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On the Entropy Increment at the Phase II to I Transition in $NaNO_3$

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Means described in the literature for calculating individual contributions to the entropy change in $NaNO_3$ at the phase II to I transformation are considered. An improved method of deriving the entropy of molecular, or ionic group, disorder is developed on the basis of a lattice dynamical model for the crystal. Application of the method yields a value of 1.7 e.u. for the entropy of orientational disorder of the nitrate groups in $NaNO_3$ at 553 K.

Using the thermodynamic principles governing the connection between entropy and the orientational disorder of coherent structural units included in a crystal lattice, Newns and Staveley [1] have applied the equation

$$\Delta S = R \ln n \qquad (1)$$

to a number of solid state phase transitions occurring in salts. ΔS is the contribution of disorder to the change in entropy at the transition, R is the gas constant, and n is the change (per formula unit) in the degree of disorder associated with the transition. The univalent nitrates are a convenient class of compounds for a study of orientational disorder properties, because of the limited number of ways in which disorder may occur, and the substantial amount of experimental data which is available on their temperature dependent characteristics.

In the instance of the solid state transition in $NaNO_3$, which occurs continuously over the temperature range ~ 423 to ~ 550 K, Newns and Staveley employed a value for the anomalous part (*i.e.* that directly attributable to disorder) of the calorimetrically determined entropy increment, $\Delta S = 1.26$ cal K^{-1} mol^{-1} (e.u.). This was derived by Mustajoki [2] by means of extrapolation of the values of specific heat C_p at temperatures below the interval of the transformation. Applying the same method to the results of several calorimetric investigations, Strømme [3] obtained a value of 2.1 e.u. for this quantity. This simple method of calculation of the appropriate part of the total entropy increment by means of extrapolation, depends on the

implicit assumption that the distribution of the normal vibrations of the lattice is only negligibly affected by the transformation; or that the characteristic temperatures associated with the various degrees of freedom remain constant. It will be shown that this is not in fact the case.

Newns and Staveley [1] pointed out that "due to the change in vibrational frequency distribution, the actual entropy increase will differ from $R \ln n$ by an amount which one would much like to calculate reliably". The latter authors showed in this connection that the suggestion of Slater,[4] that $\Delta S/\Delta V$ for the transition might be obtained from $(\partial S/\partial V)_T$ for one of the phases, does not provide a satisfactory basis for interpretation of the measured entropy increments at solid state transitions in the potassium and rubidium halides. Because of the modification of effective inter-ionic bonding forces which it is reasonable to expect at a transformation involving group orientational disorder, the method would be even less likely to succeed in such cases. Quite apart from the extra degree of freedom introduced by the onset of rotational disorder, alterations in the lattice bonding properties at the transformation will clearly produce changes in the values of the thermodynamic functions which are analogous to those found between different substances. A theoretical treatment of the thermodynamic properties of related phases or substances must therefore, as a first priority, make allowance for differences in the lattice bonding.

It was suggested by Newns and Staveley [1] that in addition to the consequences of a change in volume at a transition, an alteration in crystal structure will in principle affect the lattice vibrational frequency distribution. There is, however, an indication that a modification of the crystal structure may in itself have comparatively little influence upon the entropy. It was shown [5] that, for the alkali halides, the values of entropy at 298.15 K are consistent with the expression

$$S_{298.15} = -14.6 + 11.7\,(r_a + r_c) \qquad (2)$$

where r_a and r_c are the anion and cation radii, respectively. Since tetrahedral, octahedral, and cubic coordinations are included in the crystal structures of these compounds, it appears that this aspect is in itself comparatively unimportant among factors determining the entropy of the solid, and hence the distribution of lattice frequencies.

In respect of the univalent nitrates, it was shown [5] that at up to room temperature, a satisfactory thermodynamic model of the crystal lattice consists of three parts, *viz.*

(i) a continuous Debye solid,

(ii) an assembly of Einstein oscillators representing the dominant low frequency librational modes of the nitrate groups, and

(iii) an assembly of Einstein oscillators representing the $3N-6=6$ normal internal modes of the nitrate groups. Values of the Debye or Einstein frequencies for each part of the model were deduced from the results of IR investigations.

At higher temperatures, the above model has to be modified in order to allow for the orientational disorder which is thought to be associated with the phase II to I transformation on the basis of calorimetric,[2] electrical,[6] and

X-ray [3] measurements.* It is also convenient to adopt a different procedure in respect of parts (i) and (ii) of the earlier model.

Angular oscillations about principal axes of the nitrate groups in $NaNO_3$, which has the calcite type structure, do not occur independently of each other in the ideal way envisaged in the Einstein model of the lattice. A given nitrate group is closely coupled to six nearest neighbour cations, and six (coplanar) anions. The relative positioning of an anion in its cation environment is drawn to scale in Fig. 1. The central nitrate group is represented by a

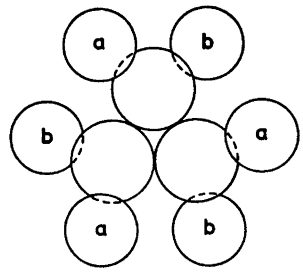

Fig. 1. Nitrate group and nearest neighbour cations in $NaNO_3$. The hard sphere model of the anion is based on the N – O separation (1.255 Å) given by Felty;[7] the cation radius is taken as 0.95 Å. The sodium atoms marked *a* are as far above the plane of the nitrate group as those marked *b* are below.

hard sphere model of the oxygen atoms based upon an N – O separation of 1.255 Å,[7] the consistent hard sphere oxygen radius being 1.10 Å. As a consequence of the anion-cation coordination, a displacement of the anion in any direction relative to the cations (*e.g.* during a normal lattice mode of vibration), imposes torsional forces on the group. A displacement parallel to the trigonal axis will, for example, produce a rotation of the group towards a position characteristic of the aragonite type structure. Similar effects occur for displacements in other directions. Librations of the groups are also directly coupled, making possible lattice modes of vibrations which involve angular degrees of freedom. A mode of oscillation of this type is shown in Fig. 2, where

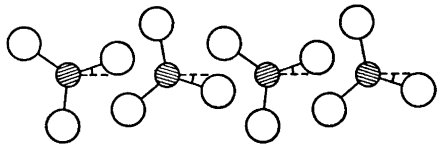

Fig. 2. Linear librational mode of oscillation of coupled nitrate groups.

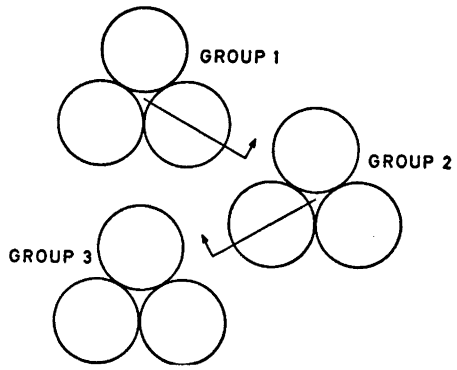

Fig. 3. Interference effect on the librational mode shown in Fig. 2 resulting from the interaction of other nitrate groups in the plane.

* These publications provide a convenient indication of current experimental work.

a small fraction of a wavelength is depicted. This mode will in fact be coherent only over short distances, owing to a dissipative interference introduced by other groups in the same plane. This mechanism is indicated in Fig. 3, where it is seen that the displacement shown for group No. 1, acting *via* group No. 2, tends to produce an in-phase rather than an anti-phase displacement of group No. 3. This effect results in a reduction of amplitude from that implied by the model shown in Fig. 1, rather than a complete neutralization; and attenuation of amplitude with the in-plane distance of propagation.

An alternative means of approach to the dynamics of the lattice is therefore to combine parts (i) and (ii) of the previous model, providing a suitable means of evaluating the Debye temperature can be found. It is also necessary to allow for the effects of the transformation on the frequency distribution of this new Debye solid. A procedure of this kind has the advantage of overcoming problems connected with the precise nature of the libration spectrum, and the drastic effects which the transformation may be expected to have on these oscillations. Since the entropy of the system is a function of state, the increment in its value over a phase transformation may be obtained by comparing the values for two such Debye solids having characteristic temperatures appropriate to the two phases. The calculation of Debye temperatures may be based upon the values of elastic constants, as have for example been obtained for $NaNO_3$ through the transition range of temperatures by Kornfel'd and Chubinov.[8]

The experimental values of S_{11}, S_{33}, S_{44}, and S_{12} obtained by the latter authors lead to values for the velocity of sound in the directions of the a and c axes of the hexagonal unit cell, as follows:

$$\begin{gathered} C_a=(\varrho S_{11})^{-\frac{1}{2}};\ C'_a=\{\varrho(\tfrac{1}{2}S_{44}+S_{11}-S_{12})\}^{-\frac{1}{2}} \\ C_c=(\varrho S_{33})^{-\frac{1}{2}};\ C'_c=(\varrho S_{44})^{-\frac{1}{2}} \end{gathered} \tag{3}$$

and mean values of the longitudinal and transverse velocities may be calculated from the equations:

$$C_l=\tfrac{1}{2}(C_a+C_c);\ C_t=\tfrac{1}{2}(C'_a+C'_c) \tag{4}$$

The effective velocity C for the calculation of the Debye temperature θ_D is then given by

$$\frac{3}{C^3}=\frac{1}{C_l^3}+\frac{2}{C_t^3} \tag{5}$$

where

$$\theta_D=\frac{hC}{k}\left(\frac{3N}{4\pi V}\right)^{1/3} \tag{6}$$

The symbols have their usual meanings, *cf.*, *e.g.*, Fowler and Guggenheim.[9] The calculation of θ_D is intrinsically somewhat arbitrary, but inaccuracies are offset here, since one is concerned with a change in properties over a comparatively small temperature interval.

Using the observed value of density ($\varrho=2.265$ g cm^{-3} at 0°C [10]) together with the results of dilatometric measurements [11] and the unit cell dimensions,[7] the derived values of θ_D at 423 and 553 K are 196 and 150 K, respectively.

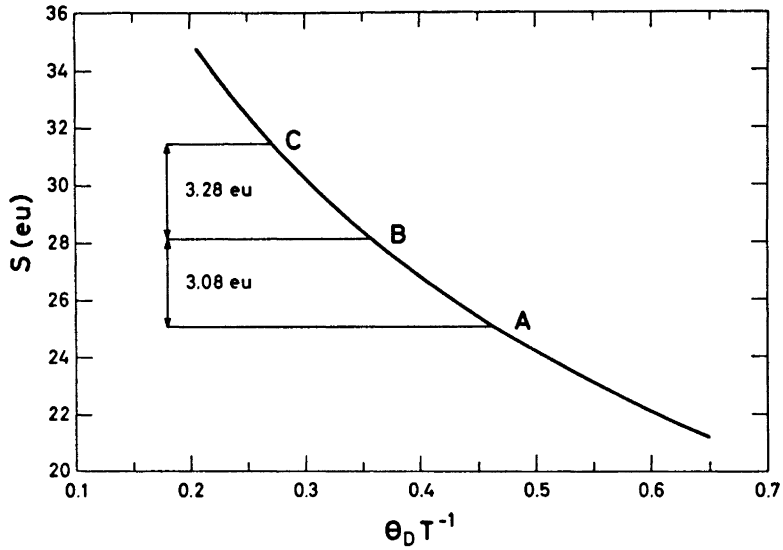

Fig. 4. Entropy of the Debye solids representing lattice modes of vibration in $NaNO_3$ below (*A*) and above (*C*) the phase II to I transformation. The point *B* represents the phase I entropy on the basis of a constant Debye temperature of 196 K.

It is not essential for the present purpose that these temperatures coincide precisely with the initiation and completion of the transformation, provided the transformation is included in the range. In Fig. 4, the Debye function entropy for the phase II and phase I solids at the temperatures 423 and 553 K are shown at the points *A* and *C*, respectively, while the point *B* represents the high temperature value which would be obtained at constant $\theta_D = 196$ K. It is seen that the effect of the transformation upon θ_D is equally important as the increase in temperature. The total increment is 6.36 e.u.

The far greater strength of the internal than the external bonding of the nitrate group permits the assumption that the internal modes of vibration are little affected by the transformation. Adopting the frequencies and designations given by Herzberg [12] for the six normal modes of the group yields values of the Einstein temperature θ_E ranging from 1050 to 2100 K. Summation of the entropy increments over the temperature range 423 to 553 K for the various modes, of which two are doubly degenerate, gives $\Delta S_{int.} = 1.6$ e.u.

From the calorimetric data of Sokolov and Schmidt,[13] the experimental value of the total entropy change

$$S_{553} - S_{423} = 9.7 \text{ e.u.} \qquad (7)$$

Equating this with the summation of the contributions from lattice modes, internal modes, and orientational disorder, yields a value of 1.7 e.u. for the latter. The probable error in this quantity cannot be assessed precisely, but is estimated at ~ 10 %.

A value of 1.9 e.u. for the entropy of disorder has been obtained by Strømme [3] on the basis of the presence of both disordered calcite and aragonite type positions of the nitrate groups. Although the present result is

consistent with this value, other possible models of disorder are not necessarily excluded. In consideration of the model proposed by the latter author it is noted that the calcite and aragonite type positions of the anion are connected by libration of the group about its threefold axis; and also that in the disordered lattice situation it seems likely that the potential at the anion varies in a more general way than required for the calcite and aragonite type situations.

The above treatment of entropy change at a transformation is not limited to gradual transitions, but does require that the elastic constants of the crystal be determinable, for example by the composite bar method employed by Kornfel'd and Chubinov.[8] It would be particularly interesting to deal in a similar way with the phase II to I transition in KNO_3, but in this case special complications arise owing to the macroscopic changes in the crystal which occur at that transformation.

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