

Application of the Method of Mott and Littleton to NaNO_3 Calculation of Enthalpies of Formation of Schottky and Frenkel Defects

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Mott and Littleton's method is applied to calculation of the enthalpy of formation of Schottky and Frenkel defects in the NaNO_3 crystal. The values obtained are equal, respectively, to 2.4 and 1.08 eV. In agreement with the experiment, it can be concluded that the Frenkel disorder is predominant in NaNO_3 .

A point defect such as a vacancy or an interstitial ion in a crystal causes a distortion. This is important close to the defect, and decreases when the distance increases.

Three approaches have been used for the investigation of atomic displacements. In Eshelby's (1) treatment the defect is considered as a point singularity in an elastic continuum. The second method, used by Kanzaki (2), Matsubara (3), and Hardy (4, 5) seems better than the first because it recognizes the discrete nature of a real lattice throughout the calculations. But we have not used this method, as certain data necessary for calculation are unknown for NaNO_3 . Chronologically speaking, the third method is the earliest: in fact Mott and Littleton (6) first carried out calculation of the enthalpy of formation of the Schottky defect in alkali halides, taking as their starting point a Jost's theory (7) which emphasized—as early as 1933—the importance of polarization phenomena in the creation of a defect. In this treatment the equilibrium of nearest neighbors is considered in detail and the rest of the medium is regarded as a polarized continuum. This theory has since been subjected to a number of modifications and improvements (8-12) which enable values to be obtained that agree well with experimental results.

But all these calculations were made for elements with a cubic structure and for monoatomic ions, which can be likened to spheres, i.e., in relatively simple cases. We proposed to extend this method to more complex crystals such as that of NaNO_3 . This salt crystallizes in the rhombohedral system up to

melting temperature and has a polyatomic anion which, in this work, we have likened to a cylinder of height 2.2 \AA and 2.3 \AA radius.

I. Polarization of a Crystal

The presence of a defect of charge q in an ionic crystal gives rise to polarization of ions and a distortion of the network. Mott and Littleton (6) showed that displacement of an ion is given by the equation

$$x = \pm \frac{M' qv}{er^2} \quad (1)$$

and dipolar moments induced by displacements and electronic polarizability on the positive and negative ions at a distance from the charge q could be expressed, respectively,

$$\mu_+ = \frac{M_+ qv}{r^2}, \quad (2)$$

and

$$\mu_- = \frac{M_- qv}{r^2}. \quad (3)$$

In Eqs. (1), (2), and (3), r is the distance from the charge q to the ion considered, v is the average volume taken up by an ion in the network and the coefficients M' , M_+ , and M_- have the following values:

$$M' = \frac{2\alpha}{2\alpha + \alpha_+ + \alpha_-} \frac{1}{4\pi} \left(1 - \frac{1}{\epsilon_r}\right),$$

and

$$M_{\pm} = \frac{2(\alpha + \alpha_{\pm})}{2\alpha + \alpha_+ + \alpha_-} \frac{1}{4\pi} \left(1 - \frac{1}{\epsilon_r}\right),$$

where ϵ_r is the relative dielectric constant, α the polarizability of displacement, α_+ and α_- the electronic polarizabilities of the anions and cations.

The NaNO_3 crystal being anisotropic, the quantities ϵ_r , α , α_+ , and α_- are represented by tensors. In practice, for lack of complete numerical data we have been obliged to use average values. For example, for the dielectric constant ϵ_r we have taken the value 6.65 obtained on pellets (13). In the case of α_- we have inferred the additivity of the polarizabilities of the ions of a crystal. Under these conditions the Lorentz formula becomes:

$$\frac{\alpha_+ + \alpha_-}{2} \frac{1}{3\epsilon_0 v} = \frac{n^2 - 1}{n^2 + 1};$$

$\alpha_- = 4.1 \times 10^{-40}$ MKSA was obtained, taking the geometrical average of the product of ordinary and extraordinary indexes for n (14), and the value 0.44×10^{-40} MKSA given by Shockley (15) for α_+ .

Finally, the method advocated by Mott and Littleton (1) was used to calculate α . It was found that $\alpha = 2.65 \times 10^{-40}$ MKSA. And from this: $M' = 3.7 \times 10^{-2}$; $M_+ = 4.3 \times 10^{-2}$; and $M_- = 9.5 \times 10^{-2}$.

Equations (1), (2), and (3) enable induced dipoles and displacements of ions at a distance from the charge q to be determined, but they are not sufficiently precise when the calculations concern the nearest neighbors of a defect. Their dipoles and their displacement must be calculated using the equations:

$$F_e + F_r = 0, \quad (4)$$

and

$$\mu_{\pm} = \alpha_{\pm} \frac{F_e}{q'}, \quad (5)$$

where the resultant of the electrostatic forces acting on the ion considered is called F_e , that of the repulsive forces F_r , and the charge of the considered ion q' .

The expression of repulsive force is obtained considering only interactions between nearest neighbors. This is the Born-Meyer model in its most simple form: the force between two ions of unlike sign at a distance r from one another may be written $b \exp[-r/\rho]$, where b and ρ are two constants. Then the total lattice energy is

$$E_c = -\frac{A_m e^2}{4\pi\epsilon_0 r_0} + 6b \exp\left(-\frac{r_0}{\rho}\right), \quad (6)$$

where r_0 is the reticular distance, A_m the Madelung constant of the crystal system under consideration. Sodium nitrate crystallizes in the rhomboedric system and the value $A_m = 1.719$ has been obtained

by direct computer calculation using Evjen's method (16), taking as the rhombohedron angle $\delta = 102^\circ 40'$ and $r_0 = 3.24 \text{ \AA}$. In the usual way, b and ρ constants have been determined using the formulae

$$\frac{dE_c}{dV} = 0,$$

and

$$\frac{d^2 E_c}{dV^2} = \frac{1}{V\beta},$$

where V is the average volume of a salt molecule in its solid state, and β the coefficient of isothermic compressibility as measured by Bridgman (17). We found that $b = 1.055 \times 10^{-14} \text{ J}$ and $\rho = 2.411 \times 10^{-11} \text{ m}$.

II. Enthalpy of Formation of Schottky Defects

It is inferred that the defect, i.e., the cationic vacancy of charge $-e$, is to be found at (0,0,0) (Fig. 1). Interposing the relative displacement $\xi = x/r_0$ of the ion and the quantity $m = -(\mu/er_0)$, the forces F_e and F_r can be expressed:

$$F_r = \frac{b}{\rho} \left\{ -\exp\left[-\frac{r_0}{\rho}(0.9920 - \xi)\right] + \frac{2\xi + 0.4664}{d_1} \exp\left(-\frac{r_0 d_1}{\rho}\right) + \frac{2\xi - 0.4289}{d_2} \exp\left(-\frac{r_0 d_2}{\rho}\right) \right\},$$

with $d_1 = (\xi^2 + 0.4664\xi + 0.9749)^{1/2}$ and $d_2 = (\xi^2 - 0.4289\xi + 0.9572)^{1/2}$ and

$$F_e = \frac{e^2}{4\pi\epsilon_0 r_0^2} \left\{ \frac{2.6910}{(1 + \xi)^2} - \frac{2(0.7796 + \xi)}{(1.5292 + 1.5292\xi + \xi^2)^{3/2}} - \frac{2(1.2204 + \xi)}{(2.4408 + 2.4408\xi + \xi^2)^{3/2}} - \frac{1}{(2 + \xi)^2} - \frac{2.4438m}{(1 + \xi)^3} - 0.1570 \right\}.$$

In this last equation, the first four terms represent the action of the vacancy and of the five other first neighbors; the fifth is due to the dipoles of these five neighbors, and the sixth represents the force created by the dipoles induced on all the other ions. In fact we have only calculated action exercised by dipoles to be found in a rhombohedron centered on the vacancy and with an aris of $40r_0$, the contribution made by the other dipoles being negligible.

Knowledge of m , ξ (Table I), and of potentials produced by dipoles on ions of the crystal, enables

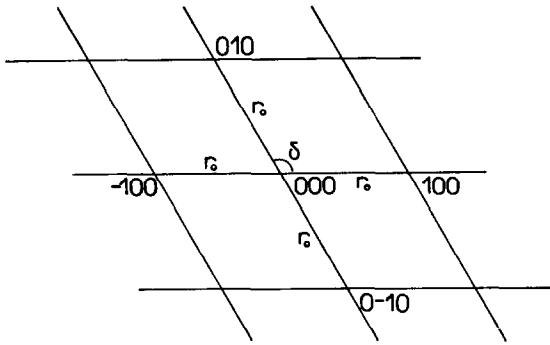


FIG. 1.

the potential of polarization V to be calculated. It is expressed thus:

$$V = \frac{e}{4\pi\epsilon_0 r_0} \left[\frac{6m}{(1+\xi)^2} + \frac{6\xi}{1+\xi} + \gamma(7.016M_+ + 4.709M_-) \right]$$

The first term represents potential created by dipoles of the first six neighbors, the second is due to displacement of these six ions, and the third and fourth result from the respective contributions of dipoles induced on all cations and all anions; γ is a numerical coefficient equal to 0.91 such as the average volume occupied by an ionic pair is $V = 2\gamma r_0^3$.

The work that must be done to move a positive ion of the crystal away to infinity is given by:

$$W_0^+ = - \left[- \frac{A_m e^2}{4\pi\epsilon_0 r_0} + \frac{1}{2} V e + 6b \exp \left(- \frac{r_0(1+\xi)}{\rho} \right) \right]$$

In the same way the work W_0^- involved in the creation of an anion vacancy can be obtained. Enthalpy of formation W_S of a pair of Schottky defects, taking into account that the enthalpy E_c is obtained by bringing ions to the surface of the crystal

is thus equal to $W_S = -(W_0^+ + W_0^-) + E_c$. Using the value $E_c = 7.1$ eV calculated from (6) this gives $W_S = 2.4$ eV.

In the calculation seen below, ion displacement has been calculated using Mott and Littleton's method, the defect causing distance being considered as isolated in the crystal. But as Hardy (5) has pointed out, theoretically ion displacement is slightly affected by the presence of other defects.

In practice, for NaNO₃, experiments justify Mott and Littleton's hypothesis: the density of disorder is at most equal to 4×10^{-5} and thus the minimal distance between two defects is on an average twenty times the interionic distance. According to formula (1) the displacement caused by the other defects is, therefore, negligible compared with that created by the neighboring defect.

III. Enthalpy of Formation of Frenkel Defects

To create a pair of Frenkel defects, it is necessary to extract a cation from the crystal and move it away to infinity: to do this work $-W_0^+$ must be supplied; afterwards this ion is put in interstitial position and the work obtained is W_1^+ . Enthalpy of formation is, therefore, $W_F = -W_0^+ + W_1^+$.

We have inferred that the interstitial ion moved into the position $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, in other words, in the center of the rhombohedron demarcated by the ions $(0,0,0)$, $(1,1,0)$, $(0,1,0)$, $(1,0,1)$, $(1,0,0)$, $(1,1,1)$, $(0,1,1)$, $(0,0,1)$ (Fig. 2). Relative displacements $(\xi_j \dots)$ of these eight ions as well as the quantities $m_j = -(u_j / e r_0)$ are taken as being unknown. For reasons of symmetry the number of unknowns is reduced to eight ($1 \leq j \leq 4$).

But it is necessary to introduce some supplementary hypothesis at this point. In effect, the interstitial

TABLE I

	Cationic vacancy	Anionic vacancy
ξ	0.041	0.042
m	0.050	0.006
E_s'	-4.86 eV	-5.33 eV
E_r'	0.33 eV	0.31 eV
$E_s' + E_r'$	$W_0^+ = -4.5$ eV	$W_0^- = -5.0$ eV
$W_S = -(W_0^+ + W_0^-) + E_c = 2.4$ eV		

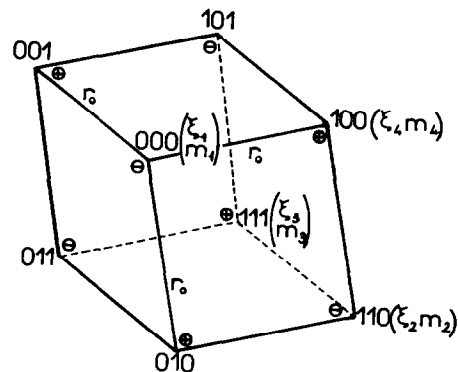


FIG. 2.

cation in the position $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is found on the ternary axis of the ion NO_3^- (0,0,0). In this direction the half-height of the anion, comparable to a cylinder, is 1.1 Å, whereas the ionic radius in the neighborhood of the ionic plane is equal to 2.3 Å. It follows that the value of repulsion energy between an anion and a cation is not the same, according to whether the latter can be found at a distance r from the former on the ternary axis or at the same distance r but in the ionic plane. In order to take this variation into account we have inferred that the coefficient ρ of the expression $b \exp[-(r/\rho)]$ was proportional to the sum of the ionic radii in the considered direction. It follows that the value for ρ is 1.525×10^{-11} m in the direction of the ternary axis.

On the other hand, the negative charge of the nitrate ion is in fact borne by the three atoms of oxygen, a more electronegative element than nitrogen, and at reduced distances this distribution of charges must be taken into account. According to Julg and Ozias (18), each atom carries the charge $-0.518 e$ and the nitrogen atom $+0.554 e$. Coulomb's force exercised on the ion NO_3^- by the interstitial ion is therefore:

$$f = \frac{e^2}{4\pi\epsilon_0 r_0^2} \left[\frac{0.554}{(0.6489 + \xi_1)^2} - \frac{1.554(0.6489 + \xi)}{[(0.6489 + \xi_1)^2 + (0.1418)]^{3/2}} \right] \\ \simeq \frac{e^2}{4\pi\epsilon_0 r_0^2} \frac{0.5}{(0.6489 + \xi_1)^2}$$

Finally, when the ion (0,0,0) is in equilibrium its electric dipole moment $\mu_1 = -m_1 e r_0$ supports the equation:

$$\mu_1 = -\alpha_- \frac{F_e^{(1)}}{e}, \quad (7)$$

and the static $F_e^{(1)}$ and repulsive forces $F_r^{(1)}$ are such that $F_e^{(1)} = -F_r^{(1)}$ (8). They are expressed thus:

$$F_r^{(1)} = \frac{b}{\rho} \left[\frac{1.5(0.8650 + 2\xi_1 - 0.4668\xi_4)}{d_1} \times \exp\left(-\frac{r_0}{\rho} d_1\right) + 1.58 \exp\left(-\frac{r_0'}{\rho'} d_2\right) - \frac{1.5(0.8912 - 2\xi_1)}{d_3} \exp\left(-\frac{r_0}{\rho} d_3\right) \right], \\ F_e^{(1)} = \frac{e^2}{4\pi\epsilon_0 r_0^2} \left[-\frac{0.5}{d_4^2} + \frac{3.7203m_4 - 3A}{d_1^3} + \frac{4.6788m_2 + 3B}{d_5^3} + \frac{1}{(d_6 - \xi_3)^2} + \right.$$

$$\left. + 0.0111 + \frac{2m_3}{d_6^3} - \frac{1}{d_6^2} + \frac{3C}{(1 + 0.8650\xi_1 + \xi_1^2)^{3/2}} - \frac{3D}{(1.5617 + 1.7300\xi_1 + \xi_1^2)^{3/2}} \right],$$

with $d_1 = (1 + 0.8650\xi_1 + \xi_1^2 + 1.5515\xi_4 + \xi_4^2 - 0.4668\xi_1\xi_4)^{1/2}$; $d_2 = 1.028 + 1.58\xi_1$; $d_3 = (1.0316 - 0.8912\xi_1 + \xi_1^2)^{1/2}$; $r_0' = 2.05$ Å; $d_4 = (0.6489 + \xi_1)$; $d_5 = (1.5615 + 1.7304\xi_1 + \xi_1^2 + 2.1572\xi_2 + \xi_2^2 + 0.4666\xi_1\xi_2)^{1/2}$; $d_6 = (1.2978 + \xi_1 + \xi_3)$; $A = (0.2807 + 1.0787\xi_1 + \xi_1^2 - 0.1514\xi_4 - 0.2333\xi_1\xi_4)d_4^{-1}$; $B = (0.5614 + 1.1502\xi_1 + \xi_1^2 + 0.2333\xi_1\xi_2 + 0.1514\xi_2)d_4^{-1}$; $C = (0.2807 + 1.0787\xi_1 + \xi_1^2)d_4^{-1}$; $D = (0.5614 + 1.5102\xi_1 + \xi_1^2)d_4^{-1}$.

By formulating it that the other ions are in equilibria, a system is obtained made up of four pairs of equations set out as follows:

$$F_e^{(j)} = -F_r^{(j)} \quad (8)$$

$$F_e^{(j)} = \frac{me^2 r_0}{\alpha_{\pm}}, \quad (9)$$

with $1 \leq j \leq 4$. For each group of values $\xi_1 \dots m_1 \dots$ we have calculated the coefficients

$$\gamma_j = \frac{F_e^{(j)} - F_e'^{(j)}}{F_e^{(j)}},$$

where $F_e^{(j)}$ and $F_e'^{(j)}$ are numerical values of force $F_e^{(j)}$, calculated, respectively, starting from Eqs. (8) and (9). The quantities γ_j are not simultaneously null: the system of eight equations allows of no solution. This can be essentially attributed to four reasons:

(1) Mott and Littleton's model is too simple (8-12). It does not take into account the phenomena of elasticity and repulsion between second nearest neighbors.

(2) For α , α_+ , α_- , and ϵ_r we have been obliged to use average values. In other words we assume that these quantities are isotropic.

(3) The values of b and ρ in the expression of the repulsive force between the anion (0,0,0) and the interstitial ion are approximate.

(4) The number of unknowns has been kept to eight, but this is too high for the model chosen. By taking only two unknowns it is possible to obtain a system that allows of solutions, but then displacements and dipoles of the other ions of the rhombohedron must be calculated using formulae (1) and (2) or (3). However, as it has already been pointed out, these are not precise enough when the calculations

concern ions in the neighborhood of the defect (at a distance less than or equal to r_0). So, rather than use this latter method we have adopted a group of values $\xi_1 \dots m_1 \dots$ which verify approximately the system of eight equations. These solutions which are $\xi_1 = 0$; $\xi_2 = 0.27$; $\xi_3 = -0.05$; $\xi_4 = 0.09$; $m_1 = 0.013$; $m_2 = 0.005$; $m_3 = 0.15$; $m_4 = 0.01$ correspond to

$$\frac{1}{4} \sum_j |\gamma_j|$$

minimum.

Polarization potential at the center of the rhombohedron is:

$$V = \frac{e}{4\pi\epsilon_0 r_0} \left\{ -\gamma(M_+ + M_-) 5.157 + 1.54 \left[\frac{\xi_1}{d_4} - \frac{\xi_3}{d_8} \right] + 3.22 \left[\frac{\xi_2}{d_7} - \frac{\xi_4}{d_9} \right] - \frac{m_1}{d_4^2} - \frac{3m_2}{d_7^2} - \frac{m_3}{d_8^2} - \frac{3m_4}{d_9^2} \right\},$$

with $d_7 = (0.9272 + \xi_2)$; $d_8 = 0.6489 + \xi_3$; and $d_9 = 0.9272 + \xi_4$.

The first term represents potential created by dipoles induced on the cations and the anions. The two following ones express displacement of each of the eight neighbors of the defect, and the last four are due to the dipoles induced on these eight neighbors. Potential being initially null at the point $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ electrostatic energy involved is reduced to $E_s' = \frac{1}{2}Ve$ and repulsion energy is expressed thus

$$E_r' = 3b \exp\left(-\frac{r_0(0.9272 + \xi_2)}{\rho}\right) + b \exp\left(-\frac{r_0'(1.028 + 1.58\xi_1)}{\rho'}\right),$$

giving $W_1^+ = E_s' + E_r' = -3.42$ eV. Enthalpy of formation of Frenkel defects is thus $W_F = -W_0^+ + W_1^+ = 1.08$ eV.

IV. Comparison with the Experiment

Enthalpy of formation of the Schottky defects which we have calculated is $W_S = 2.4$ eV and that of the Frenkel defects is much lower: it is equal to 1.08 eV. This is sufficiently small (to the figure for a

Schottky pair) for the concentration of Na⁺ interstitial to be preponderant even at melting point, and this conclusion of a theoretical origin, is well confirmed by experimental results: ionic conductivity (19) has shown that Frenkel's disorder is actually predominant in sodium nitrate.

The calculated value of W_F is 1.08 eV, whereas the experimental value is 1.14 eV. The difference reaches 6% only. It is the precision to be expected in using Mott and Littleton's theory. In order to increase the precision of results one would have to be able to take into account anisotropies of electronic polarizabilities, ion displacements, and dielectric constants, an impossible task at the moment as these are unknown data. In addition, correcting terms proper to elasticity phenomena around defects and to repulsion forces between second nearest neighbors could then be made to intervene.

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