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Equilibrium Concentration of Vacancy Pairs in Ionic Crystals

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The thermal equilibrium concentration of associated vacancy pairs in ionic crystals is calculated, taking into account the Coulomb interaction between vacancies, the entropy difference between dissociated and associated vacancy pairs, and the temperature dependence of some thermodynamic functions. Contrary to previous theoretical estimates, a formula is obtained which is consistent with the low degree of association indicated by experiments.

VACANCIES in ionic crystals are surrounded by an electrical field which favors the formation of associated vacancy pairs, i.e., pairs of positive and negative vacancies at immediately neighboring lattice sites. The degree of association has been estimated by various authors,[1–7] with the result that purely theoretical estimates predict a much larger association than is compatible with the observed coefficients of diffusion and of electrical conductivity. It is the purpose of this paper to investigate possible causes of this discrepancy, in particular the effect of Coulomb interactions between vacancies and of certain approximations in the thermodynamic formulas used in earlier studies.[1,2] As in the similar work of Lidiard,[8] the Coulomb interactions are handled by means of the Debye-Hückel theory of strong electrolytes,[9] but interaction terms in the polarization energy which were neglected by Lidiard are shown to be dominant.

THERMODYNAMIC FUNCTIONS OF A SYSTEM OF DISSOCIATED AND ASSOCIATED VACANCY PAIRS

(a) Total Energy of a System of Vacancies

The total energy of a system of vacancies can be written

$$E=n_d[W^{(0)}+W^{(1)}(n_d)]+n_a(W^{(0)}-V^{(0)})-U(n_d), \qquad (1)$$

where n_d and n_a are the numbers of dissociated and associated vacancy pairs, $W^{(0)}$ is the work required for forming an isolated ($n_d\rightarrow 0$) dissociated vacancy pair, $W^{(1)}(n_d)$ is the change of $W^{(0)}$ caused by the other vacancies, $V^{(0)}$ is the dissociation energy of an isolated associated pair,[10] and $U(n_d)$ is the remaining electrostatic energy of the whole system. $W^{(1)}(n_d)$ and $U(n_d)$ will be calculated by means of the Debye-Hückel theory.

(b) Summary of the Debye-Hückel Theory

We consider a system of n_d positive and n_d negative units with charge $\pm e$, embedded in a medium of dielectric constant ϵ, and having enough mobility to establish thermal equilibrium. These conditions are satisfied by a system of vacancies in an ionic crystal of sufficiently high temperature.

The electrostatic potential at a distance r from any unit is the sum of two contributions[11]:

$$\Psi(r)=\Psi_1(r)+\Psi_2(r)=\frac{e}{\epsilon r}-\frac{e}{\epsilon r}[1-\exp(-\kappa r)]$$
$$=\frac{e}{\epsilon r}\exp(-\kappa r), \qquad (2)$$

where $\Psi_1(r)$ is the Coulomb potential of a point charge and $\Psi_2(r)$ is contributed in the time average by the surrounding vacancy cloud of opposite sign. The net result is equivalent to an effective potential with cutoff, the range being determined by the shielding constant κ. In first approximation, κ is a simple function of n_d and the temperature T:

$$\kappa=\left(\frac{8\pi e^2 n_d}{\epsilon kT}\right)^{\frac{1}{2}}\simeq 10^{-1}\left(\frac{n_d}{T}\right)^{\frac{1}{2}}\ \text{cm}^{-1}\quad\text{if}\quad \epsilon\simeq 5. \qquad (3)$$

The electrostatic field $F(r)$, which is the derivative of the potential function with respect to r, is given by

$$|F(r)|=\frac{e}{\epsilon r^2}(1+\kappa r)\exp(-\kappa r). \qquad (4)$$

(c) Calculation of $W^{(1)}(n_d)$ and $U(n_d)$

The total energy of vacancy formation $W=W^{(0)}+W^{(1)}(n_d)$ can be represented as the sum of 2 contributions[1]:

$$W=W_L^{(0)}-\tfrac{1}{2}e\Phi(n_d), \qquad (5)$$

where $W_L^{(0)}$ is the lattice energy per ion pair and $\frac{1}{2}e\Phi(n_d)$ is the potential energy of a dissociated vacancy pair in the field produced by its polarized neighborhood.

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[1] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1940), p. 42.

[2] A. Seeger, *Handbuch der Physik* (Springer-Verlag, Berlin, 1955), Vol. 7, Part 1, p. 401.

[3] R. G. Breckenridge, J. Chem. Phys. **16**, 959 (1948).

[4] Mapother, Crooks, and Maurer, J. Chem. Phys. **18**, 1231 (1950).

[5] J. F. Aschner, Phys. Rev. **94**, 771 (A) (1954).

[6] H. W. Schamp, Jr., and E. Katz, Phys. Rev. **94**, 828 (1954).

[7] H. Witt, Z. Physik **134**, 186 (1953).

[8] A. B. Lidiard, Phys. Rev. **94**, 29 (1954).

[9] P. Debye and E. Hückel, Physik Z. **24**, 185 (1923).

[10] It will be shown that the energy $(W^{(0)}-V^{(0)})$ of an associated pair is practically independent of the vacancy concentration.

[11] Throughout this paper we use the first approximation of Debye and Hückel which is perfectly valid for the high temperatures and low vacancy concentrations encountered with crystals in thermal equilibrium.

In the case of one vacancy only, $\Phi(n_d)$ is related to the polarization P by the following equations[1]:

$$\Phi(n_d)=\int_R^\infty \frac{P}{r^2}4\pi r^2 dr, \tag{6}$$

$$P=\frac{D-F}{4\pi}=\frac{e}{4\pi r^2}\left(1-\frac{1}{\epsilon}\right)(1+\kappa r)\exp(-\kappa r). \tag{7}$$

R is an adjustable parameter with the dimension of an ionic radius. The integral (6) can be evaluated and gives

$$\begin{aligned}\Phi(n_d)&=\left(1-\frac{1}{\epsilon}\right)\frac{e}{R}\exp(-\kappa R)\\ &=\Phi(0)\exp(-\kappa R)\simeq\Phi(0)(1-\kappa R).\end{aligned} \tag{8}$$

The factor $(1-\kappa R)$, which does not occur in earlier work, represents a reduction of the polarization energy caused by the Debye shielding effect. $\Phi(0)$ and R are different for sodium and chlorine vacancies. As we are interested mainly in the order of magnitude of the interaction effects, we shall use for numerical work averages of the values given by Mott and Gurney,[1] e.g.,

$$\tfrac{1}{2}e\Phi(0)\simeq 6\text{ ev},\quad R\simeq 1.8\text{ A}\quad\text{for NaCl.} \tag{9}$$

Thus

$$\begin{aligned}W^{(1)}(n_d)&=W-W_L^{(0)}+\tfrac{1}{2}e\Phi(0)\simeq\tfrac{1}{2}e\Phi(0)\kappa R\\ &\simeq 11\kappa\text{ ev}\quad\text{for NaCl.}\quad(\kappa\text{ in A}^{-1}).\end{aligned} \tag{10}$$

A similar shielding effect for associated vacancy pairs is negligibly small, as there is practically no vacancy cloud around a dipole which could reduce the polarization.

Concerning the electrostatic energy $U(n_d)$ of the whole system, one has to calculate the potential energy of a point charge in the field of all the other charges, which is equal to the interaction energy between that charge and its companion cloud of opposite sign. Hence,

$$|U(n_d)|=n_d e\Psi_2(0)=\frac{n_d e^2}{\epsilon r}[1-\exp(-\kappa r)]_{r\to 0}=n_d\frac{e^2\kappa}{\epsilon}. \tag{11}$$

The contribution of the associated pairs to the total electrostatic energy is negligible.

(d) Entropy of a System of Vacancy Pairs.

The entropy can be written

$$S=n_d[S_d^{(0)}+S^{(1)}(n_d)]+n_a S_a+S_U(n_d)+S_C(n_d,n_a), \tag{12}$$

where $S_d^{(0)}$ is the entropy change per isolated dissociated vacancy pair of the whole crystal, S_a is the entropy change per associated pair, $S^{(1)}(n_d)$ is the entropy change related to the interaction energy $W^{(1)}(n_d)$, $S_U(n_d)$ corresponds to the electrostatic energy $U(n_d)$, and $S_C(n_d,n_a)$ is the configuration entropy or entropy of mixing.

$S^{(1)}(n_d)$ and $S_U(n_d)$ can be found by solving the Gibbs-Helmholtz equations

$$G=H+T(\partial G/\partial T)_p,\quad S=-(\partial G/\partial T)_p, \tag{13}$$

if one substitutes for the enthalpy H the energies $W^{(1)}(n_d)$ or $U(n_d)$ which depend on the temepratue via the shielding constant κ.

The particular solution of the Eqs. (13) which satisfies the third law of thermodynamics gives

$$S_U(n_d)=-\frac{1}{3}\frac{U(n_d)}{T}, \tag{14}$$

$$S^{(1)}(n_d)=-\frac{1}{3}\frac{W^{(1)}(n_d)}{T}\simeq 3.6\frac{\kappa}{T}\text{ ev}^\circ\text{K}^{-1}\text{ for NaCl.} \tag{15}$$

The configuration entropy may be written as $k\ln P$, where P is the number of different distributions of n_d dissociated and n_a associated vacancy pairs over $2N$ sites. It is convenient to calculate P as a product $P_1\times P_2$, where P_1 is the number of different distributions, *without associated pairs*, of $(n_d+n_{a/2})$ positive and $(n_d+n_{a/2})$ negative units over N positive and N negative sites and P_2 is the number of different possibilities to add the n_a remaining units in such a way that they form pairs with the units already distributed in the first phase of the procedure. P_1 and P_2 depend on the number C of next neighbors to a regular lattice site, which is 6 in sodium chloride.

The calculation of P_1 and P_2 is closely related to the problem of placing m units into M boxes with g subdivisions such that there is only one unit in each box. The number of different solutions of this problem is

$$P'=g^m\frac{M!}{m!(M-m)!}. \tag{16}$$

For calculating P_1 put $g=C+1$, i.e., number of sites "occupied" by a unit if pair formation is excluded, $M=N/C+1$, $m=n_d+n_a/2$; for calculating P_2 put $g=C$, $M=n_d+n_{a/2}$, $m=n_{a/2}$. Furthermore, consider that the number of different arrangements for the positive and negative units is equal. Then

$$\begin{aligned}P=&\left\{\frac{(C+1)^{n_d+n_a/2}(N/C+1)!}{(n_d+n_a/2)![(N/C+1)-n_d-n_a/2]!}\right\}^2\\ &\times\left\{\frac{C^{n_a/2}(n_d+n_a/2)!}{(n_a/2)!n_d!}\right\},\end{aligned} \tag{17}$$

$$\begin{aligned}\ln P=&(2n_d+n_a)\ln(C+1)+n_a\ln(2C/n_a)\\ &+(2N/C+1)\ln(N/C+1)-2n_d\ln n_d\\ &-2[(N/C+1)-n_d-n_a/2]\\ &\times\ln[(N/C+1)-n_d-n_a/2].\end{aligned} \tag{18}$$

EQUILIBRIUM CONCENTRATION OF ASSOCIATED VACANCY PAIRS

The concentration of associated vacancy pairs can be obtained from the equilibrium conditions

$$\partial G/\partial n_d = \partial G/\partial n_a = 0, \tag{19}$$

where G is the Gibbs free energy $H-TS$. The difference between H and E can be neglected for the present purpose.

Using the formulas of the preceding section and neglecting terms which are of higher order than n_d/N, one finds

$$n_d = NB_d \exp\left(\frac{S^{(0)}}{2kT}\right) \exp\left(-\frac{W^{(0)}+\Delta(n_d)}{2kT}\right), \tag{20}$$

$$n_a = 2CB_a n_d \exp\left(\frac{2S_a - S_d^{(0)}}{2kT}\right) \times \exp\left(\frac{2V^{(0)} - W^{(0)} + \Delta(n_d)}{2kT}\right), \tag{21}$$

and

$$\Delta(n_d) = \frac{\kappa}{3}\left(e\Phi(0)R - \frac{2e^2}{\epsilon}\right) \simeq 5.3\kappa \text{ ev for NaCl} \quad (\kappa \text{ in A}^{-1}). \tag{22}$$

Equation (21) which determines the degree of association contains the following three terms which were neglected in previous analyses: (i) the energy term $\Delta(n_d)$ which takes into account the Coulomb interactions between vacancies, (ii) the entropy factor, and (iii) the factor B_a which does not arise from the thermodynamic functions of the preceding section but, according to Mott and Gurney, from the temperature dependence of $W^{(0)}$ and $V^{(0)}$.

If one neglects these extra terms and uses the value -0.12 ev for the difference $V^{(0)} - W^{(0)}/2$,[12] one obtains the result that the ratio n_a/n_d is unity at about 600°K and even larger at higher temperatures. All the experimental evidence disproves this theoretical prediction.

We shall now study whether inclusion of the neglected terms can improve the situation.

Values of the interaction energy $\Delta(n_d)$ for sodium chloride are listed in Table I. They are of the same order of magnitude as the difference $V^{(0)} - W^{(0)}/2$ but because of their positive sign they favor association and cannot improve the discrepancy between theory and experiment.

According to Mott and Gurney,[1] the term B_d is larger than one and may be as large as 100. The magnitude of B_a depends on whether the temperature dependence of $V^{(0)}$ is larger or smaller than that of $W^{(0)}/2$. If it is twice as large, then B_a may be as small as 1/100 and a substantial improvement of the theory could be achieved. Nothing prevents the acceptance of this solution but one has to realize that, at present, it is not supported by additional theoretical or experimental evidence.

TABLE I. The free energy of interaction $\Delta(n_d)$ between vacancies in sodium chloride.

T, °K	800	900	1000	1070
$\Delta(n_d)$, ev	0.035	0.074	0.130	0.133

The situation is similar with the entropy factor. The entropy change per dissociated vacancy pair of the whole crystal is[1]

$$S_d^{(0)} = k \sum_{i=1}^{6N} \ln(\nu_i/\nu_i'), \tag{23}$$

where the ν_i are the frequencies of the $6N$ normal vibrations of the crystal and the ν_i' the same lattice frequencies perturbed by a vacancy pair. Mott and Gurney[1] consider only 12 frequencies of this sum which are related to the next neighbors of the vacancy pair. With this approximation there should not be much difference between a dissociated and associated pair, and if there is any, then the difference $2S_a - S_d^{(0)}$ would be positive, as an associated pair should affect the next-neighbor frequencies more strongly than a dissociated pair. However, there is undoubtedly also a long-range effect of vacancies on the lattice frequencies. Because of the anharmonicity of the lattice forces, the Coulomb forces between a vacancy and the surrounding ions produce a dilated region in the neighborhood of a vacancy in which a great number of ions is situated. Hence, *all* the lattice frequencies are reduced by a vacancy and the combined effect of all these small frequency changes may be larger than the next-neighbor effect which, probably, has been overestimated by Mott and Gurney.[13] However, the long-distance effect is negligible for *associated* vacancy pairs because of the short range of the dipole field. Thus, if the long-distance effect is dominant for *dissociated* pairs, $S_a < S_d^{(0)}$ and $2S_a - S_d^{(0)}$ may well be negative. In this case, the entropy term in Eq. (22) may reduce the degree of association by a factor of the order of magnitude 0.1.

Summarizing, one can say that Eq. (21) is consistent with the small degree of association indicated by experiments. But the formula contains several unknown parameters which, at present, prevent a complete theoretical determination of pair association. This is equally true for association in "doped crystals" [8] and should be taken into account when interpreting the ionic conductivity of such crystals.

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[12] J. R. Reitz and J. L. Gammel, J. Chem. Phys. **19**, 894 (1951).

[13] Mott and Gurney assume that $\nu/\nu' \leqslant 2$. Actually, a vacancy reduces the force constant of a nearest neighbor at best to one-half its original value such that $\nu/\nu' \leqslant \sqrt{2}$; including Coulomb repulsion, one finds $\nu/\nu' \leqslant 1.2$.