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A COMPARISON OF THE MIGRATION ENTROPY FOR THE CATION
AND THE ANION VACANCY MOTION IN ALKALI HALIDES
WITH NaCl AND CsCl TYPE STRUCTURE

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Résumé. — Les entropies de migration de lacunes cationiques et anioniques dans les halogénures alcalins ont été calculées en fonction de paramètres macroscopiques (comme le module de compression et le coefficient de dilatation) et de l'enthalpie correspondante de migration au zéro absolu. En conclusion, dans le cas d'une structure NaCl, l'entropie de migration est plus grande pour le cation que pour l'anion. Dans le cas d'une structure CsCl l'inverse est valable.

Abstract. — The entropy for the migration of a cation and an anion vacancy in alkali halides has been calculated through macroscopic parameters (such as bulk modulus and the volume expansion coefficient) and the corresponding enthalpy of motion at absolute zero. It is concluded that in the case of a NaCl structure the cation migration entropy is greater than that for an anion vacancy motion. On the other hand in the case of a CsCl structure the opposite holds.

The entropy values S_m^+ and S_m^- for cation and anion vacancy motion respectively in alkali halides are obtained experimentally from conductivity or diffusion experiments. As for their values, in recent years, a general agreement between various workers has been obtained due to the high accuracy (and the various precautions) of the recent measurements. Thus in a rough approximation we can say that in the case of an alkali halide with NaCl structure S_m^+ lies between $1k$ and $2k$ whereas S_m^- has been found to be greater than $2k$ i.e. $S_m^- = 2k - 4k$ (Table I). However we recall that both S_m^+ and S_m^- values have been derived under the following assumption : [1, 2].

The pre-exponential frequency factor appearing

in the mobilities of both cation and anion vacancy is arbitrarily set equal to the Debye frequency ν_D of the host material. Although the selection of ν_D is arbitrary and may displace both S_m^+ and S_m^- to higher or lower values, it is fairly sure [1] that the inequality $S_m^+ < S_m^-$ will be unchanged.

The scope of this paper is to discuss on theoretical grounds the relation $S_m^+ < S_m^-$ (which is valid only in the case of a NaCl structure) and to find whether in some materials this inequality must be reversed. The present treatment is based on a recently proposed method [3] for the calculation of the free energy g_m^+ for a cation vacancy migration.

In an alkali halide crystal with NaCl structure g_m^+ can be expressed as follows [3] :

TABLE I			
Crystal	S_m^+ in k units	S_m^- in k units	References
—	—	—	—
NaCl	2-3	1.5-4.4	[1]
	1.75	2.2	[8]
	1.64	1.38	[7]
KCl	1.8	4.2-6.3	[1]
	2.88	4.34	[8]
	2.40	3.20	[7]
KBr	1.7	3.7	[1]
	2.54	3.95	[8]

$$g_m^+ = \frac{A}{l} + cB\Omega$$

(1)

where

- (i) l is the nearest cation-anion distance.
- (ii) Ω is the volume per atom.
- (iii) $A = (\alpha_X - \alpha_E) e^2/\epsilon_\infty$ where α_X , α_E are the Madelung constants of a normal lattice site X and at the saddle point E respectively and ϵ_∞ the dielectric constant for high frequencies. Although ϵ_∞ depends [4] on temperature, in the following we suppose that A does not depend on temperature T .

(iv) c is a dilatation factor which is approximately equal to $1/8$ (The exact value of c is not indispensable for the arguments of the present paper).

(v) B is the local bulk modulus which is taken equal to the macroscopic bulk modulus.

Eq. (1) at $T = 0$ gives :

$$h_{m,0}^+ = \frac{A}{l_0} + cB_0 \Omega_0 \quad (2)$$

where l_0 , B_0 , Ω_0 are the corresponding values at $T = 0$ and $h_{m,0}^+$ is the migration enthalpy, also at absolute zero.

By substituting the value of c obtained from eq. (2) into eq. (1) we get :

$$g_m^+ = \frac{A}{l} + \frac{(h_{m,0}^+ l_0 - A) B \Omega}{l_0 B_0 \Omega_0} \quad (3)$$

Thus the migration entropy S_m^+ is given by :

$$S_m^+ = - \left(\frac{dg_m^+}{dT} \right)_P = \frac{A\beta}{3 l_0 b^{1/3}} - \frac{(h_{m,0}^+ l_0 - A)}{l_0 B_0} \times \frac{d(Bb)}{dT} \quad (4)$$

where

$$b = \Omega/\Omega_0 = \exp \int_0^T \beta dT,$$

β is the volume expansion coefficient.

By combining eqs. (3) and (4) we find the migration enthalpy

$$h_m^+ = g_m^+ + Ts_m^+$$

expressed by the macroscopic parameters B and β and the migration enthalpy $h_{m,0}^+$ at $T = 0$.

It is clear that similar considerations hold for an anion vacancy motion; thus the entropy S_m^- for the migration of an anion is given by the following equation which is analogous to eq. (4) :

$$S_m^- = \frac{A\beta}{3 l_0 b^{1/3}} - \frac{(h_{m,0}^- l_0 - A)}{l_0 B_0} \times \frac{d(Bb)}{dT} \quad (5)$$

Eqs. (4) and (5) give the migration entropies S_m^+ , S_m^- through the macroscopic parameters B and β (which are experimentally well known) and the migrational enthalpies $h_{m,0}^+$ and $h_{m,0}^-$.

In alkali halides with NaCl structure $h_{m,0}^+ < h_{m,0}^-$ (since we know that the experimental migration enthalpy for an anion is greater than that for a cation, and setting $h_{m, \text{exper}} \simeq h_{m,0}$).

By comparing eqs. (4) and (5) and keeping in mind [6] that $d(Bb)/dT < 0$ (for the temperature at which the usual conductivity and diffusion experiments have been made) we conclude that $S_m^+ < S_m^-$ as the experiments showed.

On the other hand in alkali halides with CsCl structure (and at temperatures in which they have not been transformed into NaCl type structure) we know that $h_{m,0}^+ > h_{m,0}^-$; thus a similar comparison of eqs. (4) and (5) gives $S_m^+ > S_m^-$.

The later result has not been well confirmed experimentally and experiments in this direction would be extremely interesting.

We add a last remark. In both eqs. (4) and (5) we have disregarded a term

$$S_{\text{vibrational}} = k \sum_i \ln \frac{\omega_i^{(2)}}{\omega_i^{(1)}},$$

where $\omega_i^{(2)}$ and $\omega_i^{(1)}$ are the frequencies of the neighbouring ions where the moving ion is at saddle point and its normal lattice site respectively. It seems probable that this term (which might have different values for a cation or an anion motion) is small as we have found [3] that the entropy values, given by differentiating eq. (3) (which must contain a term

$$- kT \sum_i \ln \frac{\omega_i^{(2)}}{\omega_i^{(1)}}),$$

are in satisfactory agreement with experimental results. Thus the addition of such a term to eqs. (4) and (5) does not change the above considerations for the comparison of the entropies S_m^+ and S_m^- .

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