and the average rate of energy loss $\bar{P}$ is then

$$\bar{P}=\frac{1}{N_aN_e}\int_0^\infty\int_0^\infty d\mathbf{V}d\mathbf{v}v\sigma_t\mu_0(\mathbf{V}_0\cdot\mathbf{v})F_e(v)F_a(V), \quad (14)$$

where $F_e(v),N_e$ and $F_a(V),N_a$ refer to electrons and atoms, respectively.

Values of $\bar{P}$ are shown in Fig. 7, the temperature of the gas atoms being taken as 293°K. The dotted curve is one calculated by Kenty,[10] using the Compton formula,[11] and total cross-section data of Ramsauer and Kollath. He assumed a Maxwell-Boltzmann distribution for the electrons, neglecting the motion of the gas atoms. He also measured the loss experimentally, over a limited range of electron temperature from 0.84 ev to 1.29 ev. His calculated values differed from his experiment by a few percent at the lower temperature and by about 20 percent at the higher temperature. If one makes the comparison using the values of elastic loss per electron derived from the phase-shifts, the agreement is better than 6 percent over the range of Kenty's experimental values.

V. DISCUSSION

The probable accuracy of these calculations is estimated to be within 10 percent for electron energy greater than 0.15 ev. The main source of error lies in the original set of phase shifts. A direct comparison with theoretical calculations is possible only for helium. The zero-order phase shift for helium used in these calculations agrees very closely with a calculation by Morse and Allis[12] using a Hartree field, and also with a recent calculation by Moiseiwitsch[13] using a variational method. For $k<1.0$ (13.5 ev) the agreement among the three is about 1 percent; and for $k<2.5(\sim 85$ ev) the agreement is better than 6 percent.

There are two features of significance in these phase shift calculations. First, the extrapolation of phase shifts to energies less than 1 or 2 ev is probably more reliable than extrapolation of the direct scattering data. Second, the transport cross sections constitute a central set of data from which many discharge parameters can be calculated; thus, if experimental agreement is established for several parameters, then one can more confidently extend the calculations to parameters which are not easily measured accurately.

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[10] Kenty, Easley, and Barnes, J. Appl. Phys. 22, 1006 (1951).

[11] K. T. Compton, Phys. Rev. 22, 333 (1923).

[12] P. M. Morse and W. P. Allis, Phys. Rev. 44, 269 (1933).

[13] B. L. Moiseiwitsch, Proc. Roy. Soc. (London) A219, 102 (1953).

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Ionic Conductivity of Impure Polar Crystals*

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Experimental determinations of the ionic conductivity of impure or "doped" alkali halide crystals are often used to find the mobility of the cation vacancies. For this purpose it is important to know to what extent the vacancies and the impurity ions have associated together to form neutral "complexes," which do not contribute to the conductivity. Previous interpretations of the experimental data have relied largely on the law of mass action to give the degree of association, but have neglected the long-range Coulomb interactions between the unassociated impurity ions and vacancies. The effect of these interactions on the calculated degree of association and upon the dc conductivity is examined in this paper. The interactions are shown to be significant even in systems containing impurities in concentrations of no more than one part in 10^4. A new analysis of the results obtained by Etzel and Maurer for the system $NaCl+CdCl_2$, leads to a binding energy of about 0.35 ev for the cadmium ion-vacancy complex. The mobility of the sodium ion vacancy is found to be about 30 percent larger, at all temperatures, than was inferred by Etzel and Maurer, using a simpler theory to interpret the data. The activation energy for the vacancy motion remains however at about 0.9 ev.

I. INTRODUCTION

THE ionic conductivity of polar crystals has in recent years engaged the attention of many investigators. The earlier work, mainly on pure crystals, has been reviewed by Mott and Gurney[1] and by Seitz.[2] More recent reviews have been given by Jacobs and Tompkins,[3] and by Jost.[4]

In general the ionic current is carried by the migration of lattice vacancies and interstitial ions. The analysis of the experimental data is complicated by the temperature dependence not only of the numbers of the various carriers but also of their mobilities. Thus the

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[1] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, Oxford, 1948), Chap. II.

[2] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. XV.

[3] P. W. M. Jacobs and F. C. Tompkins, Quart. Revs. London 6, 238 (1952).

[4] W. Jost, *Diffusion in Solids, Liquids, Gases* (Academic Press, New York, 1952), Chap. IV.

contribution of a particular carrier to the conductivity is limited both by the thermal energy needed to create it and by the energy barriers which prevent its free migration once it is formed. Uncertainties in the values of these energies limit the usefulness of the theory of conduction in the general ionic crystal.[5] Particular substances may however present simplified situations. Thus in AgBr, the ionic current is carried only by the interstitial silver ions and by the silver ion vacancies. The alkali halides are an even simpler example. Here interstitial ions do not occur to any appreciable extent and, at least for temperatures less than about 400°C,[6] the cation vacancies alone carry the current. But the situation can be refined further. Consider, for example, the solution of small amounts of $CdCl_2$ in NaCl. The Cd^{++} ions enter the Na^+ lattice substitutionally, but owing to their double charge there must also be introduced an equal number of Na^+ vacancies in order to maintain electrical neutrality. Since the number of thermally produced vacancies is very small, it only needs an impurity content of one part in 10^4 to keep the number of vacancies quite independent of temperature. Hence, by considering a "doped" alkali halide crystal we have a system with only one type of current carrier, the latter being present in known constant amount. The same situation can be obtained in the silver halides, although here much larger additions[7] of the divalent ion are required (about 1 percent).

It might appear that we have now so simplified the system as to make it of no further theoretical interest and of experimental interest only in so far as it enables a simple direct measure of the cation vacancy's mobility. That this is not so is because of the effective negative charge $(-e)$ carried by the cation vacancy and the effective positive charge $(+e)$ of the divalent impurity ions. Now charges of the same kind repel one another, and unlike charges attract, so that at the absolute zero of temperature the lowest-energy state of the system will be one in which each impurity ion has a cation vacancy attached to it in the nearest neighboring position.[8] Such a pair is spoken of as a "complex." At higher temperatures some of these attachments will be broken, and the thermodynamic state at a temperature T can be described by giving the number of complexes which remain. Now the complexes have no net charge and so do not contribute to the conductivity. In the interpretation of conductivity data it is therefore important to know the number of complexes present, particularly as a function of the impurity concentration. The law of mass action has been used for this purpose by several workers.[9–11] At any given temperature let there by n complexes present; if the total number of impurity ions is N_i there will be N_i-n unassociated vacancies, and the law of mass action states that

$$\frac{N_+ n}{(N_i-n)^2}=K(T), \tag{1}$$

where $K(T)$ is a function only of the temperature. The number of solvent cations is denoted by N_+. Equation (1) enables us to calculate the variation in the degree of association n/N_i, i.e., the variation in the conductivity, as we alter the concentration N_i/N_+ of the impurity. It was on this basis that Etzel and Maurer[11] analyzed their experimental data on the system $NaCl+CdCl_2$.

However, by requiring $K(T)$ to be independent of N_i we are implicitly neglecting the interactions between unassociated impurity ions and vacancies. As far as we are aware they have not yet been taken into account in the present connection,[12] although an indication of their possible importance has been obtained by Teltow.[10] He analyzed his data on $AgBr+CdBr_2$ both on the basis of an association described by (1) and also on the assumption that the vacancies and impurity ions formed an unassociated (strong) Debye-Hückel electrolyte. At impurity concentrations of less than one percent the data could be fitted reasonably well on either basis, although for larger concentrations it was apparent that some combination of the two assumptions was necessary We therefore propose to retain the idea of associated complexes, but in addition to treat the unassociated vacancies and impurity ions as forming a Debye-Hückel electrolyte in which the neutral complexes are immersed. It is of general interest to study the effect of neglecting the long range interactions among the unassociated charges and in the present paper we shall discuss this question with the aid of a simple model in which they are taken to be Coulombic at all distances. Although the calculations of Reitz and Gammel[13] for the system $NaCl+CdCl_2$ show that this is unlikely to be accurate at distances as small as the nearest neighbor separation, it does not seem probable that this error will materially affect our general conclusions about the influence of the

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[5] General equations giving the number of vacancies and interstitial ions, of both kinds, have been derived by R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1939), Chap. XIII.

[6] See Table XV of reference 2.

[7] The conductivity of AgCl and AgBr containing lead and cadmium ions has been studied by E. Koch and C. Wagner, Z. physik. Chem. **B38**, 295 (1937) and by J. Teltow, Ann. Physik, **5**, 63 (1949).

[8] This is, of course, the nearest neighboring position on the cation sublattice. Since the anion sublattice plays no active role in our considerations we shall speak of the cation sublattice simply as the lattice. Thus in NaCl the "lattice" is of face-centered cubic type.

[9] O. Stasiw and J. Teltow, Ann. Physik **1**, 261 (1947).

[10] J. Teltow, Ann. Physik **5**, 71 (1949).

[11] H. W. Etzel and R. J. Maurer, J. Chem. Phys. **18**, 1003 (1950).

[12] J. Frenkel [*Kinetic Theory of Liquids* (Clarendon Press, Oxford, 1946), p. 36 ff.], considering the thermal production of anion and cation vacancies in the pure salt, had earlier shown how these long range interactions would lead to a space change in the surface regions of the crystal. See also a recent paper by K. Lehovec [J. Chem. Phys. **21**, 1123 (1953)].

[13] J. R. Reitz and J. L. Gammel, J. Chem. Phys. **19**, 894 (1951). These calculations have since been extended by F. Bassani and F. G. Fumi who have calculated association energies between vacancies and Cd, Ca, and Sr impurity ions in both NaCl and KCl [Nuovo cimento (to be published)]. I am very grateful to Professor Fumi for informing me of their results prior to publication.

interaction.[14] The assumption that the interaction is purely Coulombic has the practical advantage of leading to a set of equations containing a minimum of unknown parameters. Our aim is thus not so much to account in detail for one special system as to see those effects of the long-range forces between the unassociated charges which are common to all systems. In the next section we obtain equations showing the influence of these forces on the degree of association into complexes, as a function of temperature and impurity content. Numerical results giving n/N_i as a function of T for various molar concentrations between 10^{-4} and 10^{-2} are exhibited graphically. In Sec. III we apply these results to the derivation of the steady dc conductivity. We show that departures from the simple association theory[11] may well be detectable even at impurity concentrations as low as a few parts in 10^4. A fresh analysis of the experimental data obtained by Etzel and Maurer (in Sec. IV) bears out this deduction. In the course of this analysis we obtain a value of 0.35 ev for the binding energy of the Cd^{++}: vacancy complex in NaCl. The activation energy for vacancy diffusion in NaCl deduced by Etzel and Maurer to be 0.9 ev is unaltered, although we find that the mobility is some 30 percent larger than is predicted by their Eq. (18). In subsequent papers we shall apply these calculations to a discussion of diffusion and of the ac conductivity and dielectric loss.

II. DEGREE OF ASSOCIATION INTO COMPLEXES

Our problem in this section is the calculation of the degree of association between the impurity ions and the cation vacancies. As explained in the introduction we shall take the potential energy of two such "charges" separated by a distance r to be,

$$V(r)=\pm\frac{e^2}{\epsilon r}. \tag{2}$$

The positive sign is taken when the "charges" are the same and the negative sign when they are different; ϵ is the static dielectric constant of the pure solvent salt. We may proceed therefore by considering the Helmholtz free energy F of an alkali halide crystal, which is perfect except for the presence in the cation sublattice of N_i divalent impurity ions and N_i vacancies, interacting with one another according to Eq. (2). It may be assumed that F can be written as the sum of two parts: (1) a configurational term directly dependent on the presence of the impurities and (2) a vibrational term which is independent of the arrangement of the impurities in the lattice. (That the vibrational contribution to the free energy is independent of the arrangements of the impurity ions and vacancies can easily be justified as a first approximation.) In calculating the degree of association we then need not consider the second term at all. When in the following we speak of the free energy, we shall in fact mean only the configurational free energy, since this is all we shall need.

We shall suppose that of the N_i impurity ions and N_i vacancies which are distributed among the cation lattice sites, n are paired together into complexes. Each complex has z distinguishable orientations since the vacancy can be at any one of the z nearest neighboring positions to the impurity ion. The complexes have no net charge and we shall be justified in neglecting their small dipolar interactions with one another and with the unassociated charges. If now the impurity content is *sufficiently low for us also to neglect the mutual interactions of the unassociated charges* if follows immediately that the configurational free energy is

$$F_0=-kT\ln\left\{\frac{z^n\prod_{s=0}^{n}(N_{+}+2N_i-2s)}{n!}\cdot\frac{(N_{+}+2(N_i-n))!}{N_{+}!(N_i-n)!(N_i-n)!}\right\}-\frac{ne^2}{\epsilon r_0}. \tag{3}$$

The first term is the entropy term, the expression inside the braces being the product of the number of distinguishable ways of placing the n complexes on the lattice and the number of ways of arranging the remaining N_i-n impurity ions and N_i-n vacancies. The second term in the expression (3) is the energy of association, calculated by substituting the nearest neighbor separation, r_0 into Eq. (2). We can now obtain the equilibrium number of complexes by minimizing F_0 with respect to n. Using Stirling's theorem and the condition $N_i/N_{+}\ll 1$ we find

$$\frac{N_{+}n}{(N_i-n)^2}=z\exp\left(\frac{e^2}{\epsilon r_0 kT}\right). \tag{4}$$

This is equivalent to the mass action formula (1), although (4) gives an explicit form for the temperature dependence of the equilibrium constant. If we rewrite (4), in terms of the molar concentration,

$$c=N_i/N_{+}, \tag{5}$$

and the degree of association,

$$p=n/N_{+}, \tag{6}$$

we get

$$p=1-\frac{1}{y}[-1+(1+2y)^{\frac{1}{2}}], \tag{7}$$

where

$$y=\exp\left[\frac{T_0}{T}+\ln(2zc)\right]. \tag{8}$$

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[14] We would draw attention to the theory of liquid electrolyte solutions which has achieved great success, even though it neglects specific non-Coulombic interaction forces between ions close to one another. See, for example, H. Falkenhagen, *Electrolytes* (Oxford University Press, Oxford, 1934).

Here T_0, equal to $e^2/\epsilon r_0 k$, is the binding energy in units of Boltzmann's constant. We note that to derive (7) and (8) it is not necessary to make any assumption about the source of the binding energy. In Fig. 1 we show p as a function of T/T_0 for three different concentrations.

We now have to consider how these results are modified when the interactions between the unassociated ions and vacancies are not sufficiently small as to be negligible. The necessary modification in expression (3) can be obtained from the theory of electrolyte solutions, since our system of unassociated ions and vacancies is equivalent to a solution of a binary electrolyte in a medium of dielectric constant ϵ. The fact that our "ions" can only occupy discrete lattice positions whereas the ions in a solution can move around continuously, is not likely to be significant at the small concentrations occurring in this problem. For, at these concentrations, the average separation between charges will be much larger than the lattice spacing, and the discreteness of the allowed positions will be unimportant. We shall therefore describe the effects of the Coulomb interactions between the unassociated impurity ions and vacancies by means of the equations of the Debye-Hückel theory of electrolytes.[15] In applying these equations, we have to be careful not to allow an impurity ion and a vacancy to approach closer than the next nearest neighboring distance r_1, since if they approached as close as the nearest neighboring distance they would be considered as a complex and therefore not part of our unassociated "electrolyte." We shall therefore take the ionic radius parameter of the electrolyte theories to be r_1. We are now in a position to write down the additional free energy F_{el} due to interactions, which must be added to F_0 to get the total configurational free energy. From Eq. (913.1) of reference 5 we have:

$$F_{el}=\frac{-2(N_i-n)e^2}{3\epsilon}\cdot\kappa\tau(\kappa r_1). \tag{9}$$

where κ, the Debye-Hückel screening constant, is given by

$$\kappa^2=\frac{8\pi(N_i-n)e^2}{V\epsilon kT}, \tag{10}$$

and

$$\tau(x)=\frac{3}{x^3}\left\{\ln(1+x)-x+\frac{x^2}{2}\right\}. \tag{11}$$

In Eq. (10) V is the volume of the crystal. We can now find the equilibrium value of n, the number of complexes by minimizing the sum of F_0 and F_{el} with respect to n. In place of (4) we get

$$\frac{nN_+}{(N_i-n)^2}=z\exp\left\{\frac{1}{kT}\left[\frac{e^2}{\epsilon r_0}-\frac{1}{2}\left(\frac{2e^2}{\epsilon}\right)^{\frac{3}{2}}\times\left(\frac{4\pi(N_i-n)}{VkT}\right)^{\frac{1}{2}}\cdot\frac{1}{1+\kappa r_1}\right]\right\}. \tag{12}$$

This equation is essentially the same as one derived by Bjerrum[16] in his theory of ionic association in electrolyte solutions. His definition of association is, however, more general than the association into complexes which we have used. In the language of our problem, it includes impurity vacancy pairs farther apart than nearest neighbors. The extension of our calculations in this manner is considered in the final section.

Equation (12) can be derived in a more intuitive way starting from (4), if we notice that the additional term in the exponential is merely the average potential energy of an unassociated vacancy in its surrounding Debye-Hückel charge cloud [see, for example, Eq. (911, 10) of reference 5]. The total expression in the square brackets is therefore the effective energy of excitation for a vacancy going from the associated to the unassociated state.

In order to obtain numerical results from Eq. (12) we have to make assumptions about the nature of the lattice, so that r_0 and r_1 may be related to one another and to V. Let us consider the NaCl-type lattice; here the cation sub-lattice is face-centered cubic, so that $z=12$, $r_1/r_0=\sqrt{2}$, and $V=2N_+a^3$, where a is the anion-cation separation equal to $r_0/\sqrt{2}$. With this assumption

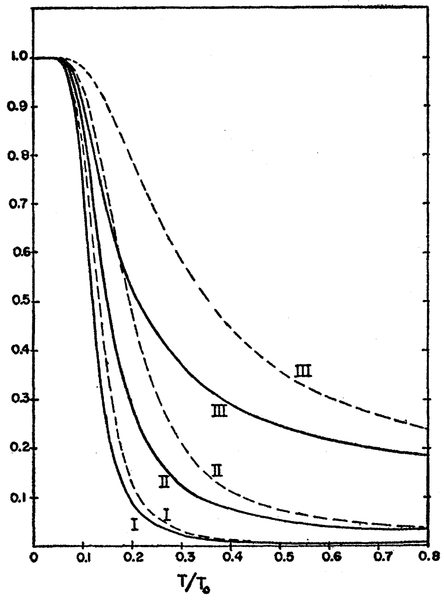

FIG. 1. Curves showing the degree of association p as a function of the reduced temperature T/T_0 at three different concentrations; I, $c=10^{-4}$; II, $c=10^{-3}$; III, $c=10^{-2}$. The dashed lines have been obtained from Eqs. (7) and (8); the full lines were calculated from Eq. (13).

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[15] For a complete account see the reference cited in footnote 14. However for the purpose of this section it is more convenient to refer to Chapter IX of reference 5, particularly Secs. 904 through 914.

[16] N. Bjerrum, Kgl. Danske Videnskab. Selskab., Mat.-fys. Medd. 7, No. 9, (1926). See also Sec. 924 of reference 5.

of a face-centered cubic lattice, Eq. (12) can be rewritten as

$$\frac{p}{(1-p)^2}=\exp\left[\frac{T_0}{T}+\ln(12c)-\frac{2(2\pi\sqrt{2})^{\frac{1}{2}}(T_0/T)^{\frac{3}{2}}[(1-p)c]^{\frac{1}{2}}}{\{1+4(\pi\sqrt{2})^{\frac{1}{2}}[(1-p)cT_0/T]^{\frac{1}{2}}\}}\right]. \quad (13)$$

For $c\leqslant 10^{-3}$ it was found convenient to solve (13) by successive approximations using the pairs of equations [see (7) and (8)]:

$$p^{(j+1)}=1-\frac{1}{y^{(j)}}[-1+(1+2y^{(j)})^{\frac{1}{2}}], \quad (14)$$

and

$$y^{(j)}=\exp\left[\frac{T_0}{T}+\ln(24c)-\frac{2(2\pi\sqrt{2})^{\frac{1}{2}}(T_0/T)^{\frac{3}{2}}[(1-p^{(j)})c]^{\frac{1}{2}}}{\{1+4(\pi\sqrt{2})^{\frac{1}{2}}[(1-p^{(j)})cT_0/T]^{\frac{1}{2}}\}}\right], \quad (15)$$

and starting with $y^{(0)}$ given by (8). For concentrations greater than 10^{-3} this process requires more than three iterations, and it is more convenient to rearrange (13) to give T/T_0 as a function of p. Thus,

$$\left(\frac{T}{T_0}\right)^{\frac{3}{2}}\ln\left(\frac{p}{12c(1-p)^2}\right)+\left(\frac{T}{T_0}\right)\cdot 4(\pi\sqrt{2})^{\frac{1}{2}}(1-p)^{\frac{1}{2}}c^{\frac{1}{2}}\ln\left(\frac{p}{12c(1-p)^2}\right)-\left(\frac{T}{T_0}\right)^{\frac{1}{2}}+(1-p)^{\frac{1}{2}}c^{\frac{1}{2}}(\pi\sqrt{2})^{\frac{1}{2}}(2\sqrt{2}-4)=0. \quad (16)$$

In Fig. 1 we show the solutions of (13) for concentrations 10^{-2}, 10^{-3}, and 10^{-4} and for comparison we also show the corresponding solutions of (7) and (8). (Results have also been obtained for a number of other concentrations; details will be supplied on request.) We notice that the effect of the Coulomb interactions is to hasten the decay of p with increasing T, and that this effect is more pronounced the greater the impurity content. Even so the transition is not especially sharp; for example, since T_0 is of the order of several thousand degrees a system containing 1 percent of impurity would have to be raised many hundreds of degrees in order to reduce the degree of association from 90 percent to 40 percent. In the normal region of experimentation on ionic conductivity the degree of association is thus an appreciable fraction of unity. The gradualness of the transition also means that any thermal effects due to the dissociation of complexes will be very slight. Thus there will be an additional specific heat which may be calculated from (3) and (9) by using the formula

$$C_v=-Td^2(F_0+F_{el})/dT^2. \quad (17)$$

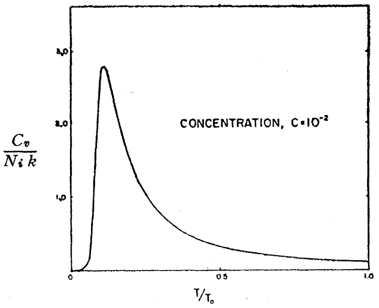

FIG. 2. The configurational specific heat, in units of the gas constant per gm-mole of impurity, as a function of the reduced temperature, T/T_0; impurity concentration, 10^{-2} mole per mole.

This is shown as a function of T in Fig. 2 for a lattice of the NaCl type and an impurity concentration of 10^{-2}. The apparent sudden rise of C_v from zero to nearly 0.03 R per gram-mole probably requires several hundred degrees to occur. This combined with the small height of the peak makes it seem quite impossible that the transition could be observed experimentally in this way. Nevertheless Dr. H. Kanzaki at the University of Tokyo in a private communication to the author, has reported the occurrence of a small λ-type anomaly in the specific heat of AgCl+1 percent $CdCl_2$ at 310°C which is not present in pure AgCl. He also reports a similar peak in the specific heat of AgBr+1 percent $CdBr_2$, occurring at about 130°C, but whose precise shape depends on the heat treatment which the specimen has undergone. As explained later in Sec. V, even our Eq. (13) probably underestimates the sharpness of the transition in real systems, and it is at least *possible* that the decomposition of the complexes could be detected thermally by measurements such as those which Kanzaki has made.

III. THE STEADY DC CONDUCTIVITY

As in the last section we can ignore the small dipolar interactions between the complexes and the unassociated impurity ions and vacancies. Furthermore, the complexes being neutral, we may forget them in this section since we shall only be concerned with the conductivity in the presence of a constant applied field E.[17] The unassociated impurity ions have no mobility *by themselves*,[18] so that they too make no direct contribution to the conductivity. They are however of indirect importance in that they form part of the Debye-Hückel

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[17] This is only permissible for fields for which Ohm's law is obeyed. At higher fields the equilibrium number of complexes depends on E; see L. Onsager, J. Chem. Phys. 2, 599 (1934).

[18] This does not imply that the impurity ions are permanently fixed at their positions in the lattice. An impurity ion may move whenever there is an adjacent vacancy into which it can jump, although not otherwise. In other words at any instant only the associated impurity ions are mobile, but since the equilibrium existing in the numbers of associated and unassociated impurity ions is a dynamical equilibrium, *every* impurity ion before long gets its chance to move. Hence it is legitimate to assume a thermodynamic equilibrium distribution of impurity ions, even though they make no direct contribution to the conductivity.

atmosphere which hinders the motion of the vacancies. We express the conductivity σ in terms of the mobility u of the unassociated vacancies, as follows:

$$\sigma=\frac{N_i(1-p)}{V}\cdot eu. \tag{18}$$

In the absence of interactions between the impurity ions and the cation vacancies, u is independent of concentration and may be calculated in the way used by Mott and Gurney.[1] To be definite let us again take the face-centered cubic lattice; we then find that

$$u=4a^2ew_0/kT, \tag{19}$$

in which w_0 is the field free probability that a vacancy will jump to one particular neighboring position in unit time. This probability w_0 is a quantity explicitly independent of the impurity concentration. We may write it in terms of a frequency factor ν and a barrier height U as

$$w_0=\nu e^{-U/kT}, \tag{20}$$

(see Seitz, reference 2, particularly Sec. 122). In general this restriction is perhaps too naive, for we must expect that the introduction into the lattice of foreign ions and their accompanying vacancies will give rise to distortions such as to alter the barrier height U. This point has not received much attention so far,[19] but at least for the system $NaCl+CdCl_2$ to which we shall apply these equations the distortion at the limit of solubility is too small to be observable (private communication from Professor H. Pick). In deriving Eq. (19) it has been assumed that the field acting to make the vacancy jump preferentially in one direction, is the macroscopic internal electric field E ("pipe" field), and not a Lorentz internal field depending on the polarization of the crystal. The reasons for regarding this as a good approximation are contained in Sec. 5 in Chapter 1, reference 1.

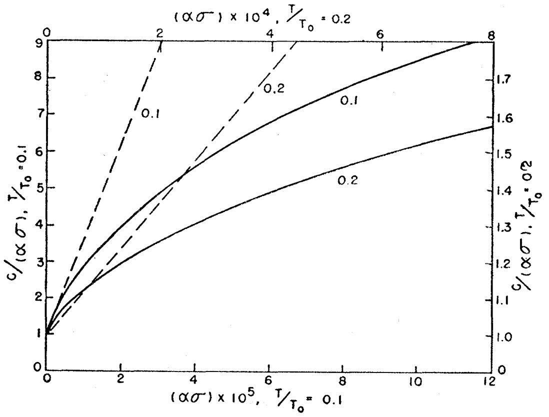

FIG. 3. Curves of $c/\alpha\sigma$ against $\alpha\sigma$ showing the difference between the simple association theory (dashed lines) and the theory presented here (full lines). The numbers on the curves are the corresponding values of T/T_0.

At impurity concentrations where the Coulomb forces become important Eq. (19) for the mobility is not sufficient. The long-range interactions lead to the same relaxation effects as occur in the electrolyte solutions.[20] The tendency of a vacancy to be held back by its "atmosphere" of impurity ions requires us to multiply (19) by some factor $f<1$, in order to get the true mobility for substitution into (18). The theory of Onsager,[21] gives

$$f_0=1-\frac{e^2\kappa}{3\epsilon kT(2+\sqrt{2})}. \tag{21}$$

Here we have dropped the electrophoretic term, which has meaning in a liquid where the ions can drag the solvent along with them, but no meaning in connection with our crystal. The factor (21) has been previously used in the present connection by Teltow.[10] However, the formula (21) omits to take account of the closest distance of approach of the ions. Fortunately the electrolyte theory has been recently extended by Pitts,[22] and in place of (21) we shall take

$$f=1-\frac{e^2\kappa}{3\epsilon kT(\sqrt{2}+1)(1+\kappa r_1)(\sqrt{2}+\kappa r_1)}. \tag{22}$$

We may substitute for κ in terms of p, c, and T, so that for our face-centered cubic lattice, (22) becomes

$$f=1-\frac{2(2\pi\sqrt{2})^{\frac{1}{2}}}{3(\sqrt{2}+1)}\cdot\frac{c^{\frac{1}{2}}(1-p)^{\frac{1}{2}}(T_0/T)^{\frac{3}{2}}}{(1+\kappa r_1)(\sqrt{2}+\kappa r_1)}, \tag{23}$$

with

$$\kappa r_1=2\kappa a=4(\pi\sqrt{2})^{\frac{1}{2}}c^{\frac{1}{2}}(1-p)^{\frac{1}{2}}(T_0/T)^{\frac{1}{2}}. \tag{24}$$

Collecting together (18), (19), and (23), we obtain as the expression for the ionic conductivity:

$$\sigma=\frac{2e^2w_0}{akT}\cdot c(1-p)\times\left[1-\frac{2(2\pi\sqrt{2})^{\frac{1}{2}}}{3(\sqrt{2}+1)}\cdot\frac{c^{\frac{1}{2}}(1-p)^{\frac{1}{2}}(T_0/T)^{\frac{3}{2}}}{(1+\kappa r_1)(\sqrt{2}+\kappa r_1)}\right], \tag{25}$$

in which p is the solution of (13). The simple association theory as expressed by Eqs. (7), (8), (18), and (19) leads to a conductivity σ' given by

$$\sigma'=\frac{2e^2w_0}{akT}c(1-p^{(0)}). \tag{26}$$

If we abbreviate $2e^2w_0/akT$ by $1/\alpha$, we may write (26) with the aid of (7) and (8) as

$$c=\alpha\sigma'+12e^{T_0/T}(\alpha\sigma')^2. \tag{27}$$

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[19] The theory of a similar problem in metals has been given by A. W. Overhauser, Phys. Rev. **90**, 393 (1953).

[20] See Chap. IX of reference 14, or alternatively H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolyte Solutions* (Reinhold Publishing Company, New York, 1950), second edition, Chaps. 2 and 4.

[21] L. Onsager, Physik. Z. **28**, 286 (1927), Eq. (45).

[22] E. Pitts, Proc. Roy. Soc. (London) **A217**, 43 (1953).

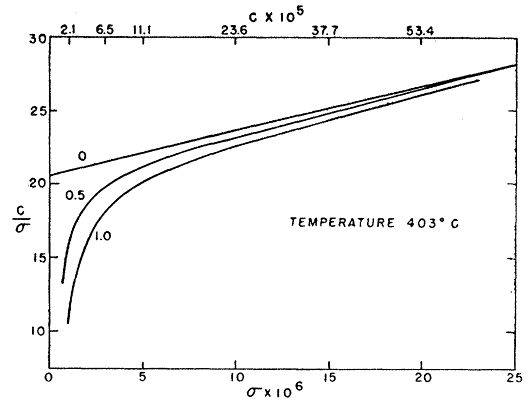

FIG. 4. Curves showing the effect of "background" impurity on plots of c/σ against σ (σ in ohm^{-1} cm^{-1}). The straight line corresponds to Eq. (29), as used by Etzel and Maurer to describe experimental results for the system NaCl+CdCl$_2$. The numbers on the curves are the concentrations c_0, of background impurity in units of 10^{-5}.

The conductivity σ given by (25) does not satisfy any such simple relation. We can see from (27) that a plot of $c/\alpha\sigma'$ against $\alpha\sigma'$ will give us a straight line. On the other hand, from Fig. 3 it is quite clear that the curves of $c/\alpha\sigma$ against $\alpha\sigma$ are only approximately straight lines at the higher concentrations; at lower concentrations the curvature increases and, in fact, as c and thus σ tend to zero the gradient $d(c/\alpha\sigma)/d(\alpha\sigma)$ diverges as $c^{-\frac{1}{2}}$. We also notice from Fig. 3 that the curves of $c/\alpha\sigma$ against $\alpha\sigma$ bear no simple relation to the particular straight lines corresponding to (27), i.e., their gradients cannot be simply related to the corresponding values of $\exp(T_0/T)$.

Before proceeding to study the experimental results in the light of Eq. (25), we must first draw attention to the effects of having a small constant background of impurity cations in the lattice, in addition to the much greater number deliberately added. This is the situation existing in practice since no crystal can be obtained absolutely pure. Suppose then that in addition to the concentration c of divalent impurity purposely added, there was also, unknown to us, an amount c_0 already present. Then taking Eq. (27) as an adequate relation between the conductivity σ and the total concentration $c+c_0$ of cation vacancies, we would have

$$c/\sigma = -c_0/\sigma + \alpha + 12\alpha^2 e^{T_0/T}\sigma. \tag{28}$$

A plot of c/σ against σ would then be a straight line only at concentrations $c \gg c_0$. As c and therefore σ decreased, the curve would bend increasingly downwards as shown in Fig. 4. Such a curvature would entirely mask the smaller effects of the long range interactions between the unassociated impurity ions and vacancies. Fortunately this difficulty is easily overcome; the experimental results may be corrected by adding to c, a value of c_0 inferred from the conductivity of a "pure" crystal in its "structure-sensitive" or low-temperature region.[1,2]

In the next section we shall consider the experimental data collected by Etzel and Maurer[11] for the system of NaCl+CdCl$_2$. As suggested by the theory, we analyze the plots of $(c+c_0)/\sigma$ against σ at various temperatures. (This has been made possible by Dr. Etzel's courtesy in supplying us with numerical data not contained in reference 11). Other systems which have been studied experimentally, but which we shall not consider here, include KCl+CaCl$_2$, BaCl$_2$, SrCl$_2$,[23] NaCl+CaCl$_2$,[24] and the silver halide systems referred to above.

IV. THE DATA OF ETZEL AND MAURER

In Table I we give the experimental values of σ and c as obtained[11] for the system of NaCl+CdCl$_2$ at four different temperatures. By a least-squares method Etzel and Maurer fitted these data directly to a parabolic equation of the type (27) resulting from the simple association theory, i.e.,

$$c = F\sigma + L\sigma^2. \tag{29}$$

The values which they deduced for F and L were given in Table III of their paper, and it appears from their Fig. 3 that the fit is very good. However, as suggested by the results of the last section, we have plotted $(c+c_0)/\sigma$ against σ at the four temperatures of Table I (Fig. 5). For c_0 we have taken the value 0.45×10^{-5}, corresponding to 10^{17} vacancies per cc in the "pure" NaCl as found by Etzel and Maurer.[11] That this is a reasonably good value may be checked by plotting σ against c from Table I; the negative intercept on the c axis is c_0. (It is nevertheless rather unsatisfactory that there is so much scattering of the experimental points in view of the importance of the c_0 correction, but we note that we can argue that c_0 cannot be *greater* than 0.45×10^{-5}.) Looking at Fig. 5 we see definite evidence at all four temperatures of that gentle curvature in the c/σ *versus* σ lines which Fig. 3 indicates should result from the Coulomb interactions of the unassociated ions and vacancies. But if this really is the case, F and L cannot have the significance they would appear to have from a comparison of (29) with (27); thus for example

TABLE I. Experimental values for the electrical conductivity of the system NaCl+CdCl$_2$ at 403°C, 344°C, 295°C, and 256°C as a function of the molar concentration of CdCl$_2$.

Concentration, $c\times10^5$	Conductivity (ohm^{-1} cm^{-1}), $\times10^9$ at 403°C	344°C	295°C	256°C
66.3[a]	24 200	6200	1440	360
38.75[a]	14 500	3900	950	242
19.0	8600	2230	565	147
8.8	4400	1170	300	81
5.0	3200	860	215	58
5.1	2580	680	173	46
3.6	2380	610	156	41
1	1080	290	73	19
0	220	64	17	5

[a] Mean of two values.

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[23] H. Kelting and H. Witt, Z. Physik. **126**, 697 (1949).

[24] C. Bean, thesis, University of Illinois, 1952 (unpublished).

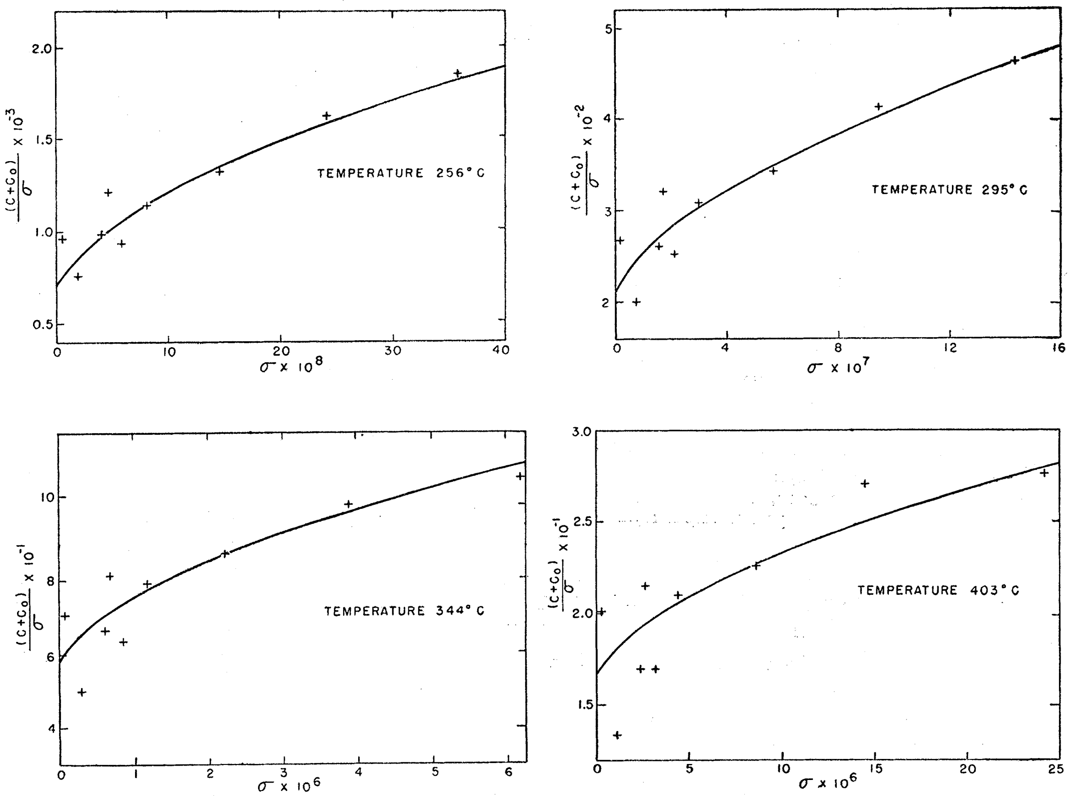

FIG. 5. The experimental data for NaCl+CdCl$_2$ given in Table I as represented by plots of $(c+c_0)/\sigma$ against σ (σ in ohm^{-1} cm^{-1}). For c_0 we have taken 0.45×10^{-5} as indicated in the text. The theoretical curves are obtained from Eq. (25) by taking $T_0=3900$°K and w_0 as given by (19) and (30).

L/F^2 is not 12 $\exp(T_0/T)$ and cannot be used to find the binding energy of the Cd^{++}: vacancy complex as Etzel and Maurer attempted to do. We therefore propose a new analysis of the data of Table I based on Eq. (25). This is complicated by our not knowing either T_0 which is a constant or w_0 which is a function of temperature.

We shall not give the details of the derivation of these unknowns but only a summary of the method. Firstly we draw a set of smooth curves (not marked) through the points shown in Fig. 5 and from these we obtain, at each temperature, the values of the conductivity σ, corresponding to selected values of the concentration, $c+c_0$. (The highest concentration we used was 5×10^{-4}, i.e., below the highest concentration studied experimentally.) We aim first to derive T_0; we therefore eliminate the factor w_0 by calculating the ratio $\sigma/\sigma(5\times10^{-4})$ at each of the selected concentrations. This ratio equals $\alpha\sigma/\alpha\sigma(5\times10^{-4})$ which by (25) depends only on c, which we know, and T/T_0 which we do not know. By graphical interpolation we can now obtain, at each concentration, a set of values of T/T_0 corresponding to the four experimental temperatures. We average these to get just one set, from which knowing the experimental temperatures we derive a set of (four) values for T_0. Despite the many uncertainties, the four values which we obtained in this way showed no systematic variation with temperature and none differed by more than 7 percent from the mean. This mean value was 3900°K, corresponding to a binding energy for the complex of 0.34 ev. This may be compared with the theoretical value of 0.44 ev calculated by Reitz and Gammel.[13]

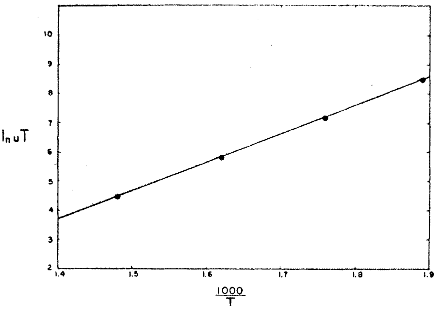

FIG. 6. The temperature dependence of the limiting mobility, u, in cm^2/volt sec; see Eqs. (19) and (30).

Having determined T_0, a direct comparison of the experimental σ *versus* c curves with the corresponding theoretical $\alpha\sigma$ *versus* c curves now gives α at each of the four temperatures. Knowing α we can calculate the limiting vacancy mobility u, in the absence of interactions [Eq. (19)]. In Fig. 6 we plot $\ln(uT)$ against $1/T$.

The four points appearing there are well fitted by the equation

$$uT = 21{,}200 \exp(-9750/T) \text{ cm}^2/\text{volt sec.} \quad (30)$$

The coefficient occurring in the exponential, which we interpret as the barrier height U in Eq. (20) is in close agreement with the value obtained by Etzel and Maurer. The theoretical curves which follow from (25) and (30) when T_0 is 3900°K are shown in Fig. 5. We have verified that these values for T_0 and U are not affected more than a few percent by starting from different "smooth curves" drawn through the experimental points.

V. CONCLUSION

We conclude with a note on the shortcomings of our theory. If we calculate T_0 from Eq. (2), it comes out to be about 7000°K for NaCl, i.e., almost twice the value we get by a direct comparison with experiment. One may therefore question the usefulness of comparing our simple model with real systems in which the impurity ion-vacancy interactions depart so appreciably from (2) at short distances. Now in our model, T_0 fixes both the binding energy of the complex and the magnitude of the interactions at large separations. Hence, by choosing T_0 so that kT_0 is the real binding energy of the complex, we alter the scale of the interactions at large distances, making them too small in this case. Therefore, as we have applied our theory, it underestimates the effect of the long-range interactions among impurity ions and vacancies. This defect can be corrected by taking explicit account of the non-Coulombic interaction between a vacancy and an impurity ion. This non-Coulombic part will only be significant at small separations, but it is not sufficient to suppose it is important only when the pair forms a complex. If it were, we would simply repeat the above calculations, replacing the binding energy $e^2/\epsilon a\sqrt{2}$ everywhere by its correct value. If we did this for the system $\text{NaCl}+\text{CdCl}_2$ and used the complex binding energy calculated by Reitz and Gammel,[13] namely, 0.44 ev, we should be employing a model in which the binding energy of a complex was less than that of a pair at the next nearest neighbor separation. The calculations can be extended therefore only when we first know the non-Coulombic part of the interaction energy at all the separations where it is not negligible. We may then proceed with the statistics of the problem by extending the definition of association so as to include all those pairs with an appreciable non-Coulombic interaction. We would, in fact, be dealing with an assembly of complexes some of which would be in their ground state while others would be in excited states.

This raises the question of the legitimacy of the idea of excited complexes; or rather, since a little reflection convinces us of the arbitrariness of the idea of association, the question is really at *what* separation ought we to draw the distinction between an unassociated pair and an associated pair. This question has been fully discussed by Fuoss,[25] for electrolyte solutions. He concludes that it is legitimate to divide the ions into two classes—those that are associated and those that are unassociated—provided the dividing distance is taken to be in the region of

$$g = e^2/2\epsilon kT. \quad (31)$$

The predicted properties of the solution are nevertheless insensitive to the exact distance which is chosen. For the temperatures of interest in connection with our problem, this implies that it makes very little difference whether we take the limiting separation to be $2a$ or $10a$. We have verified this directly for our simple model by treating pairs up to eighth neighbors (at $4a$) as associated. In regard to future calculations, which include the non-Coulombic interactions, we can therefore say that there is no point in taking the concept of association further than is necessary to include the significant non-Coulombic terms.

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[25] R. M. Fuoss, Trans. Faraday Soc. **30**, 967 (1934). For discussions of the effects of the dipolar interactions, which we have neglected, see R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc. **55**, 476, 1019, 2387 (1933), and R. M. Fuoss, J. Am. Chem. Soc. **56**, 1027 (1934).