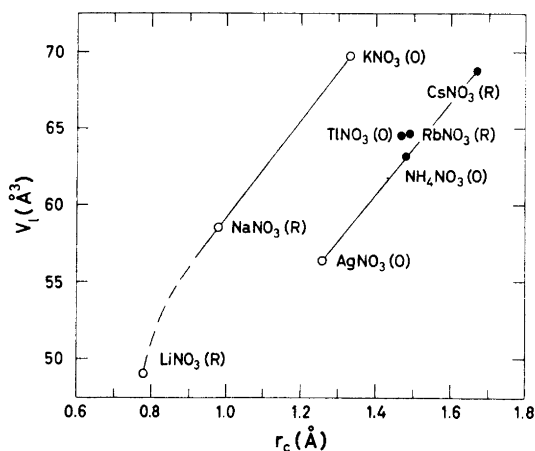


Fig. 1. Lattice volume per anion V_l versus cation radius r_c for univalent nitrates. The crystal structures of the room temperature phases are (R) rhombohedral, and (O) orthorhombic. Filled circles represent compounds adopting a cubic phase I structure ($r_c > 1.4$ Å).

INFLUENCE OF CATION RADIUS UPON PACKING

Before examining the dependence of T_a upon V_l , it is interesting to see from Fig. 1 that the connection between V_l and r_c is such that the compounds fall into two, approximately linear groups. The values of r_c employed in this diagram may be regarded as having been well established, except possibly in the case of Li^+ , for which Goldschmidt's value of 0.78 \AA ¹⁸ has been selected, consistent with its use in related work.⁶ The values of V_l are calculated for the room temperature phase in each case. There is seen to be a degree of correlation between the data for LiNO_3 ,¹⁹ NaNO_3 ,²⁰ and KNO_3 ,²¹ despite differences in structure, which may be obtained from the references given. The overall symmetries only are indicated in the figure, like symbols not necessarily indicating like structures. The data for RbNO_3 ,²² CsNO_3 ,²³ TlNO_3 ,²⁴ and NH_4NO_3 ,²⁵ form a separate group, the members of which have cubic high temperature phase I structures,²⁶ while LiNO_3 , NaNO_3 , KNO_3 , and AgNO_3 are rhombohedral, at least in their high temperature phases.²⁷ Thus, independent of the structure type at room temperature, that of the highest temperature phase depends on whether $r_c \geq 1.4 \text{ \AA}$. The separation of the room temperature data of Fig. 1 into two linear sets suggests two types of lattice bonding, independent of the crystal structures involved.

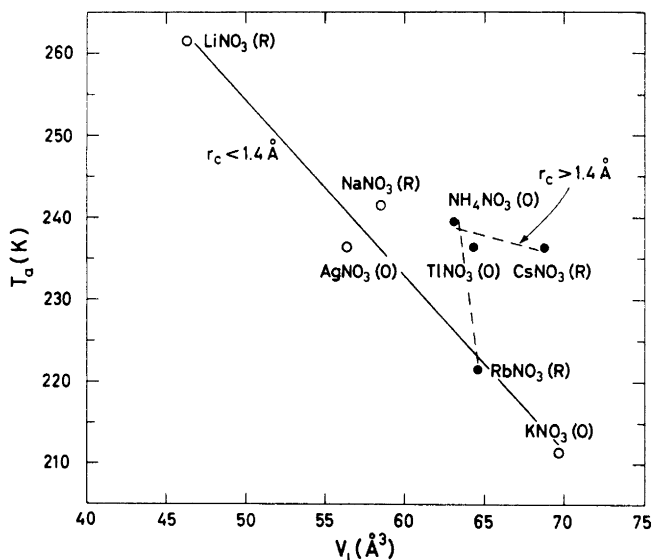


Fig. 2. The low temperature dielectric transition temperatures T_a versus the lattice volume per anion V_l for univalent nitrates. The crystal structures of the room temperature phases are (R) rhombohedral and (O) orthorhombic. Filled circles denote compounds with $r_c > 1.4 \text{ \AA}$.

DEPENDENCE OF DIELECTRIC TRANSITION TEMPERATURE ON PACKING

No consistent trend including all of the compounds is to be found on plotting T_a versus r_c , but overall correlations between T_a and V_l may be seen in Fig. 2. The results suggest that in general the lesser the ionic interaction (*i.e.* the greater V_l), the lower the transition temperature. As in Fig. 1, the influence of cation radius also appears to be in evidence in Fig. 2, since the points fall into two groups according to whether $r_c \geq 1.4$ Å. In order of increasing r_c , the group comprising LiNO_3 , NaNO_3 , AgNO_3 , and KNO_3 is approximately linear, while TlNO_3 , NH_4NO_3 , RbNO_3 , and CsNO_3 may also form a related group if RbNO_3 or CsNO_3 are excepted. It should be noted that the probable error limits in the values of T_a are not well defined, but may provisionally be set at ± 5 K. It may be relevant that RbNO_3 is unusual among these compounds in undergoing a small contraction on melting,²⁸ suggesting peculiar bonding properties. The indicated correlations, which imply T_a to be a monotonic function of V_l for each group of compounds, are of course to be regarded as suggestive rather than conclusive. It is not supposed that proximity effects alone determine the value of T_a , but the results do tend to confirm the fundamental or intrinsic nature of the anomalies, and may assist in the choice of methods suitable for their further investigation. The correlations are consistent with the order-disorder models considered above in selecting V_l as independent parameter.

The influence of packing upon the internal characteristics of nitrate groups has been demonstrated by Bues,²⁹ who showed a dependence of the symmetrical in-plane oscillation frequency ν_1 upon the free lattice volume per anion V_f (*i.e.* $V_f = V_l - V_a$, where V_a is the volume of the anion). Bues considered LiNO_3 , NaNO_3 , KNO_3 , and AgNO_3 , in solid and liquid states; finding no evidence of variation in the strength of the internal binding forces of the nitrate groups in these compounds, with the exception of AgNO_3 .

INFLUENCE OF PACKING ON THE MELTING TRANSFORMATION

It was proposed earlier³⁰ that the thermal response of the anion sublattice is primarily responsible for the anomalously low melting points T_f of the univalent nitrates, whose values are some 200 to 400 K lower than for the alkali halides. The relationship between T_f and V_l for the univalent nitrates is shown in Fig. 3, where it is seen that, with the exception of CsNO_3 , the alkali metal nitrates show an approximately linear correlation. It is important to note that KNO_3 provides an exception to the ordering of points according to cation radius. The influence of ionic radius upon T_f for the alkali halides, which provide a convenient class of compounds for comparison, has been noted earlier.³⁰ The deviation of CsNO_3 may perhaps be due to its limiting value of cation radius, possibly resulting from a screening effect. The influence of V_l upon T_f for the alkali metal nitrates is consistent with both a variation in lattice energy and a modification of the nitrate groups, on the assumption that the modes of oscillation or disorder of the latter, over and above those of spherical ions, control the melting process.

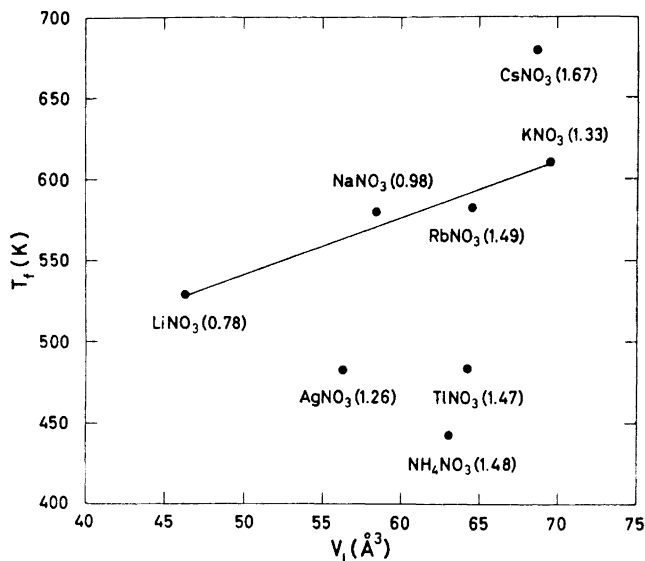


Fig. 3. Melting points T_f versus lattice volume per anion V_1 for univalent nitrates. Values of cation radii are shown in parentheses.

The positions of AgNO_3 , TlNO_3 , and NH_4NO_3 , relative to the other compounds in Fig. 3, clearly result from the operation of factors additional to those considered above. The electronic polarizabilities of the ions might be one such factor, but while the value for Tl^+ (90.1 \AA^3) exceeds even that of Cs^+ (71.3 \AA^3), that for Ag^+ (39.4 \AA^3) is less than for K^+ (47.3 \AA^3), according to the data reported by Roberts.³¹ Additional evidence for the uniformity of anion-cation bonding in univalent nitrates is presented elsewhere.⁶

In regarding ionic interactions as the controlling factor in determining T_f for LiNO_3 , NaNO_3 , KNO_3 , RbNO_3 , and CsNO_3 , variations in the internal mode frequencies of the anion have not been mentioned. According to the concept of the "Lockerungseffekt" introduced by Theimer,³² however, deformation of the anion by the electrostatic field generated between it and the surrounding cations can diminish the internal binding forces of the anion, with a consequent reduction in internal mode frequencies. This has been shown by Bues²⁹ to occur in AgNO_3 , but not in LiNO_3 , NaNO_3 , and KNO_3 , and it is possible therefore that the low value of T_f for AgNO_3 , and probably also for TlNO_3 , reflects a displacement to lower temperatures of the activation of internal modes.

Also important in an understanding of the melting process is the exceptionally high self diffusion rate of cations in the vicinity of the melting point, which has been clearly shown to exist in the high temperature disordered state of NaNO_3 by means of NMR,^{33,34} d.c. conductivity,⁸ and low frequency dispersion³⁵ experiments. These results show an instability of the cation sublattice which makes cooperative anion vibrations particularly effective in producing the disorder of melting.

In this connection, values of the partition functions for simple harmonic oscillators of the frequencies of internal oscillation of the nitrate group show that appreciable activation occurs in the temperature range of the thermal transformations above room temperature, and of the melting points.³⁶ These vibrations tend to increase the effective degree of sphericity of the group, and to cause fluctuations in the lattice barrier potentials opposing positional and orientational disorder of the ions. On increasing the temperature of a crystal, both of the above consequences of vibration tend to favour transformations into structures of a higher degree of symmetry and disorder, and lead eventually to the melt.

THE FIRST ORDER STRUCTURAL TRANSFORMATION IN KNO_3

The most common type of solid-state transformation occurring in the univalent nitrates is the discontinuous, or first order structural transition. As an example of this type of transformation, that between phases II and I in KNO_3 at ~ 402 K is extremely sharp, as may be seen from the temperature variation of the electrical resistivity.³⁷ If the characteristic modes of anion vibration are of importance in causing this and other transformations in the nitrates, the sharpness of the transition seems paradoxical in view of the gradual thermal activation of the vibrational modes. Experimental evidence of changes premonitory to the II to I transformation in KNO_3 is, however, shown in Fig. 4, where there is seen to be a gradual increase in the dielectric constant, beginning at ~ 350 K. These data were obtained for a polycrystalline *p.a.* grade (Merck) sample, according to the method described in Ref. 8. The measuring frequency used was 1 kHz, compared with the higher values (≥ 10 kHz) employed in previous determinations,³⁸⁻⁴² with which the present results are consistent. No other premon-

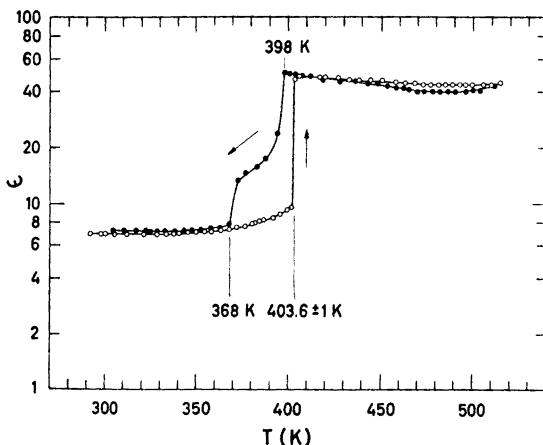


Fig. 4. Dielectric constant ϵ versus absolute temperature T for polycrystalline *p.a.* grade KNO_3 at 1 kHz. Arrows indicate the direction of temperature change.

itory effects are known to have been found in connection with this transformation. Also to be seen in the diagram is a high value of ϵ of ~ 50 in phase I ($T > 403.6$ K), where there is known to be orientational disorder of the nitrate groups,⁴³ leading to a reduction in mean energy barriers. The formation of the intermediate phase III_m ($m = \text{metastable}$; $368 < T < 398$ K, approximately) on cooling is also apparent.

The observed increase in ϵ prior to the phase II to I transformation is also relevant to the soft mode interpretation of phase transitions. According to this model, the lattice modes directly associated with the displacement of atoms to new structural positions become unstable as the transition is approached. Thus, diminished values of force constants cause the frequencies of certain lattice modes to fall to zero at the transition temperature; and the reduced force constants result in increased displacements in the presence of an externally applied electric field, thus causing the observed increase in ϵ . The stability of the phase III_m on cooling is no doubt related to the increased value of ϵ of phase II over the temperature range of existence of the phase III_m recorded here. The transitional quality of phase III_m is apparent from its values of ϵ .

Treatments of internal and librational modes of oscillation of molecules or ionic groups on the one hand, and of soft lattice modes on the other, provide complementary aspects of transformations in crystals. Whereas soft mode studies lead to insight into the transitional mechanism connecting initial and final lattice structures, consideration of spatial factors, molecular or ionic group disorder, and of internal modes and their interactions have been found of value in suggesting how solid state and melting transformations originate in the compounds considered.

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