

Estimation of the migration enthalpy and entropy for cation vacancy motion in alkali halides with the NaCl-type structure

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A method is proposed for estimating the free energy of cation vacancy migration in alkali halides with NaCl structure from macroscopic parameters. It is based on the calculation of the electrical and the dilatation work during the migration of the cation. The dilatation work can be calculated from the elastic constants and the migration volume corresponding to free-cation motion. By considering anharmonic effects the free energy is calculated as function of temperature. In the high-temperature region the temperature-independent part of the migration free energy and its temperature derivative give values which agree with the published values of the migration enthalpy and entropy.

I. INTRODUCTION

The defect properties in sodium and potassium halides, among the other alkali halides, are the best understood. As for their conductivity mechanism, it is certain that the free-cation vacancies have a higher mobility than the anion vacancies. By dc conductivity or diffusion techniques the free migration energy g_m^+ required for the free-cation motion can be determined with reasonable accuracy. On the other hand the theoretical calculation of g_m^+ is still an open question. In this paper we attempt an estimation of the migration enthalpy h_m^+ and migration entropy s_m^+ in the case of sodium and potassium halides, using only macroscopic parameters such as elastic constants and the migration volume ΔV_m^{1-4} . This has been done in cesium halides for room temperature with satisfactory results.⁵ (In the following we will drop the superscript and the subscript in the symbols g_m^+ , h_m^+ , and s_m^+ .)

NaCl structure suggests that a vacancy G should be filled by the migration of the cation E (Fig. 1). Cation E during its route EKG passes through saddle points X and X' which are the centers of the equilateral triangles AHF or HCF , respectively.⁶ Thus the migration free energy g for the cation vacancy migration process should be equal to the difference in the energy of the cation at places X and E . This energy difference can be divided as follows:

$$g = g_1 + g_2, \tag{1}$$

where g_1, g_2 are the electrical and dilatation work (static deformation contribution), respectively. The change in the vibration spectrum (vibration contribution) gives a third term $kT \sum_i \ln(\omega_i/\omega'_i)$, where ω_i , respectively, ω'_i , are the phonon frequencies at the equilibrium position, respectively, saddle point. We will come back to this contribu-

tion later.

The first term can be calculated from the relation

$$g_1 = (1/\epsilon)(\alpha_X - \alpha_E)e^2/l, \tag{2}$$

where $l = EH$ is the nearest-neighbor cation-anion distance and ϵ is the dielectric constant. α_E is the usual Madelung constant for the ion at E minus the term due to the vacancy at G , i.e., $+1.748 + 1/\sqrt{2} = +2.455$, while α_X is the Madelung constant for the ion at X (for a perfect crystal) minus the contribution of the vacancies at E and G . The Madelung constant for the ion at X can be calculated with the method of neutral cubes⁷ which gives

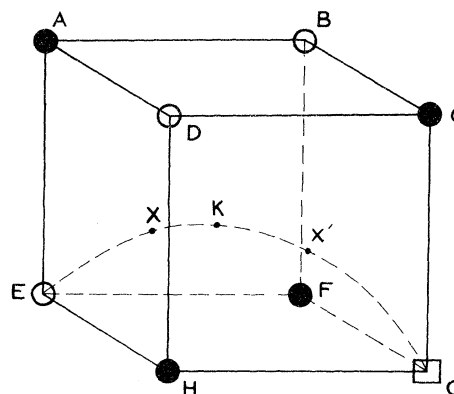


FIG. 1. Cation E during its motion $E \rightarrow G$ passes through the saddle points X and X' (the centers of the equilateral triangles AHF and CHF).

-0.1798. Hence

$$\alpha_X = -0.1798 + 3/\sqrt{3} + 1/1 = 2.552.$$

The second term g_2 can be expressed⁸ as follows:

$$g_2 = \frac{1}{2} B \delta^2 \mathfrak{V}, \quad (3)$$

where B is the bulk modulus $\frac{1}{3}(C_{11} + 2C_{12})$ of the crystal, \mathfrak{V} the local volume undergoing a strain during migration of the cation and δ its local volume dilatation, i.e., the ratio of the migration volume $\Delta V_m \equiv (\partial g / \partial P)_T$ to the volume \mathfrak{V} . Although Eq. (3) is valid only in the small-strain approximation it is used because of the great difficulties in using higher terms. The method presented in this paper is based on the assumption that $\mathfrak{V} = \mathfrak{V}_\alpha$, where \mathfrak{V}_α is the volume per atom.

II. $g(0)$ AT ABSOLUTE ZERO (ENTHALPY)

We apply the above method to NaCl at $T=0$. Inserting in Eq. (2) $\epsilon = \epsilon_\infty = 2.25$ and $l_0 = 2.79 \text{ \AA}$ we obtain $g_1(0) = 0.22 \text{ eV}$. $g_2(0)$ can be calculated from Eq. (3), using the values $B_0 = 0.273 \times 10^{12} \text{ erg/cm}^3$ and $\mathfrak{V}_\alpha = l_0^3$. For δ we insert 0.52 which is the ratio of the experimental value⁴ $\Delta V_m = 7 \text{ cm}^3/\text{mole}$ to the volume $\frac{27}{2} \text{ cm}^3$, taking 27 cm^3 as the molar volume. We thus find $g_2(0) = 0.50 \text{ eV}$ and hence $g(0) = 0.22 + 0.50 = 0.72 \text{ eV}$. If the dielectric constant were taken as $\epsilon_s = 5.25$ we would obtain alternatively $g(0) = 0.60 \text{ eV}$.

The same method has been applied to other sodium or potassium halides and the results are

given in the first column of Table I. The values of ΔV_m , and thus δ have been experimentally determined^{9,10} but some of these results were questioned in later publications.^{4,11} In the following we use the value $\delta = 0.52$ as the most probable for all alkali halides of NaCl structure.

III. TEMPERATURE VARIATION OF g

Equation (1) permits the evaluation of g for any temperature. At $T=0$ it gives

$$g(0) = (1/\epsilon_{\infty,0})(\alpha_X - \alpha_E)e^2/l_0 + cB_0\mathfrak{V}_0, \quad (4)$$

where $c \equiv \frac{1}{2}\delta^2$ is assumed independent of temperature. By substituting the value of c , obtained from Eq. (4), into Eq. (3), Eq. (1) gives

$$g = (1/\epsilon_\infty)(\alpha_X - \alpha_E)e^2/l + [g(0) - (1/\epsilon_{\infty,0})(\alpha_X - \alpha_E)e^2/l_0](B_0\mathfrak{V}_0)^{-1}B\mathfrak{V}. \quad (5)$$

l and \mathfrak{V} can be expressed from the volume expansion coefficient β . By definition we have

$$\beta = \frac{1}{\mathfrak{V}} \frac{d\mathfrak{V}}{dT} \quad \text{and} \quad \frac{1}{3}\beta = \frac{1}{l} \frac{dl}{dT},$$

which give

$$\mathfrak{V} = \mathfrak{V}_0 \exp\left(\int_0^T \beta dT\right) \quad (6)$$

and

TABLE I. Values of the migration energy, enthalpy, and entropy for different sodium and potassium halides.

	1	2	3	4	5
	$g(0)$ (eV)	$g(0) B_0/B_0$ (eV)	h_{exp} (eV)	s/k	s_{exp}/k
NaF	0.88	0.90	0.87 ^a		...
NaCl	0.72	0.74	0.72, ^b 0.715, ^c 0.65 ^d	2.50	2.07 ^b , 3.3 ^c
NaBr	0.65	0.66	0.62 ^a
NaI	0.59	0.60	0.57 ^e
KF	0.83	0.85	0.84, ^f 0.83 ^f
KCl	0.73	0.75	0.73, ^g 0.75, ^c 0.665-0.676 ^h	2.31	1.90, ^c 2.62-2.65 ^h
KBr	0.67	0.68	0.70, ^k 0.65 ^l	2	1.9 ^b , 1.28 ^k
KI	0.63	0.64	0.63, ^m 0.758 ^c	1.7	1.66 ^c , 1.58 ^m

^aJ. S. Dryden and R. J. Meakins, *Discuss. Faraday Soc.* 23, 39 (1957).

^bF. B  ni  re, M. B  ni  re, and M. Chemla *J. Phys. Chem. Solids* 31, 1205 (1970).

^cC. Naddler and J. Rossel, *Phys. Status Solidi A* 18, 711 (1973).

^dA. R. Allnatt, P. Pantelis, and S. J. Sime *J. Phys. C* 4, 1778 (1971).

^eD. Kostopoulos, P. Varotsos, and S. Mourikis, *Can. J. Phys.* 53, 1318 (1975).

^fI. M. Hoodless, J. H. Strange, and L. E. Wylde *J. Phys. (Paris) Suppl.* 11-12, C9-21 (1973).

^gM. Chemla and F. B  ni  re, *J. Phys. (Paris)* 34, 11 (1973).

^hP. W. M. Jacobs and P. Pantelis *Phys. Rev. B* 4, 3757 (1971).

^kN. Brown and P. W. M. Jacobs, *J. Phys. (Paris)* C9, 445 (1973).

^lS. Chandra and J. Rolfe *Can. J. Phys.* 49, 2098 (1971).

^mS. Chandra and J. Rolfe *Can. J. Phys.* 48, 397 (1970).

$$l = l_0 \exp\left(\int_0^T \frac{1}{3} \beta dT\right). \quad (7)$$

The combination of Eqs. (5)–(7) gives

$$g = g(0) \frac{B}{B_0} \exp\left(\int_0^T \beta dT\right) + \frac{1}{\epsilon_\infty} (\alpha_X - \alpha_E) \frac{e^2}{l_0} \exp^{-1}\left(\int_0^T \frac{1}{3} \beta dT\right) - \frac{1}{\epsilon_{\infty,0}} (\alpha_X - \alpha_E) \frac{e^2}{l_0} \frac{B}{B_0} \exp\left(\int_0^T \beta dT\right). \quad (8)$$

As the temperature variation of B , β , and ϵ_∞ is experimentally known,¹²⁻¹⁴ we can calculate g for any temperature from $g(0)$. Figure 2 shows the temperature dependence of g for KCl, NaCl, and KBr. The curves for the other alkali halides are similar.

Figure 2 shows that g at high temperatures is a linear function of T which can be written

$$g = g'(0) - sT, \quad (9)$$

where $g'(0)$ represents the intercept of the vertical axis with the extension of the straight line of Fig. 2. It is easy to obtain an analytical expression of $g'(0)$ from the fact that B is a linear function of T at high temperatures¹⁵ and can be written $B = B'_0 - bT$, where B'_0 represents the intercept of the linear extension of B . Inserting this expression into Eq. (8) and setting $T=0$ we get

$$g'(0) = g(0)B'_0/B_0 + g_1(0)(1 - B'_0/B_0).$$

As $g(0)$, respectively, $g_1(0)$, is of the order of 0.7 eV, respectively, 0.2 eV, and the ratio B'_0/B_0 is of the order of 1.03, the second term can be disregarded thus giving

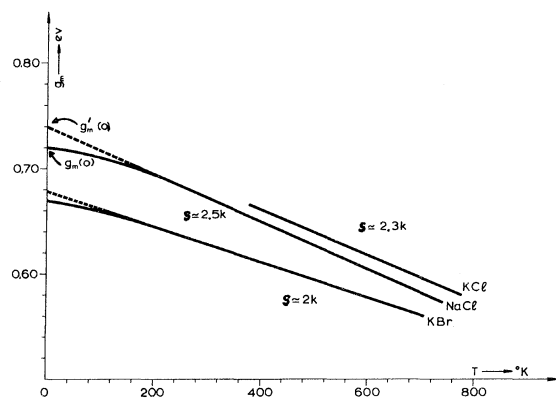


FIG. 2. Temperature variation of the migration free energy for KCl, NaCl, and KBr.

$$g'(0) = g(0)B'_0/B_0. \quad (10)$$

A combination of Eqs. (9) and (10) gives for g at high temperatures

$$g = g(0)B'_0/B_0 - sT. \quad (11)$$

IV. DISCUSSION

In the extrinsic region of the conductivity experiments, σT is proportional to the factor $\exp(-g/KT)$.

Thus we have

$$\sigma T = (4ne^2 l^2 \nu / k) \exp(-g/kT), \quad (12)$$

where ν is taken arbitrarily as the Debye frequency. A similar expression holds for the diffusion coefficient. A combination of (11) and (12) gives

$$\sigma T = (4ne^2 l^2 \nu / k) \exp(s/k) \exp[g(0)B'_0/kTB_0]. \quad (13)$$

Until now experimental investigators, using Eq. (12), plotted the function σT vs $1/T$ and determined h from the slope assuming that it is independent of T . They then determined the migrational entropy from the intercept of the vertical axis. The published values determined in this way will receive the subscript exp.

Equation (13) clearly shows that the experimentally measured slope of the curves $\ln(\sigma T) = f(1/T)$ gives $g(0)B'_0/B_0$. In column 2 of Table I we give the calculated values of $g(0)B'_0/B_0$ and in column 3 the most recent experimental values of h_{exp} . They agree within a few percent. However we recall that if we use for the calculation of $g(0)$ the ϵ_s value instead of ϵ_∞ the differences exceed 10%. A large number of older experimental¹⁶ values are not suitable for the comparison as they scatter within an extended range for each material.

Equation (13) further shows that the intercept of the vertical axis in the graph of $\ln(\sigma T)$ vs $1/T$ gives information on the value of s which should be equal to s_{exp} . The values of s at high temperatures are found by solving Eq. (8) graphically and determining its slope according to Eq. (11). The results are listed in column 4. In column 5 we give the most recent values of s_{exp}/k . We notice that they agree reasonably with s/k . If the s_{exp} values were found larger than s it would mean that Eq. (1) should have an important third term due to vibrational entropy. The agreement between s_{exp} and s shows that it is unimportant. To the best of our knowledge its theoretical evaluation has not been attempted.

Although the assumptions upon which the present calculation is based are undoubtedly crude approximations to the real situation, the results agree sufficiently with the experimental values, so as to justify their presentation.

Note added in proof. At very high temperatures (higher than those of Fig. 2), Eq. (8) shows that both h and s depend on T .

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¹M. Beyeler and D. Lazarus, *Z. Naturforsch.* A 26, 291 (1971).

²D. N. Yoon and D. Lazarus, *Phys. Rev. B* 5, 4935 (1972).

³C. B. Pearce, *Phys. Rev.* 123, 253 (1960).

⁴G. Martin, D. Lazarus, and J. L. Mitchell, *Phys. Rev. B* 8, 1726 (1973).

⁵P. Varotsos, K. Alexopoulos, and F. Bénéière, *Phys. Rev. B* 12, 4403 (1975).

⁶J. S. Dryden and R. J. Meakins, *Discuss. Faraday Soc.* 23, 39 (1957).

⁷C. Kittel, *Introduction to Solid State Physics*, 4th ed. (Academic, New York, 1971), p. 117.

⁸Reference 7, p. 142.

⁹M. Beyeler (private communication).

¹⁰D. L. Lazarus, D. N. Yoon, and R. N. Jeffrey, *Z. Naturforsch.* A 26, 56 (1971).

¹¹D. Lazarus and J. L. Mitchell, *J. Phys. (Paris)* 34, C9-37 (1973).

¹²*Point Defects in Solids*, edited by J. H. Crawford and L. M. Slifkin (Plenum, New York, 1972), pp. 506-507.

¹³K. K. Srivastava and H. D. Merchant, *J. Phys. Chem. Solids* 34, 2069 (1973).

¹⁴S. Haussühl, *Z. Phys.* 159, 223 (1960).

¹⁵H. B. Huntington, *The Elastic Constants of Crystals in Solid State Reprints* (Academic, New York, 1958), pp. 117, 110, 65, 64.

¹⁶*Point Defects in Solids*, edited by J. H. Crawford and L. M. Slifkin (Plenum, New York, 1972), pp. 76, 135, 139.