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Lattice Energies of Some Univalent Nitrate Phases

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The lattice bonding energies of univalent nitrates in calcite-like modifications are calculated using a method in which dispersion and multipolar forces are implicitly accounted for. The results accord well with experimental data. It is deduced from the temperature dependences of the energies that there are significant departures from the calcite type structure at higher temperatures in $LiNO_3$, $NaNO_3$, and KNO_3. The nature and extent of the deviations are discussed.

The evaluation of crystal lattice energies can be approached from both theoretical and experimental points of view, permitting tests regarding the nature of the bonding forces in the compounds. The results also have implications in connection with many bulk and defect properties of the crystals, and their behaviour on being dissolved, or transformed to the vapour state.

The lattice energy of a crystal may be defined relative to that of the constituent atoms at infinite dispersion *in vacuo* at absolute zero temperature, but for ionic crystals, the usual procedure is to employ as reference level the energy of the fully ionized atoms and groups of atoms at infinite dispersion. This is evidently realistic when the internal bonding forces of an ionic group are large compared with the external interionic forces, so that the group behaves as a discrete entity, and physical characteristics such as interionic separations and charge distribution are little affected by the state of aggregation. The infrared frequencies of internal and lattice oscillations provide a convenient indication of whether this condition is fulfilled, as it is in the nitrates, where the frequency ratio approaches 10:1.

The chief contribution to the lattice energy of an ionic crystal is the classical electrostatic (Coulomb) energy, which for an ion labelled i in an aggregate of ions, each having a spherically symmetric distribution of charge, is given by

$$U_i = q_i \sum_j q_j r_{ij}^{-1} \qquad (1)$$

where r_{ij} is the separation of the charges q_i and q_j. For one mol of a binary crystal, the total electrostatic energy may be written in the form

$$U_E = -NMz^2e^2r_0^{-1} \quad (2)$$

where N is Avogadro's number, M is the Madelung constant for the crystal structure, ze is the ionic charge, and r_0 the separation of adjacent anion and cation in the lattice. More difficult to calculate are the attractive forces arising between the fixed dipoles which are mutually induced on the ions as a result of their individual polarizabilities; and the dispersion (van der Waals) forces, arising from the fluctuations of charge about their mean positions. Where a non-uniform distribution of charge exists on an ionic group, as, *e.g.*, in NO_3^-, there is an opportunity for allowing (to some extent) for the multipolar and dispersion forces, since these may be included in eqn. 2 by means of a suitable adjustment of a hypothetical charge distribution for the group.

U_E is a negative quantity, whereas the repulsive energy U_R originating from the overlap of electrons between ions of both like and opposite charge is positive, and usually of the order of $-0.1U_E$. Exponential and inverse power laws of force have been used in calculating the energy due to these short range forces. A discussion of repulsive, multipolar, dispersion, and zero point energies has been given by Waddington [1] for alkali nitrates and other crystals.

Using an effective radius of 1.89 Å for the nitrate group, Yatsimirsky [2] derived values for the lattice energies of $NaNO_3$, KNO_3, $RbNO_3$, and $CsNO_3$ from a modified empirical equation due to Kapustinsky, and values based on the use of lyotropic numbers have been published by Morris.[3] Other experimentally based data have been presented by Ladd and Lee,[4] who utilized the Born-Haber cycle and direct calculation. All of these data relate to room temperature, where $LiNO_3$ and $NaNO_3$ alone have the calcite type structure;[5,6] the latter compounds retaining trigonal symmetries up to the melting points (253.1 [7] and 404°C,[8] respectively). KNO_3 has a closely related phase I structure over the range from 128.5°C [9] to the melting point (338°C [10]),[11] and $RbNO_3$ is rhombohedral in phase II (219 – 281°C [12]),[13] and this is also the case for phase I $AgNO_3$ [5] from ~159°C [14] to the melting point 209.6°C.[15]

CALCULATION OF LATTICE ENERGIES

Calculations of the electrostatic energy of crystals with the calcite type structure, from a point charge approximation for both anion and cation, were performed by Højendahl [16] and Evjen,[17] both authors obtaining values of the Madelung constant from rapidly converging series. In two earlier articles, Chapman *et al.*[18] and Topping and Chapman [19] considered the stability of the calcite type structure using a model which allows for the non-spherical charge distribution of the anion. Their method will be discussed in some detail, as it is used in modified form to calculate the lattice bonding energies of univalent nitrates with calcite-like structures. A numerical treatment of complex ions was recently described by Jenkins and Waddington.[20]

The rhombohedral, calcite type structure of $LiNO_3$, is shown in Fig. 1. The nitrogen atoms are situated at the centres of equilateral triangles defined by the oxygen atoms, and are indicated in the diagram by lattice points only. The layer-like nature of the structure is shown in Fig. 1b, where the first

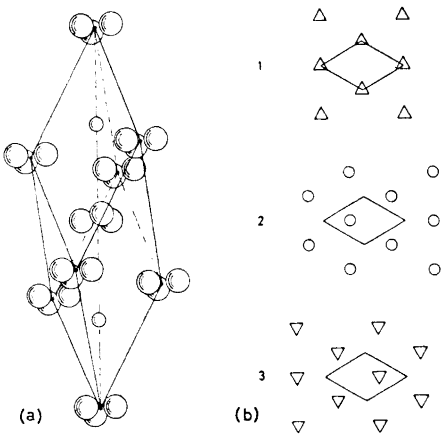

Fig. 1. (a) Calcite type structure of $LiNO_3$, (b) three strata of ions perpendicular to the hexagonal *c*-axis.

three of twelve strata occurring along the diagonal of the rhombohedron are shown. Also shown in Fig. 1b are the projections of the alternative, hexagonal unit cell, the *c*-axis of which coincides with the diagonal of the rhombohedral cell, and is of the length shown in Fig. 1a. The nitrate group is thought to be planar, or practically so, and for present purposes the charge distribution is arbitrarily regarded as $+5e$ at the centre of the nitrogen atom, and three charges of $-2e$ each, at a distance l (Chapman *et al.* used the notation b for this dimension) from the centre of the nitrogen atom, in the directions of the oxygen atoms. l is regarded here as an empirical quantity, adjustable for each compound so that the model has the same stable configuration and unit cell dimensions as are found in the crystal. In this way, multipolar and dispersion forces are implicitly incorporated in the model for each compound, whereas Topping and Chapman considered l to be constant for the group. The restriction of dipoles to the plane of the group is consistent with their greater polarizability in the plane than perpendicular to it.

Chapman *et al.* introduced the parameters $t=\pi a/3\sqrt{3}d$ and $\lambda=l/a$ where a is the hexagonal unit cell dimension, and d $(=c/12)$ is the separation of ionic planes perpendicular to the *c*-axis. The relationship between λ and t was then plotted for a constant size of the anion group, and constant separation between oxygen atom and adjacent cation (configuration curves); these being superimposed on curves of constant electrostatic potential. The locus of points of contact between these curves defines possible structural configurations, as shown in Fig. 2, where the inset diagram shows how the locus is related to the configuration curve C and equipotential curve P. The points marked on the curve refer to $LiNO_3$ at 20 and 251.4°C, and $NaNO_3$ at 25 and 300°C, according to structural data from Refs. 5 and 6.

From a comparison of the experimental and theoretical values of the rhombohedral angle (of a unit cell other than that of Fig. 1), Chapman *et al.* obtained good agreement for five carbonates using the appropriate λ *versus* t curve, and a constant value of 0.92 Å for l. At that time, the results could be applied to only a single nitrate compound, *viz.* $NaNO_3$, for which they found

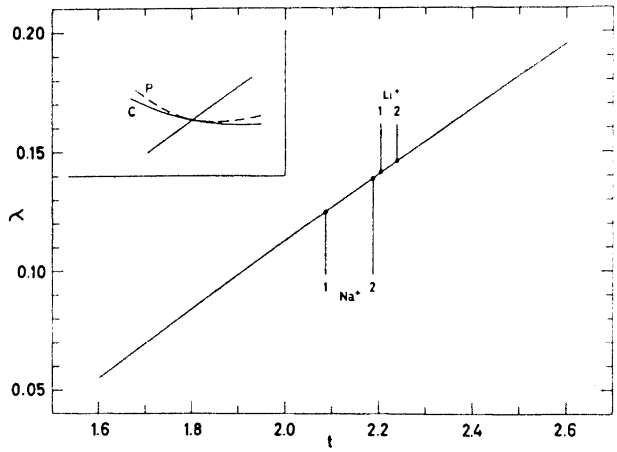

Fig. 2. λ *versus* t for univalent crystals with the calcite type structure according to the results of Chapman *et al.*[18] The inset diagram shows how the curve is derived as the locus of points of contact of configuration curves C and equipotential curves P.

$l = 0.72$ Å. These values of l were modified slightly on dealing differently with the repulsive energy, but this is of no consequence here.

The values of λ and t for a given compound determine the Madelung constant, the actual expression used being

$$U_E = -\frac{96e^2NF(\lambda,t)}{lJ} \tag{3}$$

where J is the mechanical equivalent of heat. As the values of $F(\lambda,t)$ are not readily obtained from the original work, they are plotted in Fig. 3 for both

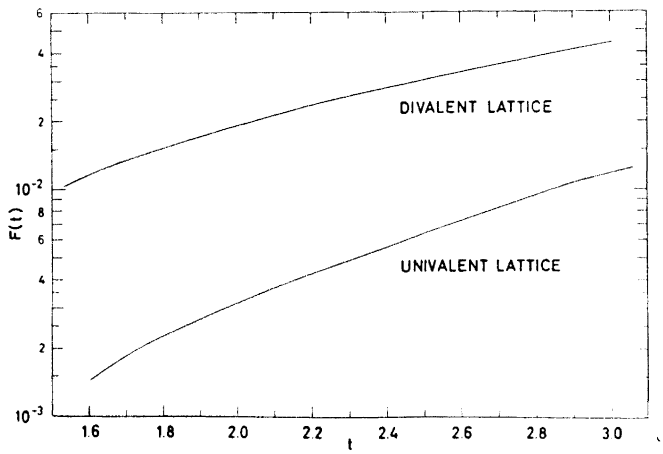

Fig. 3. $F(t)$ derived from the results of Chapman *et al.*[18] for univalent (nitrate) and divalent (carbonate) lattices.

univalent (nitrate) and divalent (carbonate) lattices. The curves are seen to have an approximately logarithmic dependence on t.

Information is now available on the variation of unit cell dimensions of $LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$, and $AgNO_3$ with temperature, and the modified method may be used to determine the corresponding values of electrostatic energy on the assumption that the crystal structures are of the calcite or orientationally disordered calcite types over certain ranges of temperature. Besides yielding values of the electrostatic energies of the compounds, the results also reflect the influence of temperature upon the structures.

NUMERICAL RESULTS

The calculated values of l and U_E at selected temperatures are presented in Table 1, together with the structural data on which they are based. It is seen that l varies considerably between the various compounds. Topping and

Table 1. Values of the adjustable parameter l and lattice bonding energy U_E for univalent nitrates in rhombohedral modifications.

Compound	Temp. (°C)	Phase	Unit cell dimensions a (Å)	c (Å)	Ref.	l (Å)	$-U_E$ (kcal/mol)
$LiNO_3$	Rm.temp.	I	4.693	15.224	21	0.687	208
$NaNO_3$	25	II	5.0694	16.8200	6	0.703	191
KNO_3	128	I	5.423	19.277	5	0.640	170
$RbNO_3$	250	II	5.48_3	21.41_0	5	0.526	162
$AgNO_3$	210	I	5.174	17.018	5	0.730	187

Chapman show how the repulsive energy may be calculated from an inverse eleventh power law for the repulsive force. The values of U_R for $NaNO_3$ and KNO_3 corresponding to the data of Table 1 are $NaNO_3$, 22 kcal/mol, and KNO_3, 11.3 kcal/mol. These results are not of high precision owing to the fact that the positions of the centres of repulsion of the oxygen atoms are not well defined. For both $NaNO_3$ and KNO_3, approximately equal contributions to the repulsive energy derive from cation-oxygen and oxygen-oxygen interactions, while cation-cation contact is negligible. A lack of suitable coefficients prevented a similar calculation for $LiNO_3$.

The present data are shown together with literature values in Table 2. There is seen to be good consistency between the present results and those published earlier. $AgNO_3$ has an anomalously high value of lattice energy, as may be seen from the results of Ladd and Lee plotted in Fig. 4; the dependence of U upon ionic separation (the crystal structure being of secondary importance), has been observed by Kapustinsky.[22] It seems likely that the high value of U for $AgNO_3$ results from the exceptionally large electronic polarizability of Ag^+.[23]

Table 2. Lattice energy U and electrostatic energy U_E for univalent nitrates. [a] indicates use of the Born-Haber cycle, [b] semi-empirical data, the remaining results being calculated.

Author(s) and year	Energy (kcal/mol)	$LiNO_3$	$NaNO_3$	KNO_3	$RbNO_3$	$CsNO_3$	NH_4NO_3	$AgNO_3$	$TlNO_3$
Topping and Chapman[19] (1927)	$-U$		178						
Højendahl [16] (1938)	$-U_E$		180						
Yatsimirsky [2] (1956)	$-U$		181.1[b]	164.2[b]	157.6[b]	151.1[b]			
Morris [3] (1958)	$-U$	198.8[b]	177.6[b]	162.5[b]	155.8[b]	149.7[b]	158.2[b]	195.6[b]	164.6[b]
Ladd and Lee [4] (1960)	$-U$	193[a]	172[a]	156[a]	147	143	143	189[a]	158[a]
Present work	$-U_E$	208	191	170	162			187	
	$-U$		169	159					

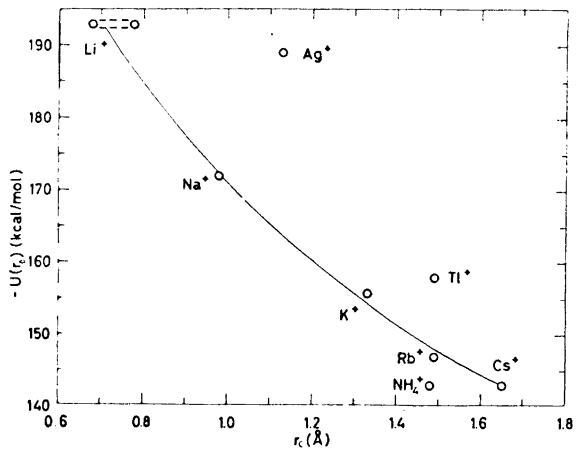

Fig. 4. Lattice energies $-U$ for univalent nitrates *versus* cation radius r_c. Values of $-U$ from Ladd and Lee.[4]

INFLUENCE OF TEMPERATURE INCREASE ON BONDING ENERGIES

With increasing temperature and distortion of the average unit cell due to anharmonicity of thermal vibration, there is in general an increase in the electrostatic contribution to the lattice energy (*i.e.* it becomes less negative). Since the attractive and repulsive forces are virtually in equilibrium at all stages of the expansion, the increase in lattice energy depends on the far smaller force constants which are, for example, reflected in lattice mode frequencies. Even where a sharp polymorphic phase transformation occurs, the enthalpy increment of the crystal may in most cases be largely accounted for by the effects of positional or orientational disorder of the ions,[24] without the necessity of introducing terms expressing increments in bonding energies. The effects of alterations in the lattice bonding forces over the continuous phase II to I transformation in $NaNO_3$ have, however, been considered in relation to changes in the Debye temperature and entropy of the compound.[25]

Although the change in U_R due to this transformation is difficult to calculate, the increment in U_E may be derived from the expansion properties of the lattice as determined by X-ray diffraction.[5] The amount calculated according to the present method is $\Delta U_E = 10.7$ kcal/mol over the temperature interval 25 to 300°C. This is a considerable change in energy, especially when compared with the repulsive energy at 25°C, $U_R = 22$ kcal/mol, or the experimentally determined enthalpy increment of ~ 9 kcal/mol over the same temperature interval.[10] Thus it seems that the only way in which ΔU may be of the correct order of magnitude (*i.e.* negligible compared with these amounts) is for there to be a significant departure from the assumed calcite type structure in $NaNO_3$ I. This interpretation is consistent with the findings of Strømme,[26] from X-ray diffraction data, of the displacement of a proportion of the nitrate groups parallel to the *c*-axis in the phase. It also seems probable that some groups undergo metastable angular displacements about axes perpendicular to the threefold axis, the overall effect being to expand the thickness of the planar distribution of negative charge associated with the anions. Such a mechanism is consistent with the relative constancy of the *a*-axis of $NaNO_3$ over the temperature interval.[5]

The apparent increase in U_E with temperature may be used as a measure of the distortion from the ideal structure, and a comparison of values obtained for the various compounds is complementary to (and at present a substitute for) complete structure determinations. There is no direct information on lattice changes in $LiNO_3$ above room temperature, but anomalies have been detected in the range 120 to 230°C by means of UV [27] and electrical measurements.[28] The increment ΔU_E for $LiNO_3$ over the range 20 to 251.4°C is 4.6 kcal/mol, which may be taken as a measure of the corresponding lattice distortion. The corresponding value for KNO_3 I over the temperature interval 128 to 335°C is 8.9 kcal/mol.

It would be of interest to extend the present approach to the calculation of lattice energies to other compounds, *e.g.* the remaining nitrates, and to examine in detail the problem of repulsive energies. The barrier separating alternative metastable positions of the anion might then be determinable on the assumption (which was also used here) that the cation sublattice remains virtually undisturbed.

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