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Space Charge in Ionic Crystals. I. General Approach with Application to NaCl†

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The defect distribution in an ionic crystal is calculated for both pure crystals and crystals containing divalent cationic impurities. By taking the electrostatic energy into account explicitly, it is shown that bulk electrical neutrality and space-charge regions surrounding the vacancy sources are an inherent aspect of thermal equilibrium. Interactions among defects of the opposite charge are taken into account using the nearest-neighbor-binding model. Inclusion of the long-range effects of the Coulomb interaction and the question of the sign of charged dislocations are discussed.

I. INTRODUCTION

IT was Frenkel[1] who first pointed out that pure ionic crystals in which Schottky disorder predominates should, in thermal equilibrium, possess a charged surface and a region of space charge of the opposite sign adjacent to the surface as a consequence of the fact that the free energies of formation of the anion and cation vacancies differ. Qualitatively the surface dipole region arises in the following manner: Suppose the free energy necessary to form a cation vacancy is less than that required to form an anion vacancy. Then, at any finite temperature, there will be a tendency to form an excess of cation vacancies resulting in a positively charged surface and a region of negative space charge beneath the surface. This charge distribution will retard the further formation of cation vacancies while enhancing the formation of anion vacancies. The result is that, in equilibrium, there will exist a dipole region at the surface across which there exists a potential difference which serves to change the innate free formation energies of the vacancies into effective free formation energies in such a way that the bulk of the crystal is electrically neutral if the crystal is sufficiently large.

Eshelby, Newey, Pratt, and Lidiard[2] noted that edge dislocations, being sources and sinks for vacancies, would also give rise to such charging effects, the analog of the surface charge being a charge on the dislocation line itself with the space charge distributed with cylindrical symmetry around the dislocation line.

When a crystal contains a small concentration of impurities which possess an absolute value of charge different from that of the host ions of the crystal, there also arises a space-charge region near the surface and around edge dislocations.[2] Consider a NaCl crystal containing divalent cations. At temperatures where the vacancy concentrations are essentially determined by the divalent cation concentration, the surface develops a negative charge and the space charge is positive. The resulting potential distribution serves to enhance the cation-vacancy concentration while reducing the anion-vacancy concentration with the result that electrical neutrality is again maintained in the bulk of the crystal.

In contrast to previous work on the problem, we show that electrical neutrality within the bulk of the crystal is a consequence of thermal equilibrium and need not be postulated to demonstrate the existence of the space-charge regions. Thus, the space-charge regions are an inherent aspect of thermal equilibrium.

We restrict our discussion in this paper to ionic crystals for which Schottky disorder predominates. The crystal model used in the calculations is presented in Sec. II. In Sec. III the general mathematical procedure is utilized to calculate the defect distribution in a pure crystal. Crystals containing divalent cationic impurities are discussed in Sec. IV where we have taken into account effects due to the association of impurities and cation vacancies using the nearest-neighbor-binding point of view. Inclusion of the long-range effects of the Coulomb interactions among defects is the subject of Sec. V. The physical nature of the space-charge formation is emphasized in the discussion of Sec. VI.

II. CRYSTAL MODEL

We restrict our discussion to crystals of the type M^+X^- with the NaCl structure for which the intrinsic disorder is of the Schottky type. For our calculations involving the surface region we consider an electrically neutral crystal having free (100) surfaces at $x=0$ and $x=2L$ and of infinite extent in the y and z directions so that the problem becomes one dimensional. We assume that the charged-defect distribution can be suitably smoothed so that the potential Φ arising from this distribution will satisfy Poisson's equation for a medium with static dielectric constant ϵ. The boundary conditions for the potential are

$$\Phi=0 \quad \text{at} \quad x=0 \quad \text{and} \quad x=2L, \tag{2.1}$$

and

$$d\Phi/dx=0 \quad \text{at} \quad x=L. \tag{2.2}$$

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[1] J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, New York, 1946), p. 36.

[2] J. Eshelby, C. Newey, P. Pratt, and A. Lidiard, Phil. Mag. 3, 75 (1958).

The physical nature of boundary condition (2.1) will be discussed later. Boundary condition (2.2) follows immediately from symmetry and expresses the fact that, since we demand that our entire crystal be neutral, each half will also be electrically neutral. Thus we need concern ourselves only with the section of crystal from $x=0$ to $x=L$.

In the case of the edge dislocations we assume that we have an edge dislocation density d with the dislocations regularly spaced and parallel in the crystal. Assuming the dislocation core radius to be b, the boundary conditions on Φ in a cylindrical coordinate system with the z axis along the dislocation line and r measured from the center of the core are

$$\Phi=0 \quad \text{at} \quad r=b, \tag{2.3}$$

and

$$d\Phi/dr=0 \quad \text{at} \quad r=R, \tag{2.4}$$

where

$$R=(\pi d)^{-1/2}. \tag{2.5}$$

Condition (2.4) expresses the fact that each dislocation and the region surrounding it out to a radius R comprise an electrically neutral system. Condition (2.3) will be discussed later.

We further assume that we are always in a state of thermal equilibrium. That is, the defects all have mobilities sufficiently high that the state predicted by a minimization of the free energy can be attained. At low temperatures such an assumption is of dubious validity and we will comment further on this later.

In addition, we consider the pressure to be zero such that the equilibrium state will be given by a minimization of the Helmholtz free energy F

$$F=U-TS, \tag{2.6}$$

where U is the internal energy of the crystal, T is the absolute temperature, and S is the entropy.

III. SPACE-CHARGE DISTRIBUTION FOR A PURE CRYSTAL

For the case of a pure crystal, electrical neutrality of the system means we have equal numbers of anions and cations. Since we are considering the case of Schottky disorder, there are three types of defects which arise. These are anion vacancies, cation vacancies, and bound vacancy pairs. The pairs arise from the Coulomb attraction between the cation vacancies with virtual charge $-e$ (e is the absolute value of the electronic charge) and the anion vacancies with virtual charge e. As a model for this interaction we consider the pairs to have a binding energy B when they are nearest neighbors in the lattice and no binding energy otherwise. This model ignores the long-range effects of the Coulomb interaction and this deficiency will be discussed later. A vacancy pair, being neutral, does not contribute to the charge density. Since we will neglect all interactions involving dipoles, vacancies forming pairs are essentially eliminated from further consideration. We retain the pairs in the theory as a prototype of important such pairings to be discussed later.

The free energy per unit area of the half of the disordered crystal we are considering, to within an additive quantity depending only on the temperature, is

$$F=\int_0^L dx[n_+(x)F^+ + n_-(x)F^- + n_B(x) \times\{F^+ + F^- - B\} + \tfrac{1}{2}\rho(x)\Phi(x)] - TS_c, \tag{3.1}$$

where $n_+(x)$ is the density of cation vacancies at x, $n_-(x)$ is the density of anion vacancies at x, $n_B(x)$ is the density of bound vacancy pairs at x, and S_c is the configurational entropy. The charge density $\rho(x)$ is given by

$$\rho(x)=e\{n_-(x)-n_+(x)\} \tag{3.2}$$

and $\Phi(x)$, the electrostatic potential, is to be determined from Poisson's equation

$$\nabla^2\Phi(x)=d^2\Phi(x)/dx^2=-4\pi\rho(x)/\epsilon, \tag{3.3}$$

where ϵ is the static dielectric constant.

The quantities F^+ and F^- are the free energies of formation of the cation and anion vacancies and include the change in vibrational entropy of the crystal because of the presence of the defect. In the same sense B should also be considered to be a free energy including the binding energy of the defects together with an entropy term arising from the modification of the vibrational spectrum due to the presence of the pair. We assume the quantities F^+, F^-, and B are independent of x, an assumption that will be discussed later.

We now make a variation of F with respect to the three independent quantities, $n_+(x)$, $n_-(x)$, and $n_B(x)$. Thus

$$\delta F=\int_0^L dx[\delta n_+(x)F^+ + \delta n_-(x)F^- + \delta n_B(x) \times\{F^+ + F^- - B\} + \tfrac{1}{2}\delta\{\rho(x)\Phi(x)\}] - T\delta S_c. \tag{3.4}$$

The variation of the term involving $\rho(x)\Phi(x)$ is discussed in Appendix A and δS_c is evaluated in Appendix B. Using Eq. (B5) of Appendix B and the results of Appendix A, Eq. (3.4) becomes

$$\delta F=\int_0^L dx\Bigg[\delta n_+(x)\left\{F^+ - e\Phi(x) - kT\ln\left[\frac{N-n_+(x)-n_B(x)}{n_+(x)}\right]\right\} + \delta n_-(x)\left\{F^- + e\Phi(x) - kT\ln\left[\frac{N-n_-(x)-n_B(x)}{n_-(x)}\right]\right\}$$
$$+\delta n_B(x)\left\{F^+ + F^- - B - kT\ln\left[\frac{z_n(N-n_-(x)-n_B(x))(N-n_+(x)-n_B(x))}{(N-n_B(x))n_B(x)}\right]\right\}\Bigg], \tag{3.5}$$

where N is the density of anion or cation sites in the crystal, z_n is the number of nearest unlike neighbors of an ion, and k is Boltzmann's constant. Since there exist no restrictions on the quantities varied, the conditions for a minimum of free energy are that the coefficients of δn_+, δn_-, and δn_B in (3.5) must all vanish. Assuming n_+/N, n_-/N, and n_B/N are much less than one, these conditions become

$$\begin{aligned} n_+(x) &= N\exp\{-(F^+ - e\Phi(x))/kT\}, \\ n_-(x) &= N\exp\{-(F^- + e\Phi(x))/kT\}, \\ n_B(x) &= Nz_n\exp\{-(F^+ + F^- - B)/kT\}. \end{aligned} \tag{3.6}$$

Using Eqs. (3.2), (3.3), and (3.6), we have

$$\frac{d^2\Phi}{dx^2} = -\frac{4\pi eN}{\epsilon}\left[\exp\left\{-\frac{F^- + e\Phi}{kT}\right\} - \exp\left\{-\frac{F^+ - e\Phi}{kT}\right\}\right]. \tag{3.7}$$

Let us now define Φ_∞ as that potential which makes the right-hand side of (3.7), that is ρ, equal to zero. Thus

$$e\Phi_\infty = \tfrac{1}{2}(F^+ - F^-). \tag{3.8}$$

We attach no physical significance to Φ_∞ at this point. If we now define

$$z(x) \equiv \{e\Phi(x) - e\Phi_\infty\}/kT, \tag{3.9}$$

$$\kappa^2 \equiv \frac{8\pi Ne^2}{\epsilon kT}\exp\{(e\Phi_\infty - F^+)/kT\}, \tag{3.10}$$

and

$$s \equiv \kappa x, \tag{3.11}$$

Eq. (3.7) can be rewritten as

$$d^2z/ds^2 = \sinh z. \tag{3.12}$$

The solution to this equation, using boundary condition (2.2), is[3]

$$\kappa L = kF\left(\sin^{-1}\left\{\frac{\cosh z_0 - \cosh z_L}{\cosh z_0 - 1}\right\}^{1/2}, k\right), \tag{3.13}$$

where $F(\Phi,k)$ is the elliptic integral of the first kind,

$$k = \left(\frac{2}{\cosh z_L + 1}\right)^{1/2}, \tag{3.14}$$

$$z_0 \equiv z|_{x=0} = -e\Phi_\infty/kT, \tag{3.15}$$

and

$$z_L \equiv z|_{x=L} = \{e\Phi(L) - e\Phi_\infty\}/kT. \tag{3.16}$$

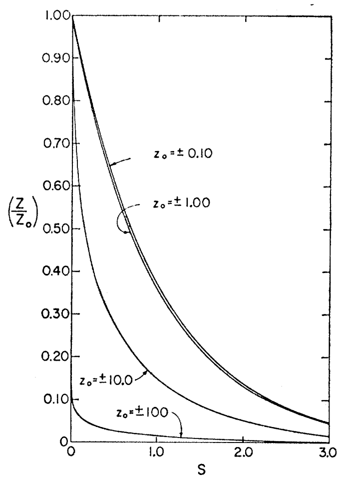

FIG. 1. z/z_0 as a function of s with $z = 4\times\tanh^{-1}\{e^{-s}\tanh(z_0/4)\}$.

Let us consider for illustration a NaCl crystal with $L = 1$ cm at 500°K. Using for F^+ and F^- the values[4]

$$\begin{aligned} F^+ &= 0.80\text{ eV} - 3.1kT, \\ F^- &= 1.32\text{ eV} - 3.1kT, \end{aligned} \tag{3.17}$$

together with[5]

$$\begin{aligned} N &= 2.25\times 10^{22}/\text{cm}^3, \\ \epsilon &= 5.62, \end{aligned} \tag{3.18}$$

we find $\kappa L = 1.22\times 10^4$. From (3.13) this then means that $\cosh z_L = 1 + u$ with $u \ll 1$. Since $\cosh z_L \simeq 1$, $z_L \simeq 0$, and $\Phi(L) \cong \Phi_\infty$. Since Φ_∞ was defined as the potential for which $\rho = 0$, we see that *the state of thermal equilibrium includes electrical neutrality within the bulk of the crystal as long as* $\kappa L \gg 1$, and we need not postulate this condition initially as has been done in the past.

As long as $\kappa L \gg 1$, we can obtain the solution of (3.12) in a form more amenable to computation. The result is

$$z = 4\tanh^{-1}\{e^{-s}\tanh(\tfrac{1}{4}z_0)\}, \tag{3.19}$$

where z_0 is still given by (3.15).

Thus we see that the potential, zero at the surface, becomes Φ_∞ within the bulk of the crystal where there exists electrical neutrality, but only when $\kappa L \gg 1$. Note that the vacancy concentrations when $\Phi = \Phi_\infty$,

$$n_+ = n_- = Ne^{-(F^+ + F^-)/2kT}, \tag{3.20}$$

are the concentrations normally assumed to exist throughout the crystal.

In Fig. 1 are shown curves of z/z_0, using (3.19), as a function of s for $z_0 = 0.10$, 1.0, 10.0, and 100. The value of s for which $z/z_0 = 0.368$ is seen to decrease as $|z_0|$

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[3] The first integration of (3.12) yields, using (2.2),

$$ds = -\frac{1}{\sqrt{2}}\frac{dz}{(\cosh z - \cosh z_L)^{1/2}}.$$

Making the substitution $t = \cosh z$, Eq. (3.13) results.

[4] These values were selected rather arbitrarily using as a basis the experimental work summarized in R. Dreyfus and A. Nowick, J. Appl. Phys. Suppl. 33, 473 (1962), and the theoretical summary given by F. Fumi and M. Tosi, Discussions Faraday Soc. 23, 92 (1957).

[5] For actual applications, the temperature dependence of ϵ should be considered.

increases, being $\simeq 1$ for $|z_0| \lesssim 1$, 0.30 for $z_0=10$, and decreasing to 2×10^{-8} for $z_0=100$. Thus, the potential achieves its bulk value essentially exponentially for $|z_0| \lesssim 1$ and even more rapidly as $|z_0|$ increases beyond 1.

TABLE I. Quantities characteristic of pure NaCl.

T (°K)	κ^{-1} (cm)	x_e (cm)	σ (esu/cm^2)	E (V/cm)
1100	1.45×10^{-7}	1.27×10^{-7}	3.58×10^{3}	2.40×10^{6}
900	4.55×10^{-7}	3.77×10^{-7}	1.32×10^{3}	8.87×10^{5}
700	2.83×10^{-6}	2.10×10^{-6}	2.72×10^{2}	1.83×10^{5}
500	8.21×10^{-5}	4.80×10^{-5}	1.60×10^{1}	1.07×10^{4}
300	2.20×10^{-1}	6.67×10^{-2}		
100	8.45×10^{16}	6.58×10^{14}		

Using the data representing NaCl given in (3.17) and (3.18) κ^{-1} is tabulated in Table I for various temperatures. Also shown in Table I are values of x_e, the value of x for which $z/z_0=0.368$. Note that κ^{-1} is a reasonable measure of the thickness of the transition region down to near room temperature. As the temperature decreases below room temperature we see that the condition $\kappa L \gg 1$ is not satisfied for crystals of reasonable size. Then Eq. (3.19) is no longer valid and $z(s)$ is given by

$$s=kF\left(\sin^{-1}\left\{\frac{\cosh z_0-\cosh z_L}{\cosh z_0-1}\right\}^{1/2},k\right)$$

$$-kF\left(\sin^{-1}\left\{\frac{\cosh z(s)-\cosh z_L}{\cosh z(s)-1}\right\}^{1/2},k\right),$$

where $F(\Phi,k)$ is the elliptic integral of the first kind and k is defined by (3.14).

In terms of z the vacancy concentrations are

$$\begin{aligned} n_+/N&=\exp\{-(F^+ + F^-)/2kT\}\exp\{z\}, \\ n_-/N&=\exp\{-(F^+ + F^-)/2kT\}\exp\{-z\}. \end{aligned} \qquad (3.21)$$

These quantities are sketched schematically in Fig. 2 as a function of x for the case $F^- > F^+$ corresponding to NaCl. We see that in the region near the surface there are more cation than anion vacancies resulting in a region of negative space charge. The excess charge in the space-charge region is compensated by a layer of positive charge lying on the surface at $x=0$, the result of an excess of cations. The quantity of positive charge on the surface can be obtained by integrating the negative of the charge density over the range $0 \leq x \leq L$ or, alternatively, from the fact

$$D_n = 4\pi\sigma, \qquad (3.22)$$

where σ is the surface charge per unit area, and D_n is the normal component of the displacement at the surface in the direction of increasing x. Now

$$dz/ds = -(e/kT\kappa)E_x, \qquad (3.23)$$

where E_x is the x component of the electric field and so, using Eq. (3.21),

$$\sigma = (kT\kappa\epsilon/2\pi e)\sinh(z_0/2) \qquad (3.24)$$

as long as $\kappa L \gg 1$. Values of σ and the electric field at $x=0$ are given in Table I for those temperatures for which $\kappa L \gg 1$ with $L=1.0$ cm. Note that the electric field becomes very high at high temperatures.

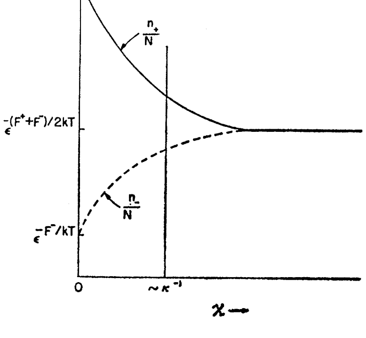

FIG. 2. Sketch of n_+/N and n_-/N as a function of x for a pure crystal with $F^- > F^+$.

Several important aspects of the problem relating to the considerations of electrostatics should be mentioned. We used the boundary condition that the potential was zero at the surface and found (at high enough temperature) that the potential became $\Phi_\infty(=\Phi(L))$ in a distance $\sim\kappa^{-1}$, and then remained at Φ_∞ to $x=L$. Thus the structure of the surface region is essentially a dipole. It is well known that the potential change in traversing a dipole layer of strength τ,

$$\tau = \sigma\xi, \qquad (3.25)$$

where $|\sigma|$ is the charge per unit area of each sheet of charge and ξ is the separation of the charge sheets, in a medium of dielectric constant ϵ is $4\pi\tau/\epsilon$. In the model we have used, we have an infinite dipole layer. Thus, when we assume a zero potential surface, we have a potential which is zero for all $x \leq 0$, rises to a value Φ_∞ near $x=\kappa^{-1}$, and remains at Φ_∞ until the reverse transition occurs near $x=2L$. So we have immediately,

$$\Phi_\infty = 4\pi\tau/\epsilon. \qquad (3.26)$$

For simplicity we have been considering a crystal of infinite extent in the y and z directions. In the case of a finite crystal the dipole layer will cover the entire surface. Therefore the potential will be zero at all points outside the crystal (a reasonable state for a neutral entity) and Φ_∞ within the crystal as long as one is further than κ^{-1} from a surface. The representation of the surface region as a dipole layer breaks down of course when $\kappa L \lesssim 1$ or whenever one is interested in potential variations over dimensions $\sim\kappa^{-1}$.

The above discussion, together with the results of Appendix A, provides the justification for our neglect of effects due to image charges. Let us assume that the crystal extends to infinity in the x direction so we need worry only about the dipole layer near $x=0$. In the model where the crystal is effectively infinite in the y and z direction the image dipole layer will produce a constant potential throughout the real crystal. It is shown, however, in Appendix A that an arbitrary reference level for the potential produces no physical effect. Thus the image dipole layer can be neglected.

The fact that the potential assumed to exist at the surface is immaterial is physically clear since the defects are affected only by the potential difference between the surface and the interior of the crystal. This potential difference enters the problem as a correction to the free formation energies of the vacancies [see (3.6)] and serves to change these energies in just such a manner that within the bulk of the crystal electrical neutrality exists as long as $\kappa L \gg 1$.

For the case of dislocations much of the above formalism can be retained. We assume that F^+ and F^- are independent of whether the vacancy source is the surface or a dislocation for the present. Equations (3.6) remain unchanged if we interpret Φ as $\Phi(r)$ and (3.12) becomes, in this cylindrically symmetric case,

$$\frac{1}{s_D}\frac{d}{ds_D}\left(s_D\frac{dz_D}{ds_D}\right)=\sinh z_D\,, \tag{3.27}$$

where now

$$z_D=\{e\Phi(r)-e\Phi_\infty\}/kT \tag{3.28}$$

and

$$s_D=\kappa r\,, \tag{3.29}$$

with κ given by (3.10) and $e\Phi_\infty$ by (3.8).

If we are at a temperature such that $\kappa R \gg 1$, then $\Phi_\infty=\Phi(R)$ and the solution of (3.27) has been shown to be similar to that for the surface.[6] The potential, zero at the dislocation core, $r=b$, achieves its bulk value Φ_∞ in a distance $\sim\kappa^{-1}$. Since the potential is always negative for pure NaCl, the region around the dislocation contains an excess of cation vacancies giving rise to a negative space charge which is neutralized by charging of the dislocation line.

IV. SPACE-CHARGE DISTRIBUTION IN A CRYSTAL CONTAINING DIVALENT CATIONIC IMPURITIES

For our discussion of the surface region we consider the model presented in Sec. II and assume there is present within the crystal an average concentration $\bar{C}$ of divalent cation impurities. $\bar{C}$ is defined to be the ratio of impurity ions to normal cations. There exists a considerable body of evidence that when, for example, a NaCl melt is doped with a substance such as $CaCl_2$, the Ca enters the crystal as Ca^{++} ions in cation sites[7] and we consider this to be the case. The over-all neutrality of the crystal then means that each divalent cation which enters the crystal brings with it two anions.

There are now, in addition to the three types of defects discussed in Sec. III, two types of impurity defects which enter into our considerations. The first consists of isolated impurities having an effective charge of $+e$, and the second consists of impurities which are close neighbors of cation vacancies. These complexes are neutral and will not contribute to the charge density ρ.

For our initial considerations we take as a model for the impurity-vacancy association the supposition that the complex has a binding free energy B_+ if the impurity and vacancy are in adjacent cation sites and no binding free energy otherwise. Thus we are again ignoring the long-range effects of the Coulomb interactions.

The free energy of the crystal per unit area now is (again to within an additive constant dependent only on temperature)

$$F=\int_0^L dx[n_+(x)F^+ + n_-(x)F^- + n_B(x)\{F^+ + F^- - B\} + n_{ib}(x)\{F^+ - B_+\} + \tfrac{1}{2}\rho(x)\Phi(x)] - TS_c\,, \tag{4.1}$$

where n_{ib} is the density of impurity-cation vacancy complexes, and now

$$\rho=e(n_{if}+n_- - n_+)\,, \tag{4.2}$$

where n_{if} is the density of unassociated impurities.

We now make a variation of F permitting n_+, n_-, n_B, n_{if}, and n_{ib} to vary. Proceeding as in Sec. III (the variation of the configurational entropy is evaluated in Appendix C for this case), the conditions for the free energy to be a minimum are

$$\begin{aligned}
&\frac{n_{if}}{(N-2n_{ib}-n_B-n_{if}-n_+)}=\exp\left\{-\frac{e\Phi+\alpha_H{}^+}{kT}\right\},\\
&\frac{n_{ib}(N-2n_{ib})^2}{(N-2n_{ib}-n_B-n_{if}-n_+)^2N}=z_{nn}\exp\left\{-\frac{F^+-B_++\alpha_H{}^+}{kT}\right\},\\
&\frac{n_+}{(N-2n_{ib}-n_B-n_{if}-n_+)}=\exp\left\{-\frac{F^+-e\Phi}{kT}\right\},\\
&\frac{n_-}{(N-n_--n_B)}=\exp\left\{-\frac{F^-+e\Phi}{kT}\right\},\\
&\frac{n_B(N-n_B)}{(N-2n_{ib}-n_B-n_{if}-n_+)(N-n_B-n_-)}=z_n\exp\left\{-\frac{F^++F^--B}{kT}\right\}.
\end{aligned} \tag{4.3}$$

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[6] J. Koehler, D. Langreth, and B. von Turkovich, Phys. Rev. **128**, 573 (1962).

[7] A. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 20, p. 290.

The Lagrange multiplier α_H^+ has been introduced to take account of the fact that the total number of impurities in the system must remain constant, that is,

$$\int_0^L dx(n_{if}+n_{ib})=N\bar{C}L. \tag{4.4}$$

Anticipating forthcoming results, we assume n_{ib}/N, n_+/N, n_-/N, and n_B/N are much less than one. In addition we will assume in this paper that $n_{if}/N\ll 1$.[8] Using the assumption that all concentrations are small, (4.3) can be simplified to

$$\begin{aligned} n_+/N&=\exp\{-(F^+-e\Phi)/kT\}\,,\\ n_-/N&=\exp\{-(F^-+e\Phi)/kT\}\,,\\ n_{if}/N&=\exp\{-(e\Phi+\alpha_H^+)/kT\}\,,\\ n_{ib}/N&=z_{nn}\exp\{-(F^+-B_++\alpha_H^+)/kT\}\,,\\ n_B/N&=z_n\exp\{-(F^++F^--B)/kT\}\,. \end{aligned} \tag{4.5}$$

The charge density ρ as given by (4.2) becomes, using Eq. (4.5),

$$\begin{aligned}\rho=eN[&\exp\{-(e\Phi+\alpha_H^+)/kT\}\\ &+\exp\{-(F^-+e\Phi)/kT\}\\ &-\exp\{-(F^+-e\Phi)/kT\}]\,. \end{aligned}\tag{4.6}$$

We again define Φ_∞ by the condition that $\rho=0$ when $\Phi=\Phi_\infty$. Thus,

$$\begin{aligned}0=&\exp\{-(e\Phi_\infty+\alpha_H^+)/kT\}\\ &+\exp\{-(F^-+e\Phi_\infty)/kT\}\\ &-\exp\{-(F^+-e\Phi_\infty)/kT\}\,. \end{aligned}\tag{4.7}$$

With z given by (3.11), s_+ by

$$s_+=\kappa_+x\,, \tag{4.8}$$

and κ_+ by (3.12) with Φ_∞ now understood to refer to a crystal containing divalent cations, Poisson's equation becomes (3.12) with s replaced by s_+. As long as $\kappa_+L\gg 1$ [so that $\Phi(L)=\Phi_\infty$], the solution is again given by Eq. (3.19) with s replaced by s_+. The quantity z_0 is given by (3.15). As in the case of the pure crystal, the potential goes from zero at the surface to its bulk value Φ_∞ in a distance of the order of κ_+^{-1}. Before determining Φ_∞ we need to evaluate α_H^+. This evaluation is carried out in Appendix D.

Having now an expression for α_H^+, we could solve Eq. (4.7) for $e\Phi_\infty$. However, if one inserts α_H^+ [see Eq. (D20)] into (4.7), the result is a cubic equation for $e^{e\Phi_\infty/kT}$, which, though solvable as it stands, yields a solution which tends to obscure the physics. Thus we shall present some preliminary arguments which lead to useful approximations in the solution of Eq. (4.7). Keep in mind that we are discussing the situation for $\kappa_+L\gg 1$.

In view of the fact that the free impurities will be either attracted or repelled by the surface, depending upon the sign of Φ_∞ [see Eq. (4.5)], while the concentration of impurity-vacancy complexes is uniform throughout the crystal, it is most useful to define the degree of association p of the impurities in terms of the total impurity concentration beyond the transition region. Thus,

$$\begin{aligned}p\equiv&\frac{n_{ib}}{n_{ib}+n_{if}|_{z=0}}\\ &=\left[1+z_{nn}^{-1}\exp\left\{\frac{F^+-B_+-e\Phi_\infty}{kT}\right\}\right]^{-1}\end{aligned} \tag{4.9}$$

such that beyond the transition region, when Φ is effectively Φ_∞,

$$n_{if}/N=(1-p)C_1 \tag{4.10}$$

and

$$n_{ib}/N=pC_1\,, \tag{4.11}$$

where C_1 is the total impurity concentration beyond the transition region which means the region $\kappa_+^{-1}\lesssim x\leq L$. Using (4.5), (4.9), (4.10), and (4.11),

$$C_1=\bar{C}\left[\frac{z_{nn}\exp\{-(F^+-B_+)/kT\}+\exp\{-e\Phi_\infty/kT\}}{z_{nn}\exp\{-(F^+-B_+)/kT\}+\xi_+\exp\{-e\Phi_\infty/kT\}}\right], \tag{4.12}$$

where ξ_+ is defined in Eq. (D18). Thus we now have an expression for the "bulk" impurity concentration as well as an expression for the degree of association in terms of this concentration.

In terms of the quantities just defined, our neutrality condition (4.7) can be written

$$\begin{aligned}(1-p)C_1&+\exp\{-(F^-+e\Phi_\infty)/kT\}\\ &-\exp\{-(F^+-e\Phi_\infty)/kT\}=0\,,\end{aligned} \tag{4.13}$$

so that

$$\begin{aligned}e^{e\Phi_\infty/kT}=e^{F^+/kT}\big((1-p)C_1/2&+\{[(1-p)C_1/2]^2\\ &+\exp[-(F^++F^-)/kT]\}^{1/2}\big)\,.\end{aligned} \tag{4.14}$$

For reasonable impurity concentrations and moderate temperatures we expect the first term in the square root to completely dominate the second. Physically, this means we have a negligible number of anion vacancies which is mathematically equivalent to assuming $F^-\rightarrow\infty$. Using this assumption we find

$$\begin{aligned}\exp\{e\Phi_\infty/kT\}=(2z_{nn})^{-1}&\exp\{(F^+-B_+)/kT\}\{-\xi_+\\ &+[\xi_+^2+4\bar{C}z_{nn}\exp(B_+/kT)]^{1/2}\}\,.\end{aligned} \tag{4.15}$$

This solution for $e\Phi_\infty$ is valid for intermediate temperatures. The failure of this expression as the temperature is lowered is due to the breakdown of the approximation $n_{if}/N\ll 1$[8] (see below). At high temperatures it is no longer valid to consider $F^-\rightarrow\infty$. The highest tempera-

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[8] The assumption $n_{if}/N\ll 1$ will be eliminated in the following paper. Its use prevents us from discussing arbitrary temperatures.

TABLE II. Maximum temperature for which Eq. (4.15) is valid for $L=1.0$ cm. (All temperatures in °K.)

B_+ (eV) \ $\bar{C}$	10^{-6}	10^{-5}	10^{-4}	10^{-3}
0.20	639	727	840	994
0.40	639	725	833	967
0.60	630	705	791	891

tures of validity for Eq. (4.15) using the parameters representing NaCl are given in Table II for various combinations of B_+ and $\bar{C}$.

At sufficiently high temperatures, as is evident from Eq. (4.14), $e\Phi_\infty$ will become that for the pure crystal, Eq. (3.10), corresponding to the $\bar{C}\rightarrow 0$ limit in Eq. (4.15). Using the aforementioned NaCl parameters, the temperatures above which $e\Phi_\infty$ is essentially that of the pure crystal are given in Table III. For temperatures between those given in Tables II and III, Eq. (4.14) must be solved as it stands.

TABLE III. Minimum temperature for which $e\Phi_\infty$ is given by pure crystal solution, Eq. (3.8), for $L=1.0$ cm.[a] (All temperatures in °K.)

B_+ (eV) \ $\bar{C}$	10^{-6}	10^{-5}	10^{-4}	10^{-3}
0.20	945	>1100	>1100	>1100
0.40	939	>1100	>1100	>1100
0.60	907	1053	>1100	>1100

[a] Melting point for NaCl ≅1073°K.

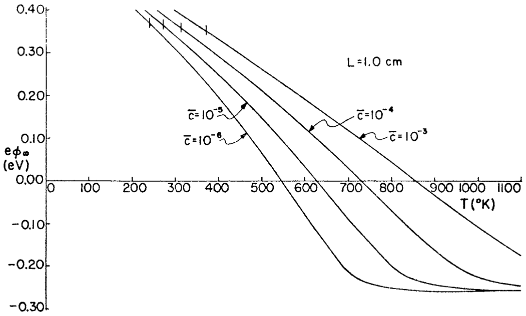

FIG. 3. The temperature dependence of $e\Phi_\infty$ for a NaCl crystal containing divalent cations with $B_+=0.40$ eV. The vertical lines on the curves mark the temperature below which the solution (4.15) is no longer valid.

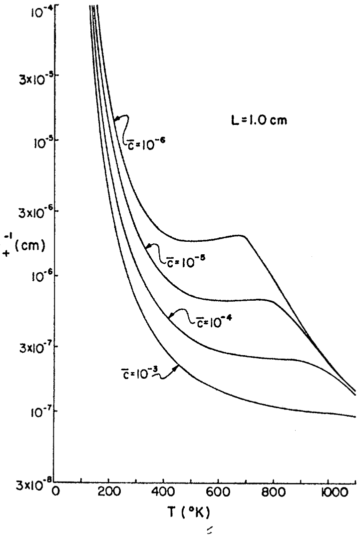

FIG. 4. The temperature dependence of κ_+^{-1} for a NaCl crystal containing divalent cations with $B_+=0.40$ eV.

Curves of $e\Phi_\infty$ for $\bar{C}=10^{-6}$, 10^{-5}, 10^{-4}, and 10^{-3} are given in Fig. 3 for $B_+=0.40$ eV using the NaCl parameters.[9] Note that at moderate temperatures the potential is positive, becomes zero at a temperature T_0 depending upon B_+ and $\bar{C}$, and approaches the potential for the pure crystal at still higher temperatures. Physically, T_0 is that temperature at which the intrinsic concentration of free cation vacancies is equal to the free impurity concentration, that is,

$$\exp\{-F^+/kT_0\}$$
$$=\bar{C}/[z_{nn}\exp\{-(F^+-B_+)/kT_0\}+1] \quad (4.16)$$

since $\xi_+\cong 1$ for $T=T_0$. Values of T_0 for various combinations of $\bar{C}$ and B_+ are given in Table IV for the NaCl parameters.

Increasing B_+ results in less free charge in the crystal, the slope of $e\Phi_\infty$ in the impurity-dominated region is less steep and the potential for a given temperature is reduced. Decreasing B_+ has the opposite effect. These features are evident in Table IV.

TABLE IV. Values of T_0, the temperature for which the potential becomes zero, in °K, for $L=1.0$ cm.

B_+ (eV) \ $\bar{C}$	10^{-6}	10^{-5}	10^{-4}	10^{-3}
0.20	549	635	753	915
0.40	546	628	731	860
0.60	509	568	643	739

Curves of κ_+^{-1} as a function of temperature are given in Fig. 4 using the data representing NaCl and $B_+=0.40$ eV. These can be interpreted as the thickness of the space-charge region only for $|e\Phi_\infty|/kT\lesssim 1$ as discussed above. Thus, for $T>T_0$, κ_+^{-1} will be an adequate representation for the double layer thickness while the thickness becomes increasingly less than κ_+^{-1} as T decreases below T_0. Increasing B_+ to 0.6 eV increases significantly the value of κ_+^{-1} in the region where the impurity content is significant as a consequence of the reduced free-charge content within the crystal.

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[9] The temperatures below which Eq. (4.15) becomes invalid are noted on these curves. For high values of the binding energy B_+, Eq. (4.15) is valid down into the temperature range in which the existence of thermal equilibrium becomes questionable whereas such is not the case for low values of the binding energy.

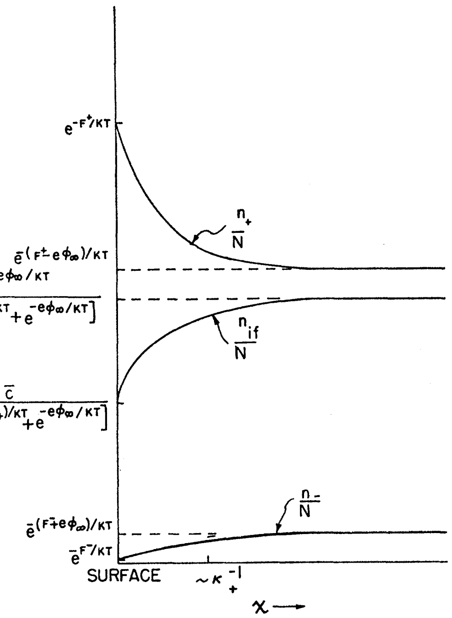

FIG. 5. Sketch of charged defect concentrations for a crystal with $F^- > F^+$ containing divalent cations and $T > T_0$.

Reducing B_+ to 0.2 eV produces minima in the curves of κ_+^{-1} which are more pronounced than those of Fig. 4. For example, $\bar{C}=10^{-6}$ produces a minimum of $\kappa_+^{-1}\sim 10^{-6}$ cm at $T\simeq 250$°K, whereas $\bar{C}=10^{-4}$ corresponds to a minimum at ~ 350°K, where $\kappa_+^{-1}\sim 2\times 10^{-7}$ cm. It should be pointed out that our present assumption that $\kappa_+ L \gg 1$ will be satisfied for crystals of reasonable size down to well below room temperature.

The concentrations of the charged defects can be obtained from (4.5) and (D13). Sketches of these quantities for temperatures greater than and less than T_0 are given in Figs. 5 and 6. Note that for $T<T_0$, the impurities tend to congregate near the surface whereas for $T>T_0$, the opposite occurs. The tendency for the impurities to congregate near the surface for $T<T_0$ is the reason the solution discussed to this point breaks down at low temperatures.[8]

The charge on the surface serving to neutralize the space charge, negative for $T<T_0$ and positive for $T>T_0$, is given by (3.24) with κ replaced by κ_+ since we are still considering $\kappa_+ L \gg 1$.

To this point in the discussion of crystals containing divalent cations we have dealt solely with the problem of the surface. As pointed out in Sec. III, edge dislocations, being sources and sinks for vacancies, behave in many respects like a surface.

The equation determining the potential around the dislocation is (3.27) with z_D given by (3.28) and s_{D+} by

$$s_{D+}=\kappa_+ r. \tag{4.17}$$

We are considering all defect concentrations to be small everywhere. The neutrality condition (4.7) will be satisfied at $r=R$ provided $\kappa_+ R \gg 1$ so that $\Phi(R)=\Phi_\infty$. It is not immediately obvious that the Lagrange multiplier should be the same for both the dislocation and the surface. The reason why $C_1 \neq \bar{C}$ is the tendency toward depletion of the bulk impurity concentration by the high concentration near the surface for $T<T_0$. This effect is negligible in the case of dislocations for normal dislocation densities ($\sim 10^6$ lines/cm^2) with $\bar{C}\gtrsim 10^{-8}$. Considering the dislocations to be in a region of impurity concentration C_1, we find for the dislocations

$$\exp\left\{-\frac{\alpha_H{}^+}{kT}\right\}$$

$$=\frac{C_1}{z_{nn}\exp\{-(F^+-B_+)/kT\}+\exp\{-e\Phi_\infty/kT\}}. \tag{4.18}$$

Using for C_1 the expression (4.12), we see that $\alpha_H{}^+$ for the dislocation is identical to that for the surface. Keep in mind that we are still considering F^+ and F^- to be constant for a given crystal, independent of the vacancy source.

A numerical method for the solution of Eq. (3.27) is given in Ref. 6. It is shown there that the structure of the solution is similar to that for the surface. For $T<T_0$, the potential, zero at $r=b$, increases to Φ_∞ in a distance $\lesssim \kappa_+^{-1}$, resulting in a negatively charged dislocation and a region of positive space charge, comprised essentially of divalent ions, surrounding the dislocation. For $T>T_0$, the space charge, now consisting of an excess of cation vacancies, is negative and the dislocation is charged positively. The charge on the dislocation line per unit

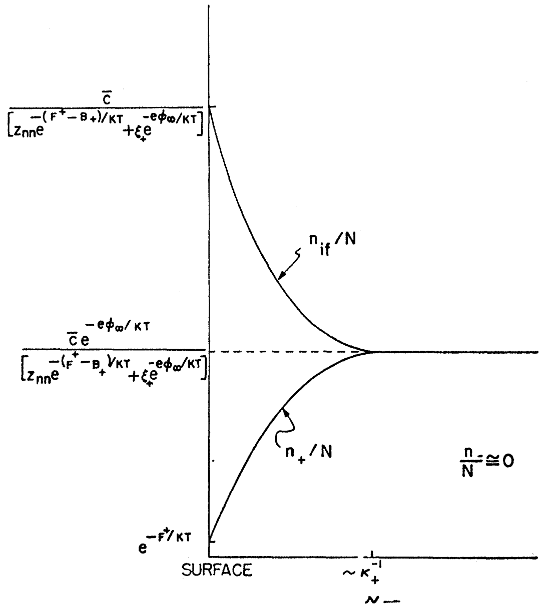

FIG. 6. Sketch of charged defect concentrations for a crystal with $F^- > F^+$ containing divalent cations. The temperature is less than T_0 but within the realm of validity of Eq. (4.15).

length Q is given by

$$Q=-\frac{\epsilon kT}{2e}(\kappa_+ b)\frac{dz_D}{ds_{D+}}\bigg|_{s_{D+}=\kappa_+ b} \tag{4.19}$$

for $\kappa_+ R \gg 1$ and all defect concentrations small. Note that the equation which gives the temperature for which the dislocation charge vanishes is (4.16).

V. INCLUSION OF LONG-RANGE FORCES BETWEEN DEFECTS

From Eq. (4.5) it follows that

$$\frac{n_{ib}}{n_+ n_{if}}=\frac{z_{nn}}{N}e^{B_+/kT}. \tag{5.1}$$

Lidiard[10] showed that the inclusion of Coulomb effects, within the context of the Debye-Hückel theory, resulted in Eq. (5.1) becoming

$$\frac{n_{ib}}{n_+ n_{if}}=\frac{z_{nn}}{N}\exp\{(B_+ - V_{DH})/kT\}, \tag{5.2}$$

where V_{DH}, the Debye-Hückel potential energy, is given by

$$V_{DH}=e^2\kappa_+/\epsilon(1+\kappa_+ a). \tag{5.3}$$

If an impurity and a cation vacancy have a separation less than a, they are considered to form a neutral complex whereas they interact with other charged defects via the long-range forces if the separation is greater than a. We consider the vacancy and the impurity to be a complex if they are in adjacent cation sites. For all larger separations the interaction is assumed to be Coulombic.

Equation (5.2) was derived under the assumption that the defect distribution was uniform and that local neutrality existed throughout the crystal. In the present problem this is clearly not the case near surfaces or dislocations. However, near surfaces or dislocations the preponderance of defects of one sign and the resultant high electric field means that the dominant Coulomb effects have been included in these regions. Thus it is reasonable to utilize Lidiard's formalism for including the Coulomb interactions within the bulk of the crystal where the assumptions apply. If we do so, we see that the long-range forces result in the binding energy B_+ becoming B_+^{eff} where

$$B_+^{\text{eff}}=B_+ - V_{DH}. \tag{5.4}$$

The same modification is clearly appropriate for the binding energy B as well. In addition the long-range forces result in F^+ becoming F_{eff}^+ and F^- becoming F_{eff}^- where

$$F_{\text{eff}}^+=F^+ - \tfrac{1}{2}V_{DH}$$

and

$$F_{\text{eff}}^-=F^- - \tfrac{1}{2}V_{DH}. \tag{5.5}$$

Physically, Eqs. (5.5) are statements of the fact that the existence of the Debye-Hückel charge clouds reduce the energy of formation of a vacancy by half of the Debye-Hückel potential energy on the average.

That the combination produced by Eqs. (5.4) and (5.5) is correct can be seen from the following argument. Consider a cation vacancy and an anion vacancy which form a complex. The change in the crystal energy due to the addition of a complex is independent of whether or not long-range effects are included since the complex is neutral. If long-range effects are not included the energy of the crystal, with respect to that of the crystal prior to the introduction of the pair of defects being considered, will be $F^+ + F^-$ when the defects are widely separated. When the complex is formed the energy will drop to $F^+ + F^- - B_+$. If long-range forces are included, the introduction of the pair of defects will require an energy $F_{\text{eff}}^+ + F_{\text{eff}}^-$. The final energy of the resulting complex will then be $F_{\text{eff}}^+ + F_{\text{eff}}^- - B_+^{\text{eff}}$ which is, using (5.4) and (5.5), $F^+ + F^- - B_+$ as it must be. An identical argument can obviously be made for impurity-vacancy complexes.

The inclusion of the long-range forces requires self-consistent solutions in general since F_{eff}^+, F_{eff}^-, and B_+^{eff} all depend upon Φ_∞. This introduces some degree of complexity but the long-range effects are important and should be included when the defect concentrations are substantial.

VI. DISCUSSION

Let us briefly consider a pure sodium chloride crystal. From (3.6) it is clear that the effective free energies of formation which must be supplied to put a cation vacancy and an anion vacancy into the bulk of the crystal are $F^+ - e\Phi_\infty$ and $F^- + e\Phi_\infty$. The potential difference Φ_∞ appears across the surface dipole layer and thus the dipole layer serves as the agent whereby information as to the electrical state of the bulk of the crystal is transmitted to the surface, and thereby to any potential vacancies. That is, in equilibrium the presence of the dipole layer changes the innate free energies of formation F^+ and F^- into effective free energies of formation $F^+ - e\Phi_\infty$ and $F^- + e\Phi_\infty$, such that the actual free energy which must be supplied in putting an anion vacancy or a cation vacancy into the bulk of the crystal is the same thus ensuring electrical neutrality within the bulk. It is then obvious that if $F^+ = F^-$ no dipole layer will exist since the innate free energies of formation give rise to electrical neutrality automatically.

Similar considerations apply to the edge dislocation since it also is a vacancy source. There must exist a sheath of negative space charge counterbalanced by the positive charge on the dislocation line itself such that

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[10] A. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 20, p. 307.

the effective free energies of formation of the two types of vacancies become equal because of the fact that the vacancies must traverse the potential field around the dislocation before reaching the bulk.

Consider now the situation for a NaCl crystal containing a small concentration of divalent cation impurity. At sufficiently high temperatures where the concentrations (3.20) are much greater than the divalent ion concentration, the situation is essentially the same as for the pure crystal. The surface (and the edge dislocations) will have a positive charge due to the excess evaporation of cation vacancies, the space-charge region will be negative, and the potential across the dipole layer will be such that the effective free formation energies of the two types of vacancies are equal. As we reduce the temperature, the bulk concentration of both types of vacancies will be reduced in equal parts in accordance with (3.20) and $e\Phi_\infty$ will remain at (3.8) as long as the concentrations (3.20) remain large compared with the divalent cation concentration. When the concentration of free divalent cations becomes an appreciable fraction of the concentrations (3.20) it is clear that the potential change from surface to bulk must become smaller in magnitude, though still remaining negative, such that the precipitation of anion vacancies is enhanced while the precipitation of cation vacancies is retarded. Physically this occurs since the precipitation of equal numbers of both types of vacancy would, when the presence of the divalent impurities becomes noticeable, produce a positively charged bulk which would serve to attract into the bulk some of the vacancies comprising the negative space charge thereby reducing the potential across the space-charge region. The result of this process is that ρ is zero within the bulk of the crystal or

$$n_-(\infty)+n_{if}(\infty)=n_+(\infty), \tag{6.1}$$

where ∞ indicates the bulk of the crystal. Since we are now considering decreasing temperatures, the surface (and the edge dislocations) serves as a vacancy sink and the reduction in the magnitude of the potential means that the precipitation of an anion vacancy becomes energetically more favorable than the precipitation of a cation vacancy.

With a further decrease in temperature this trend will continue. That is, the potential difference continues to decrease in magnitude resulting in a further enhancement of anion vacancy precipitation compared with cation vacancy precipitation until the temperature is reached where the innate difference between the concentrations of anion and cation vacancies is precisely equal to the concentration of free cation impurities, or

$$Ne^{-F^+/kT_0}-Ne^{-F^-/kT_0}=n_{if}\big|_{T=T_0}. \tag{6.2}$$

The temperature where (6.2) is satisfied, designated T_0 in Sec. IV, is the temperature where the potential difference between the surface and the bulk becomes zero since the innate free formation energies F^+ and F^- are of such a magnitude that bulk electrical neutrality is ensured without need of modification of F^+ and F^- by a dipole layer. Thus the surface and the dislocations are uncharged at this temperature. We saw in Sec. IV that, when $T=T_0$, the anion vacancy concentration using the NaCl parameters has become essentially zero. In this case (6.2) is to a good approximation

$$Ne^{-F^+/kT_0}=n_{if}\big|_{T=T_0}, \tag{6.3}$$

indicating clearly that at $T=T_0$ we have within the crystal essentially equal numbers of free impurities and free vacancies.

As the temperature is reduced slightly from $T=T_0$, the cation vacancies will continue to precipitate out on the surface (and the dislocations) since the initial tendency is to maintain a concentration based solely on thermal considerations, a concentration given by

$$n_+=Ne^{-F^+/kT}. \tag{6.4}$$

However, this precipitation of negative charge will attract positively charged impurities (the only remaining source of positive charge) and the result will be a dipole layer with a potential rise from the surface to the bulk which decreases the effective free energy of formation for cation vacancies from F^+ to $F^+-e\Phi_\infty$, thus making further precipitation energetically unfavorable and preserving bulk neutrality.

For temperatures less than T_0 then, the dipole layer arises through the precipitation on the surface (and the edge dislocations) of cation vacancies possessing a negative charge and the resultant attraction by this negative charge of positively charged impurities into the region beneath the surface (and around the dislocation). Thus, in the temperature range where the cation vacancy concentration is governed by the quantity of divalent cations present, the surface charge and the charge on the dislocation line will be negative and the sign of this charge depends in no sense upon the fact that $F^->F^+$, but only upon the charge possessed by the impurities. Hence, for a crystal containing divalent anions, the surface charge in the temperature range of extrinsic conductivity will be positive because anion vacancies will be appearing at the surface. The fact that $F^->F^+$ is important for a doped crystal only in that there will exist a temperature such that the potential is zero everywhere for a crystal doped with divalent cations whereas no such temperature exists for a crystal doped with divalent anions.

It is now clear that the presence of the dipole layer is an inherent aspect of thermal equilibrium and a question as to the ability of the dipole layer to form at an arbitrary temperature is really a question of whether or not the crystal is in thermal equilibrium at the temperature under consideration.

As pointed out by Eshelby *et al.*,[2] it is by no means certain that the free energy of formation of individual vacancies at dislocations is equal to that for a surface even though the free energy of formation of a Schottky pair should be essentially the same for the two sources. The possibility that the individual formation free energies for the two sources can differ is a consequence of the fact that the transfer of a cation say from a dislocation jog to a kink in a surface step involves the transition of a positive jog into a negative jog and a negative kink into a positive kink. Since the environments in the two cases are not identical, these are not necessarily compensating processes. Thus the surface and the dislocations might be uncharged at different temperatures.

We have assumed that, in a crystal containing divalent impurities, all the impurities are present either in the free state or associated with a vacancy of the opposite charge. Thus we have not considered higher complexes which might exist such as impurity precipitates and aggregates of impurity-vacancy complexes. The presence of such complexes would serve to reduce $\tilde{C}$. Studies made by Ninomiya,[11] Chiba *et al.*,[12] and Dryden[13] on KCl and NaCl crystals doped with divalent cations indicate that the predominant higher complex formed around room temperature is an aggregate of impurity-vacancy complexes. Since this type of aggregation has only a small effect upon the theory, it seems possible that the attainment of the state predicted herein will be principally limited by the mobility of the defects.

Electrical charge developed during plastic deformation of alkali halides has been reported in several publications.[14–19] In each of these studies crystals with electrodes plated or pressed onto the surfaces were deformed and potentials appeared at the electrodes. These potentials were attributed to the motion of charged dislocations.

Since alkali halide crystals commonly designated pure contain concentrations of divalent cations of the order of 10^{-6} such that the room-temperature conductivity is in the extrinsic range, the present theory predicts that dislocations in "pure" crystals at room temperature should be negatively charged. However, there is no unanimity of opinion as to the sign of the dislocation charge as determined experimentally in such crystals. Some investigators have concluded, on the basis of their interpretation of the dislocation motion involved, that the dislocations are negatively charged whereas others have concluded the opposite. Rueda and Dekeyser[18] found that dislocations in "pure" and $CdCl_2$-doped NaCl were charged negatively, while doping with Na_2O_2 produced positively charged dislocations. This behavior is completely consistent with the ideas presented above and the sign change when the concentration of divalent anions exceeds that of the divalent cations merits particular mention. Hikata *et al.*[16] have not measured the dislocation charge directly, but have constructed a model based upon their results which suggests that the dislocations are positively charged in "pure" NaCl at room temperature. They have also demonstrated the fact that screw dislocations in NaCl are uncharged.

Several important questions emerge in connection with these deformation studies. First of all, are the dislocations being observed dislocations which were present initially and presumably in an equilibrium state with their charge cloud and then extracted from their charge cloud, or are they freshly produced dislocations which might be uncharged at production? Secondly, when a dislocation is torn from its charge cloud by a stress does it carry with it the entire charge it had originally, a part of the original charge, or does it emerge uncharged? Thirdly, what will be the charge state of an initially uncharged dislocation after it has moved a distance through the crystal?

Let us consider a NaCl crystal at room temperature containing a concentration of the order of 10^{-6} divalent cation impurity. The equilibrium theory says the dislocations should be negatively charged, so if we can extract the dislocation in its original state the charge will remain negative. Suppose now that through the action of a dislocation source an uncharged edge dislocation is produced within the crystal. If the dislocation feels it is in a pure crystal, the fact $F^+ < F^-$ and the absence of a potential field would lead to the dislocation acting as a source of cation vacancies principally and the dislocation would develop a positive charge. However, this tendency is counteracted by the presence of a concentration of cation vacancies greater than that based on thermal considerations due to the presence of the impurities. These vacancies will attempt to establish the equilibrium configuration around the dislocation. That is, they will tend to precipitate on the dislocation until the potential difference between the core and the bulk, which was initially zero, reaches the equilibrium value. The result is a dislocation charged negatively. This effect depends upon the ability of the vacancy to reach and attach itself to the moving dislocation. Based on the present theory, in equilibrium the dislocations at room temperature possess a significant negative charge since the precipitation of vacancies is an energetically favorable condition. This fact, together with the small charging resulting if the dislocation attempted to act as if it were in a pure crystal, suggests that for divalent cation concentrations at least as low as 10^{-6} the moving dislocation should accrue a negative charge and that the effect should be enhanced for greater impurity concen-

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trations.[20] This is suggested by the work of Rueda and Dekeyser[18] since adding $CdCl_2$ to the "pure" crystal did not change the sign of the charge. This is not conclusive, however, since no distinction is made between effects due to dislocations present prior to deformation and freshly formed dislocations although the method of deformation they used would probably contribute a large number of new dislocations. We must conclude that the questions posed above remain unanswered and the dynamic problem of an initially uncharged dislocation moving through the crystal should be investigated. In addition, the dislocation motion involved in the experimental studies must be established before the sign of the dislocation charge can be determined unequivocally.

VII. ACKNOWLEDGMENTS

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APPENDIX A: VARIATION OF THE ELECTROSTATIC ENERGY

We consider I to be the variation of the electrostatic energy term in Eq. (3.4)

$$I=\frac{1}{2}\int_0^L dx\{\delta\rho(x)\Phi(x)+\rho(x)\delta\Phi(x)\}. \tag{A1}$$

The variation of $\rho(x)$ follows immediately from (3.2).

Consider the second part of (A1),

$$I_1=\frac{1}{2}\int_0^L dx\rho(x)\delta\Phi(x). \tag{A2}$$

Using Eq. (3.3), Eq. (A2) becomes

$$I_1=-\frac{\epsilon}{8\pi}\int_0^L dx\frac{d^2\Phi}{dx^2}\delta\Phi. \tag{A3}$$

We have stated earlier that the boundary conditions on the potential are given by Eqs. (2.1) and (2.2). Let us retain boundary condition (2.2) but, for the moment, assume that the potential at the surface is fixed at $\Phi=\Phi_1$. Now integrate (A3) by parts. Using (2.2) together with the fact that Φ_1 is fixed, we have, after interchanging the order of differentiation and variation,

$$I_1=\frac{\epsilon}{8\pi}\int_0^L \delta\left(\frac{d\Phi}{dx}\right)\left(\frac{d\Phi}{dx}\right)dx. \tag{A4}$$

Integrating by parts once again, we have

$$I_1=\frac{\epsilon}{8\pi}\left[\Phi_1\delta\left(\left.\frac{d\Phi}{dx}\right|_{x=0}\right)-\int_0^L dx\Phi\delta\left(\frac{d^2\Phi}{dx^2}\right)\right] \tag{A5}$$

which can be written

$$I_1=\frac{\epsilon}{8\pi}\Phi_1\delta\left(\left.\frac{d\Phi}{dx}\right|_{x=0}\right)+\frac{1}{2}\int_0^L dx\Phi\delta\rho. \tag{A6}$$

The imposition of the condition of electrical neutrality on each half of the crystal requires the charge per unit area on the surface σ to be

$$\sigma=-\frac{\epsilon}{4\pi}\left(\left.\frac{d\Phi}{dx}\right|_{x=0}\right)=-\int_0^L dx\rho \tag{A7}$$

so that the first term of (A6) becomes

$$-\frac{1}{2}\int_0^L dx\Phi_1\delta\rho. \tag{A8}$$

Thus

$$I=\int_0^L dx\{\Phi(x)-\Phi_1/2\}\delta\rho(x) \tag{A9}$$

or

$$I=e\int_0^L dx\{\Phi(x)-\Phi_1/2\}\{\delta n_-(x)-\delta n_+(x)\}. \tag{A10}$$

Since we are now assuming that the potential at the surface is Φ_1 there is an additional term in the free energy Eq. (3.1) due to the surface charge. This contribution F_{surf} is

$$F_{\mathrm{surf}}=\tfrac{1}{2}\sigma\Phi_1 \tag{A11}$$

or, using (A7)

$$F_{\mathrm{surf}}=-\frac{1}{2}\int_0^L dx\Phi_1\rho(x). \tag{A12}$$

Thus the variation of the total electrostatic energy $I+\delta F_{\mathrm{surf}}$ yields

$$\delta F_{\mathrm{elec}}=e\int_0^L dx\{\Phi(x)-\Phi_1\}\{\delta n_-(x)-\delta n_+(x)\}. \tag{A13}$$

Note that the surface potential enters in such a way that if we now redefine our potential as

$$\Phi'(x)=\Phi(x)-\Phi_1, \tag{A14}$$

then (A13) becomes

$$\delta F_{\mathrm{elec}}=e\int_0^L dx\Phi'\{\delta n_--\delta n_+\}. \tag{A15}$$

Since this is equivalent to (A10) with $\Phi_1=0$, we see there is no loss of generality by requiring the potential at the surface to be zero and ignoring the surface electrostatic energy. Thus, we conclude that the varia-

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[20] The possibility that impurity precipitation could reduce the effective impurity concentration to the point where the dislocation became positively charged remains. In addition compensation for the divalent cations by other impurities can occur. [B. Fritz, F. Lüty, and J. Anger, Z. Physik **174**, 240 (1963); M. V. Klein, Phys. Rev. **122**, 1393 (1961).]

tion of the electrostatic energy term in (3.4) is

$$I=e\int_0^L dx\Phi(x)\{\delta n_-(x)-\delta n_+(x)\}. \tag{A16}$$

We want to emphasize that the potential $\Phi(x)$ in (A16) is the difference in potential between the point x and the surface as is most clearly seen from (A13). Thus the surface potential is completely arbitrary.

APPENDIX B: CONFIGURATIONAL ENTROPY OF A PURE CRYSTAL IN WHICH SCHOTTKY DISORDER PREDOMINATES

Consider a macroscopically small volume of the crystal ΔV_i still containing a large number of defects in a region where the defect concentration is essentially constant. Suppose this region contains $n_+{}^i\Delta V_i$ cation vacancies, $n_-{}^i\Delta V_i$ anion vacancies, $n_B{}^i\Delta V_i$ bound vacancy-pairs, and $N\Delta V_i$ anion and cation sites. The number of ways these components can be arranged over the available sites is

$$\begin{aligned}w_i=z_n{}^{n_B{}^i\Delta V_i}[N\Delta V_i]![(N-n_B{}^i)\Delta V_i]!\\ \times\{[n_+{}^i\Delta V_i]![n_-{}^i\Delta V_i]![(N-n_+{}^i-n_B{}^i)\Delta V_i]!\\ \times[(N-n_-{}^i-n_B{}^i)\Delta V_i]![n_B{}^i\Delta V_i]!\}^{-1},\end{aligned} \tag{B1}$$

where z_n is the number of nearest unlike neighbors of a given ion. In the NaCl structure, $z_n=6$. Because of an assumption, we can use Stirling's approximation for the factorials.

Varying $\ln w_i$ with respect to $n_+{}^i$, $n_-{}^i$, and $n_B{}^i$, we find

$$\begin{aligned}\delta(\ln w_i)=\Delta V_i\Bigg\{\delta n_B{}^i \ln\left[\frac{z_n(N-n_+{}^i-n_B{}^i)(N-n_-{}^i-n_B{}^i)}{(N-n_B{}^i)n_B{}^i}\right]\\ +\delta n_+{}^i\ln\left[\frac{N-n_+{}^i-n_B{}^i}{n_+{}^i}\right]\\ +\delta n_-{}^i\ln\left[\frac{N-n_-{}^i-n_B{}^i}{n_-{}^i}\right]\Bigg\}.\end{aligned} \tag{B2}$$

For the entire crystal the configurational entropy S_c is given by

$$S_c=k\ln(\prod_i w_i)=k\sum_i \ln w_i, \tag{B3}$$

where k is Boltzmann's constant and the sum is over the set of volume elements comprising the crystal. A variation of S_c yields

$$\delta S_c=k\sum_i \delta(\ln w_i). \tag{B4}$$

Using (B2), (B4) becomes, in a continuous representation where all quantities are functions only of x,

$$\begin{aligned}\delta S_c/\text{unit area}=k\int_0^L dx\Bigg\{\delta n_B(x)\ln\left[\frac{z_n(N-n_-(x)-n_B(x))(N-n_+(x)-n_B(x))}{(N-n_B(x))n_B(x)}\right]\\ +\delta n_+(x)\ln\left[\frac{N-n_+(x)-n_B(x)}{n_+(x)}\right]+\delta n_-(x)\ln\left[\frac{N-n_-(x)-n_B(x)}{n_-(x)}\right]\Bigg\}.\end{aligned} \tag{B5}$$

As stated above, ΔV_i must contain many defects in a region where the defect concentration is essentially constant. In transforming from Eq. (B4) to Eq. (B5) where all quantities are a function of x, these conditions become

$$nA|\Delta x|\gg 1 \tag{B6}$$

and

$$|dn/dx||\Delta x|\ll n, \tag{B7}$$

where n is any defect density, A is the area in question, and the integration in (B5) should be thought of as a sum over successive Δx's which satisfy (B6) and (B7). Conditions (B6) and (B7) must be satisfied in order that (B5) be valid.

APPENDIX C: CONFIGURATIONAL ENTROPY OF A CRYSTAL FOR WHICH SCHOTTKY DISORDER PREDOMINATES CONTAINING DIVALENT CATIONS

As in Appendix B we consider a macroscopically small volume of the crystal ΔV_i still containing a large number of defects in a region where the defect concentration is essentially constant.

Suppose this region contains: $n_+{}^i\Delta V_i$ cation vacancies, $n_-{}^i\Delta V_i$ anion vacancies, $n_B{}^i\Delta V_i$ bound vacancy pairs, $n_{if}{}^i\Delta V_i$ free impurities, $n_{ib}{}^i\Delta V_i$ vacancy-impurity pairs, and $N\Delta V_i$ anion and cation sites. The number of ways these constituents can be arranged over the sites is

$$\begin{aligned}w_i=z_{nn}{}^{(n_{ib}{}^i\Delta V_i)}\Big[\prod_{j=0}^{(n_{ib}{}^i\Delta V_i-1)}(N\Delta V_i-2j)\Big]\frac{[(N-2n_{ib}{}^i)\Delta V_i]!}{[n_{ib}{}^i\Delta V_i]!}\,\frac{z_n{}^{(n_B{}^i\Delta V_i)}[(N-n_B{}^i)\Delta V_i]!}{[n_B{}^i\Delta V_i]![n_{if}{}^i\Delta V_i]![n_+{}^i\Delta V_i]![n_-{}^i\Delta V_i]!}\\ \times\frac{1}{[(N-2n_{ib}{}^i-n_B{}^i-n_{if}{}^i-n_+{}^i)\Delta V_i]![(N-n_B{}^i-n_-{}^i)\Delta V_i]!},\end{aligned} \tag{C1}$$

where z_{nn} is the number of nearest like neighbors of a given ion, 12 for NaCl. Because of our assumption we can use Stirling's approximation for the factorials with the result

$$\begin{aligned}\ln w_i = \Delta V_i\{ & n_{ib}{}^i \ln z_{nn} + n_B{}^i \ln z_n - n_{ib}{}^i \ln[n_{ib}{}^i \Delta V_i] + n_{ib}{}^i + (N-2n_{ib}{}^i) \ln[(N-2n_{ib}{}^i)\Delta V_i] \\ & + (N-n_B{}^i) \ln[(N-n_B{}^i)\Delta V_i] - (N-2n_{ib}{}^i-n_B{}^i-n_{if}{}^i-n_+{}^i) \ln[(N-2n_{ib}{}^i-n_B{}^i-n_{if}{}^i-n_+{}^i)\Delta V_i] \\ & - (N-n_B{}^i-n_-{}^i) \ln[(N-n_B{}^i-n_-{}^i)\Delta V_i] - n_B{}^i \ln[n_B{}^i \Delta V_i] - n_{if}{}^i \ln[n_{if}{}^i \Delta V^b] - n_+{}^i \ln[n_+{}^i \Delta V_i] \\ & - n_-{}^i \ln[n_-{}^i \Delta V_i] + (\Delta V_i)^{-1} \sum_{j=0}^{(n_{ib}{}^i \Delta V_i - 1)} \ln[N\Delta V_i - 2j]\}\,. \end{aligned} \quad \text{(C2)}$$

This last term of (C2) is equal to

$$n_{ib}{}^i \ln(N\Delta V_i) - \frac{2}{N(\Delta V_i)^2} \sum_{j=0}^{(n_{ib}{}^i \Delta V_i - 1)} j \quad \text{(C3)}$$

as long as $n_{ib}{}^i/N \ll 1$. Now

$$\sum_{j=0}^{(n_{ib}{}^i \Delta V_i - 1)} j = \tfrac{1}{2}[(n_{ib}{}^i \Delta V_i)^2 - (n_{ib}{}^i \Delta V_i)]$$

and since $(n_{ib}{}^i \Delta V_i) \gg 1$ by assumption, (C3) becomes

$$n_{ib}{}^i \ln[N\Delta V_i] - (n_{ib}{}^i)^2/N\,. \quad \text{(C4)}$$

Using (C4), a variation of (C2) with respect to $n_+{}^i$, $n_-{}^i$, $n_{if}{}^i$, $n_{ib}{}^i$, and $n_B{}^i$ yields

$$\begin{aligned}\delta(\ln w_i) = \Delta V_i\Bigg\{ & \delta n_{if}{}^i \ln\left[\frac{N-2n_{ib}{}^i-n_B{}^i-n_{if}{}^i-n_+{}^i}{n_{if}{}^i}\right] + \delta n_{ib}{}^i \ln\left[\frac{z_{nn}(N-2n_{ib}{}^i-n_B{}^i-n_{if}{}^i-n_+{}^i)^2 N}{(N-2n_{ib}{}^i)^2 n_{ib}{}^i}\right] \\ & + \delta n_B{}^i \ln\left[\frac{z_n(N-2n_{ib}{}^i-n_B{}^i-n_{if}{}^i-n_+{}^i)(N-n_B{}^i-n_-{}^i)}{(N-n_B{}^i)n_B{}^i}\right] \\ & + \delta n_+{}^i \ln\left[\frac{N-2n_{ib}{}^i-n_B{}^i-n_{if}{}^i-n_+{}^i}{n_+{}^i}\right] + \delta n_-{}^i \ln\left[\frac{N-n_B{}^i-n_-{}^i}{n_-{}^i}\right]\Bigg\}\,. \end{aligned} \quad \text{(C5)}$$

For the entire crystal, the configurational entropy S_c and its variation are given by (B3) and (B4) of Appendix B with $\delta(\ln w_i)$ given by (C5). Converting to a continuum representation with all quantities functions of x only, the final result is

$$\begin{aligned}\frac{\delta S_c}{\text{unit area}} = k\int_0^L dx\Bigg\{ & \delta n_{if}(x) \ln\left[\frac{N-2n_{ib}(x)-n_B(x)-n_{if}(x)-n_+(x)}{n_{if}(x)}\right] \\ & + \delta n_{ib}(x) \ln\left[\frac{z_{nn}(N-2n_{ib}(x)-n_B(x)-n_{if}(x)-n_+(x))^2 N}{(N-2n_{ib}(x))^2 n_{ib}(x)}\right] \\ & + \delta n_B(x) \ln\left[\frac{z_n(N-2n_{ib}(x)-n_B(x)-n_{if}(x)-n_+(x))(N-n_B(x)-n_-(x))}{(N-n_B(x))n_B(x)}\right] \\ & + \delta n_+(x) \ln\left[\frac{N-2n_{ib}(x)-n_B(x)-n_{if}(x)-n_+(x)}{n_+(x)}\right] + \delta n_-(x) \ln\left[\frac{N-n_B(x)-n_-(x)}{n_-(x)}\right]\Bigg\}\,. \end{aligned} \quad \text{(C6)}$$

Conditions (B6) and (B7) of Appendix B must be satisfied in this case also.

APPENDIX D: EVALUATION OF THE LAGRANGE MULTIPLIER $\alpha_{H}{}^{+}$

The condition determining the Lagrange multiplier is that the total number of impurities must be conserved,

$$\int_0^L dx(n_{if}+n_{ib}) = \text{number of impurities in the crystal per unit area.} \quad \text{(D1)}$$

The densities n_{if} and n_{ib} are given in (4.5) assuming all defect concentrations to be small.

Consider a unit area of the crystal. The number of bound impurities is

$$\int_0^L dx n_{ib} = z_{nn} N L \exp\{-(F^+ - B_+ + \alpha_H{}^+)/kT\}, \quad \text{(D2)}$$

and the number of free impurities is

$$\int_0^L dx n_{if} = N\kappa_+{}^{-1} \exp\{-(\alpha_H{}^+ + e\Phi_\infty)/kT\} \times \int_0^{\kappa_+ L} \exp\{-z\} ds, \quad \text{(D3)}$$

with z given by (3.19) since $\alpha_H{}^+$ is the multiplier when $\kappa_+ L \gg 1$. Defining the integral in (D3) as I,

$$I = \int_0^{\kappa_+ L} \exp(-z) ds, \quad \text{(D4)}$$

and making the substitution

$$e^{-s} \tanh(z_0/4) = \tanh(\eta/2),$$

I can be shown to be

$$I = \int_{2\gamma_+}^{z_0/2} \frac{d\eta \cosh 2\eta}{\sinh\eta} - \int_{2\gamma_+}^{z_0/2} \frac{d\eta \sinh 2\eta}{\sinh\eta}, \quad \text{(D5)}$$

where

$$\gamma_+ = \tanh^{-1}\{e^{-\kappa_+ L} \tanh(\tfrac{1}{4}z_0)\}. \quad \text{(D6)}$$

The integrals in (D5) can be readily evaluated so that

$$I = \kappa_+ L + 2\exp\{-\tfrac{1}{2}z_0\} - 2 \times \exp\{-2\tanh^{-1}(e^{-\kappa_+ L} \tanh(\tfrac{1}{4}z_0))\}. \quad \text{(D7)}$$

Since the mean impurity concentration within the crystal is $\bar{C}$, the number of impurities per unit area is $\bar{C}NL$. Hence $\bar{C}NL$ is equal to the sum of (D2) and (D3) using (D7) so that

$$\bar{C} = z_{nn} \exp\{-(F^+ - B_+ + \alpha_H{}^+)/kT\} + \exp\{-(\alpha_H{}^+ + e\Phi_\infty)/kT\} \times [1 + 2(\kappa_+ L)^{-1}(\exp(-\tfrac{1}{2}z_0) - \exp\{-2\tanh^{-1}(e^{-\kappa_+ L} \tanh\tfrac{1}{4}z_0)\})]. \quad \text{(D8)}$$

Since $\kappa_+ L \gg 1$, $\exp[-2\tanh^{-1}\{\exp(-\kappa_+ L)\tanh(\tfrac{1}{4}z_0)\}] \simeq 1$ and the term containing $(\kappa_+ L)^{-1}$ is significant only for $\exp(-\tfrac{1}{2}z_0) \gg 1$. Thus we have

$$\bar{C} \simeq z_{nn} \exp\{-(F^+ - B_+ + \alpha_H{}^+)/kT\} + \exp\{-(\alpha_H{}^+ + e\Phi_\infty)/kT\} \times [1 + 2(\kappa_+ L)^{-1} \exp\{-\tfrac{1}{2}z_0\}]. \quad \text{(D9)}$$

Defining

$$\zeta_+ = \left[\frac{8\pi N e^2}{\epsilon kT} \exp\left\{-\frac{F^+}{kT}\right\}\right]^{1/2} = \kappa_+ \exp(z_0/2) \quad \text{(D10)}$$

and

$$\xi_+ = 1 + 2(\zeta_+ L)^{-1}, \quad \text{(D11)}$$

we conclude

$$\bar{C} = z_{nn} \exp\{-(F^+ - B_+ + \alpha_H{}^+)/kT\} + \xi_+ \exp\{-(\alpha_H{}^+ + e\Phi_\infty)/kT\} \quad \text{(D12)}$$

so that

$$\exp\left\{-\frac{\alpha_H{}^+}{kT}\right\} = \frac{\bar{C}}{z_{nn} \exp\{-(F^+ - B_+)/kT\} + \xi_+ \exp\{-e\Phi_\infty/kT\}}. \quad \text{(D13)}$$

Note that L in the present model is the volume-to-surface ratio.