

Application of the Method of Mott and Littleton to NaNO_3 : Calculation of Enthalpies of Migration of Frenkel Defects

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The principles of Mott and Littleton's method are applied to calculation of enthalpies of migration of interstitial ions and cationic vacancies in NaNO_3 . The ensuing results, 1.75 eV for the first mechanism, and 0.75 eV for the second, enable the conclusion to be drawn, in accordance with the experiment, that the transport of current is due to a migration of vacancies.

Introduction

It is known that an ionic crystal has, at a given temperature, a specific number of structural defects and that certain transport phenomena, such as the diffusion of matter or electric conductivity, are due to the migration of these defects. An interstitial ion, for example, moves under the action of an electric field in a succession of jumps between interstitial sites and this changing of place necessitates a certain quantity of energy, called enthalpy of migration.

We have undertaken to determine theoretically the value of this enthalpy for interstitial cations and for cation vacancies in NaNO_3 , this salt presenting in effect a Frenkel cationic disorder (1). For this calculation we shall use the principles of Mott and Littleton's method (2), which enabled us in earlier work (3) to determine the value of the enthalpy of formation of a pair of Frenkel defects in NaNO_3 .

In accordance with this method, we have therefore considered two regions in the crystal: region I constituted by the ions neighboring the defect and region II containing the rest of the crystal ions. The presence of a defect disturbs the network. In the first region, the displacement x of each ion and the induced dipole μ of each of these ions is calculated by writing that the electric and repulsion forces which affect it, and of which the resultants are F_e and F_r , balance one another out. That is,

$$F_e + F_r = 0.$$

In the whole of this work, forces are counted positively when there is repulsion. A second equation is obtained by writing, in the classical way, that the electric dipole μ_{\pm} induced on the ion under consideration satisfies the equation

$$\mu_{\pm} = \alpha_{\pm}(F_e/q'),$$

α_{+} (or $-$) being the electronic polarizability of the cation (or of the anion) and q' the cation (or anion) charge.

The expression of the repulsion force between two ions is naturally

$$f = -\partial E_r / \partial x.$$

For E_r , repulsion energy, we make use of an expression of the Born and Meyer type:

$$E_r = b \exp(-r/\rho) = \omega(r),$$

with $b = 1.055 \times 10^{-14}$ J and $\rho = 2.411 \times 10^{-11}$ m (3). As in (3), we have considered only the repulsion forces between first neighbors.

In region II the crystal is considered as a continuous and polarized medium. The displacements of ions and induced dipoles are given by

$$x = M' qv/q' r^2 \quad (1)$$

and

$$\mu_{\pm} = M_{\pm}(qv/r^2), \quad (2)$$

q being the defect charge. The values of M' , M_{+} and M_{-} are, respectively, 3.7×10^{-2} , 4.3×10^{-2} , and 9.5×10^{-2} (3).

Enthalpy of Migration of Interstitial Ions

Sodium nitrate crystallizes in the rhombohedral system, the characteristics of whose network are $r_0 = 3.24 \text{ \AA}$ and $\alpha = 102^\circ 40'$. We have supposed that the interstitial cation occupies the center of an elementary rhombohedron, that is to say, the position $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 1).

To migrate from this position towards one of the six possible neighboring positions, this cation may take either of two ways. It can pass through the center of the reticular plane where the electric potential is negative (way $I_1 I_2 I_3$ in Fig. 1) or by the centers of the two other planes equivalent to this point of view (that is to say, the negative ions are on the small diagonal of the side crossed). It can also pass through the centers of reticular planes where the electric potential is positive (way $I_1 I_2' I_3'$ in Fig. 1).

But the migrant ion being positive, the second way would necessitate an enthalpy of migration greater than that demanded by the first. In practice, the migration of an interstitial cation therefore takes place by the type 1 way only; it is at least according to this hypothesis that we calculate the enthalpy of migration U_i of this cation. To make the position clear, let us consider the way going from the interstitial position I_1 $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ to the interstitial position I_3 $(\frac{3}{2}, \frac{1}{2}, \frac{1}{2})$ and passing through the point I_2 $(1, \frac{1}{2}, \frac{1}{2})$. If W_1^+ and W_2^+ indicate the enthalpies of the cation at the points I_1 and I_2 , the enthalpy of migration is $U_i = W_2^+ - W_1^+$.

Calculation of W_2^+

We consider that region I is constituted by the anions $(1,0,0)$ and $(1,1,1)$, and by the cations $(1,0,1)$ and $(1,1,0)$. There are therefore four

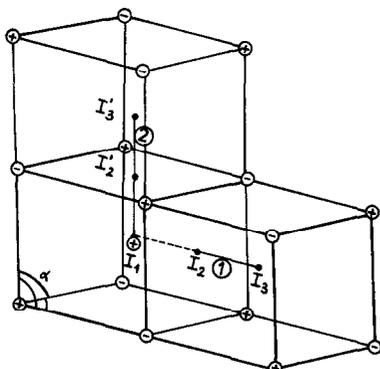


FIG. 1. Different ways for migration of interstitial ion.

unknowns: they are the relative displacements $\xi = x_-/r_0$ of the anions and $\eta = x_+/r_0$ of the cations and the quantities $m_- = \mu_-/er_0$ and $m_+ = \mu_+/er_0$ which are proportional to the dipoles induced on these same ions. To calculate the repulsion forces, we write that each of the region I ions is submitted to an interaction from its six nearest neighbors [whose displacements are calculated by formula (1)] and possibly from the defect, when the interionic distance is equal to or less than the total of the ionic radii (that is to say, when there is contact).

For example, if d_1-d_5 indicate, respectively, the distances between the ion $(1,0,0)$ on the one hand and the ions $(1,1,0)$ or $(1,0,1)$, $(1,-1,0)$ or $(1,0,-1)$, $(0,0,0)$, $(2,0,0)$, and the defect $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ on the other hand, the repulsion energy of the ion $(1,0,0)$ is

$$\sum \omega(r) = 2\omega(d_1) + 2\omega(d_2) + \omega(d_3) + \omega(d_4) + \omega(d_5),$$

whence

$$\begin{aligned} F_i^{(-)} = & - \frac{d(\sum \omega(r))}{dx} \\ = & \frac{b}{\rho} \left\{ \frac{1.2496 + 2\xi}{d_1} \exp\left(\frac{-r_0}{\rho} d_1\right) \right. \\ & - \frac{1.2749 - 2\xi}{d_2} \exp\left(\frac{-r_0}{\rho} d_2\right) \\ & - \frac{0.3645 - \xi}{d_3} \exp\left(\frac{-r_0}{\rho} d_3\right) \\ & + \frac{0.3411 + \xi}{d_4} \exp\left(\frac{-r_0}{\rho} d_4\right) \\ & \left. + \exp\left(\frac{-r_0}{\rho} d_5\right) \right\}, \end{aligned}$$

with

$$d_1 = [(0.6248 + \xi)^2 + (0.7808 + \eta)^2]^{1/2},$$

$$d_2 = (1.0287 - 1.2749\xi + \xi^2)^{1/2},$$

$$d_3 = (1.0330 - 0.7290\xi + \xi^2)^{1/2},$$

$$d_4 = (1.0574 + 0.6822\xi + \xi^2)^{1/2},$$

and

$$d_5 = (0.6248 + \xi).$$

In the same way if d_6, d_7 and d_1 represent the distances between the cation $(1,1,0)$ and its six neighbors $(0,1,0)$ or $(2,1,0)$, $(1,2,0)$ or $(1,1,-1)$,

(1,0,0) or (1,1,1), the repulsion force acting on one of these cations from region I is

$$F_r^{(+)} = \frac{b}{\rho} \left\{ \frac{0.0258 - 2\eta \exp\left(\frac{-r_0}{\rho} d_6\right)}{d_6} - \frac{1.5396 - 2\eta \exp\left(\frac{-r_0}{\rho} d_7\right)}{d_7} + \frac{1.5617 + 2\eta \exp\left(\frac{-r_0}{\rho} d_1\right)}{d_1} \right\},$$

with

$$d_6 = (0.9677 - 0.0258\eta + \eta^2)^{1/2},$$

$$d_7 = (0.9758 - 1.5396\eta + \eta^2)^{1/2}.$$

The force of electrical origin F_e^- acting on (1,0,0) is the resultant of several forces: in region I, Force created by the defect:

$$f_1 = (-e^2/4\pi\epsilon_0 r_0^2)(1/d_5^2);$$

Force due to the displacement of (1,1,1):

$$f_2 = \frac{e^2}{4\pi\epsilon_0 r_0^2} \left(-\frac{1}{(1.2496 + \xi)^2} + \frac{1}{4d_5^2} \right);$$

Force due to the displacements of (1,0,1) and (1,1,0):

$$f_3 = \frac{2e^2}{4\pi\epsilon_0 r_0^2} \left[\frac{d_5}{(1 + 1.2496\xi + \xi^2)^{3/2}} - \frac{d_5}{d_1^3} \right];$$

Force created by the dipole of (1,1,1):

$$f_4 = (e^2/4\pi\epsilon_0 r_0^2)(m_-/4d_5^3);$$

Force created by the dipoles of (1,0,1) and (1,1,0):

$$f_5 = (e^2/4\pi\epsilon_0 r_0^2)(2.9262m_+/d_1^3).$$

In region II, the force created by the polarization of all the medium is

$$f_6 = \gamma(1.1636M_- + 1.4474M_+),$$

γ being a characteristic number of the crystalline structure of NaNO_3 (3). Whence:

$$F_e^- = \sum_1^6 f_i.$$

In the same way the force F_e^+ acting on (1,0,1) can be expressed thus:

$$F_e^+ = \frac{e^2}{4\pi\epsilon_0 r_0^2} \left\{ \frac{1}{d_9^2} - \frac{m_+}{4d_9^3} - \frac{2.9626m_-}{d_1^3} - \frac{1}{(1.5617 + \eta)^2} + \frac{1}{4d_9^2} - \frac{2d_9}{d_1^3} + \frac{2d_9}{(1 + 1.5617\eta + \eta^2)^{3/2}} - \gamma(0.4477M_- + 1.9106M_+) \right\},$$

with

$$d_9 = 0.7808 + \eta.$$

The solutions of the system of equations I:

$$I \begin{cases} F_e^{(-)} + F_r^{(-)} = 0; \\ F_e^{(+)} + F_r^{(+)} = 0; \\ m_- = -F_e^{(-)} \alpha_- / r_0 e^2; \\ m_+ = +F_e^{(+)} \alpha_+ / r_0 e^2; \end{cases}$$

are $\xi = 0.25$, $\eta = 0.108$, $m_+ = 0.0171$ and $m_- = 0.1078$. The polarization potential at the center of the face is thus:

$$V = \frac{e}{4\pi\epsilon_0 r_0} \left\{ \frac{3.2\xi}{0.625 + \xi} - \frac{2.56\eta}{0.78 + \eta} - \frac{2m_-}{(0.625 + \xi)^2} - \frac{2m_+}{(0.78 + \eta)^2} - \gamma(6.2750M_- + 7.9987M_+) \right\}.$$

The first two terms are due to the displacement of the ions of region I, the following two represent the potential created by the dipoles of these ions and, lastly, the fifth is the potential produced by region II.

The electrostatic energy of the ion at point I_2 is

$$E_s = Ae^2/(4\pi\epsilon_0 r_0) + \frac{1}{2}Ve = -2.67 \text{ eV},$$

(where $A = -0.325$ represents the Madelung constant of the network related to point I_2) and that of repulsion $E_r = 0.97 \text{ eV}$. Whence, $W_2 = E_s + E_r = -1.7 \text{ eV}$ as $W_1 = -3.45 \text{ eV}$ (3). It results from this that $U_i = W_2 - W_1 = 1.75 \text{ eV}$.

Enthalpy of Migration of a Cation Vacancy

Most authors suppose that, in halides, the defect takes a direct way (2, 4). We work from the same hypothesis, that is, we presume that the migration of a cation vacancy takes place on one face of the elementary rhombohedron (Fig. 2). The site of the vacancy may be taken up by one of the 12 neighboring cations, such as $(-1, -1, 0)$

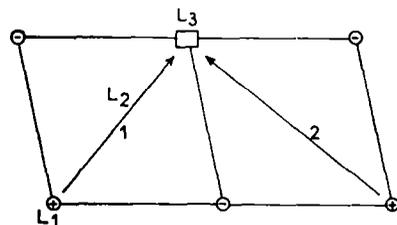


FIG. 2. Different ways for migration of cationic vacancy.

or $(1, -1, 0)$. As in the preceding paragraph, there are therefore two possible ways of migration according to whether the ion moves along a small diagonal (way 1 of Fig. 2), or on the contrary along a large diagonal (way 2). In this present work we consider in detail the case of way 1 only, which corresponds to the weakest enthalpy U_i . To evaluate the value of U_i , two successive operations are carried out: First, the ion from site L_1 $(-1, -1, 0)$ is removed and put in crystal. In order to do this, energy $-W_3$ must be supplied. It is then replaced in the crystal in L_2 $(-\frac{1}{2}, -\frac{1}{2}, 0)$ and the energy received is W_4 , whence $U_i = W_4 - W_3$.

Calculation of W_3

This is the energy necessary to create a vacancy in L_1 in the presence of the vacancy taking up site L_3 $(0, 0, 0)$. We suppose that the repulsion energy E_r and that the polarization potential V_p brought into play on the creation of this second vacancy are equal to those of an isolated vacancy. Electrostatic energy is easily calculated by $E_s = e(V + \frac{1}{2}V_p)$, where V is the electrostatic potential which exists in L_1 before the creation of the second vacancy. The potential V is the sum of several terms which represent: Potential created by all the crystal ions:

$$-(e/4\pi\epsilon_0 r_0) A_m \quad (\text{with } A_m = 1.719);$$

Potential created by the vacancy L_3 :

$$-(e/4\pi\epsilon_0)(1/1.2496r_0);$$

Potential created by the dipoles induced by polarization in region II:

$$(e/4\pi\epsilon_0 r_0) \gamma(4.781M_+ + 4.368M_-);$$

Potential created by the electronic polarization and the displacement of the six neighbors of L_3 (region I):

$$e/(4\pi\epsilon_0 r_0) 0.1407.$$

We have obtained $E_s = -5.28$ eV, now $E_r = 0.33$ eV (3), whence $W_3 = -4.95$ eV.

Calculation of W_4

It is the enthalpy brought into play to place the cation in the site $(-\frac{1}{2}, -\frac{1}{2}, 0)$ in the presence of the two vacancies in L_1 and L_3 . To calculate the value of the polarization potential due to the presence of this extra defect (Fig. 3) using Mott and Littleton's method, we suppose that the region I is limited to the ions $(-1, 0, 0)$ and $(0, -1, 0)$.

If d_1, d_2, d_3 and d_4 represent, respectively the

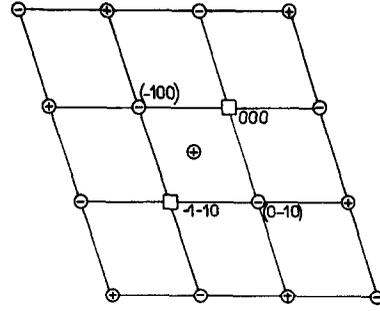


FIG. 3. The saddle-point configuration for the vacancy migration.

distance of the ion $(0, -1, 0)$ at $(2, 0, 0)$ or $(1, -1, 0)$, $(1, 0, 1)$, $(1, 0, -1)$ and L_2 , the repulsion force acting on one of the ions of region I is:

$$F_r = \frac{b}{\rho} \left\{ \frac{2\xi - 1.3727}{d_1} \exp\left(-\frac{a}{\rho} d_1\right) + \frac{\xi - 0.0173}{d_2} \exp\left(-\frac{a}{\rho} d_2\right) + \frac{\xi + 0.0053}{d_3} \exp\left(-\frac{a}{\rho} d_3\right) + \exp\left(-\frac{a}{\rho} d_4\right) \right\},$$

with

$$d_1 = (0.8537 - 1.3737\xi + \xi^2)^{1/2},$$

$$d_2 = (0.9851 - 0.0347\xi + \xi^2)^{1/2},$$

$$d_3 = (0.9851 + 0.0116\xi + \xi^2)^{1/2},$$

and

$$d_4 = 0.7808 + \xi.$$

The electrostatic force is the resultant of several forces which are:

Force exerted by the two vacancies and the interstitial ion:

$$f_1 = + \frac{e^2}{4\pi\epsilon_0 r_0^2} \left[\frac{2d_3}{(1 + 1.5617\xi + \xi^2)^{3/2} - d_3^2} - \frac{1}{d_3^2} \right];$$

Force created by the dipole of the other ion of region I:

$$f_2 = (e^2/4\pi\epsilon_0 r_0^2)(m/4d_3^3);$$

Force due to the displacement of the other ion of region I:

$$f_3 = \frac{e^2}{4\pi\epsilon_0 r_0^2} \left(\frac{1}{4d_3^2} - \frac{1}{(1.5616 + \xi)^2} \right);$$

Force created by the polarization induced in region II by the three defects and which can be split up, in its turn, into several terms by calculating the action due to each defect taken in isolation. These are:

(1) Force created by the polarization induced by the interstitial cation:

$$f_4 = \frac{e^2}{4\pi\epsilon_0 r_0^2} \gamma(0.448M_+ + 1.911M_-);$$

(2) Force created by the polarization induced by the vacancy L_3 . For the ions far from the vacancy (that is, all the ions of the crystal except $(+1,0,0)$, $(0,1,0)$, $(0,0,1)$ and $(0,0,-1)$), this force is:

$$f_5 = -\frac{e^2}{4\pi\epsilon_0 r_0^2} \gamma(1.873M_+ + 0.508M_-).$$

For the four ions near the vacancy, the force acting on the ion $(-1,0,0)$ or $(0,-1,0)$ can be calculated easily, if we know that the displacement of the ions is $0.041r_0$, and the dipole is $\mu = 0.059er_0$ (3). For example, the force due to the displacement of $(2,0,0)$ can be expressed thus:

$$f = -\frac{e^2}{4\pi\epsilon_0 r_0^2} \left[\frac{(2.5396 + 3.1874\xi + \xi^2)^{1/2}}{(4.1657 + 3.1874\xi + \xi^2)^{3/2}} - \frac{(2.3739 + 3.1232\xi + \xi^2)^{1/2}}{(4 - 3.1232\xi + \xi^2)^{3/2}} \right].$$

(3) Finally, the force created by the polarization induced by the vacancy L_1 which is equal to that of L_3 .

The solutions of system II,

$$\text{II} \begin{cases} F_e + F_r = 0; \\ m = -F_e \alpha_- / e^2 r_0, \end{cases}$$

are $\xi = 0.0646$ and $m = 0.0231$. Now in the presence of the two vacancies only the ion $(-1,0,0)$ or $(0,-1,0)$ is displaced from $\xi = 0.0640$, and m has the value -0.0921 . Thus, practically, the introduction of the interstitial cation in L_2 provokes no displacement of the ions in the region I, but on the contrary the induced dipole undergoes an increase, $\Delta m = 0.115$, and the polarization potential V_p is:

$$V_p = \frac{e}{4\pi\epsilon_0 r_0} \left[\frac{2\Delta m}{(0.78 + \xi)^2} - \gamma(6.273M_+ + 7.499M_-) \right].$$

The electrostatic energy existing in L_2 is $E_s = e(V + \frac{1}{2}V_p)$, where V represents the potential existing in L_2 before the introduction of the ion, that is, in the presence of the two L_1 and L_3 . It represents, therefore, the potential created by all the ions, by the two vacancies, and by the polarization induced by these latter. We shall

find $E_s = 5.74$ eV and $E_r = 1.54$ eV, whence $W_4 = -4.20$ eV, and $U_i = W_4 - W_3 = 0.75$ eV can be deduced.

Discussion

It is not easy to calculate precision on values U_i and U_l because it depends on the one with which the quantities M_+ , M_- , M' , b and ρ are known. And these are calculated by supposing the crystal to be isotropic, and starting from experimental values which are themselves tainted with errors as they have generally been obtained at room temperature. Thus the error on U_l has been estimated at about 10%. That on U_i is greater, in the region of 20-25%, because of the important relaxations which occur in the presence of the interstitial ion.

If one wishes to compare the theoretical and experimental values of U_l , a difficulty is met with, for this magnitude depends on the temperature field. In fact, sodium nitrate crystallizes in the rhombohedral system from room temperature up to fusion, but between 150 and 275°C a progressive thermal transformation takes place linked to the disorder of the anions, which has repercussions on electrical conductivity: The $\log \sigma$ vs $1/T$ shows a change in slope at these temperatures (1, 5-7).

When $t > 275^\circ\text{C}$, we obtained $U_l = 0.67$ eV (1); From 150 to 275°C, U_l varies from 0.74 to 0.67 eV, which corresponds, on curves $\log \sigma$ vs $1/T$, to an apparent activation enthalpy of 0.99 eV (1), whereas Mariani and colleagues (5) obtain a fixed value of 0.87 eV; the value of U_l for $t < 150^\circ\text{C}$ was not determined but transformation being continuous, it can be estimated at 0.74 eV. Finally the calculated value, which is 0.75 eV, agrees well with the different experimental values which range from 0.67 to 0.87 eV. In the case of U_i no experimental value exists; Mariani (6) estimates it higher than 1.4 eV at low temperature, which agrees with our value.

In conclusion, the method we use enables migration enthalpies of defects in nitrates to be calculated. But as the properties of these salts (polarizability, dielectric constant, repulsion strength, etc.) are not known very well, it is not possible at the moment to calculate the values of these enthalpies in each temperature field and to effect a prediction *a priori* of the transport properties of electric current in these salts.

Nevertheless, this method is altogether general. It can be applied in particular to cubic crystals

such as those of alkali halides. Their structure, less complicated than that of NaNO_3 and their better known physical properties allow a greater number of interactions to be taken into account, such as repulsion between second nearest neighbors or elasticity phenomena.

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