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Pressure effect on ionic conductivity in NaCl

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Ionic conductivity in polycrystalline NaCl was measured using a dc technique to 35 kbar in a modified Bridgeman anvil device at ambient temperatures. An analysis was made of the pressure effect on the vacancy-impurity complexes contribution to ionic conductivity using the Pierce-Lazarus conductivity expression with an extension of the Lidiard theory of vacancy-impurity association to include pressure effects. Using a value of 5 cm^3/mole for the activation volume of motion of free Na vacancies inferred from this measurement and the strain energy model of Keyes, this analysis obtained a good fit to the existing data in the "extrinsic" region obtaining values of 0.43 eV/atom for the free energy of association of complexes and 14 cm^3/mole for the activation volume of reaction. Thermal Schottky disorder was found to be negligible below 600°K, whereas "extrinsic" vacancy effects are not negligible even at the melting point according to this model. Although this model suggests a large increase in apparent activation volume near the melting point using Etzel and Maurer's early results for the concentration and an activation volume of 28 cm^3/mole of Schottky defects, the agreement of this calculation with previously measured results is poor. This suggests that additional conduction mechanisms may be operable above 900°K in agreement with the conclusions of Martin *et al.*

INTRODUCTION

At normal pressures and temperatures, electrical conduction in NaCl is accomplished by the drift of Na cations through the lattice in response to an electric field.[1] In pure crystals, thermal Schottky defects, i.e., pairs of Na and Cl vacancies, provide the mechanism by which diffusion of the Na ions and conduction occurs.

Mapother, Crooks, and Maurer[2] demonstrated the validity of the Nernst-Einstein relationship between the electrical conductivity σ and the cationic diffusivity D in NaCl above 850 °K:

$$\sigma/D = Ne^2/kT, \tag{1}$$

where N is the number of sodium ions per unit volume having a charge e and kT is the usual Boltzmann temperature factor.

However, small concentrations of multivalent cationic impurities have a profound effect on both the ionic conductivity and cation diffusion below 850 °K in the "extrinsic" region. Here Mapother *et al.*[2] observed large deviations from the Nernst-Einstein relation even in the purest crystals available. They proposed that this deviation was due to "extrinsic" vacancies introduced in the crystal by the multivalent cationic impurities and the requirement of electroneutrality. Using the theory of association of impurity-vacancy complexes of Stasiw and Teltow[3] and an elementary treatment of complexes due to Seitz,[4] they proposed that closely bound cationic impurity-vacancy complexes contributed to the diffusivity. However, these complexes, which are electrically neutral, did not contribute to the measured conductivity. Using this analysis they were able to account qualitatively for the measured discrepancy from Eq. (1) and for the variation in diffusivity and conductivity with divalent impurity concentration.

Lidiard[5] extended the Stasiw-Teltow association theory by application of the mass-action law to the quasichemical reaction:

$$\text{(unassociated impurity)} + \text{(unassociated vacancy)} \rightleftharpoons \text{(impurity-vacancy complex)}$$

to determine the degree of association p of impurity-vacancy complexes. He obtained

$$p/n_i(1-p)^2 = z\, e^{\Delta\xi/kT}, \tag{2}$$

where n_i is the concentration of divalent impurities, z is the orientation number ($z = 12$ for NaCl), and $\Delta\xi$ is the free-energy change of association. This result neglected the effect of thermal disorder and assumed nearest-neighbor interactions only; however, Lidiard pointed out that "intrinsic" Schottky defects could be introduced as a separate molecular species without affecting the equilibrium relationship described in Eq. (2). Of course, this is only strictly correct when there is no interaction between molecular species, i.e., ideal solutions. Nonideality can be evaluated by the replacement of concentrations with appropriate activity coefficients.

Lidiard[5] introduced nonideality by applying the Debye-Hückel screening constant χ involved in the interaction between unassociated defects to the free energy of association $\Delta\xi$ and the related effects of defect mobilities.

The first measurements of the pressure effect on conductivity by Lazarus[6,7] and Pierce[7] demonstrated that the apparent activation volume, $RT(\partial \ln\sigma/\partial P)_T$ was very temperature dependent in the range of 500–800 °K. They found the apparent activation volume to vary from 9 cm^3/mole at the extremes of this range to a clear maximum of 13 cm^3/moles near 600 °K. These volumes are significantly larger than the ionic volume of 5 cm^3/mole for Na in NaCl.

Pierce[8] analyzed his results using an explicit relationship for the conductivity from reaction rate theory. He obtained

$$\sigma = (n_f e^2 a^2 \nu_0 / kT)\, e^{-(\Delta G_m / kT)}, \tag{3}$$

where n_f is the total concentration of free vacancies, a is the lattice jump distance, ν_0 is the atomic attempt frequency normally of the order of the Debye frequency, and ΔG_m is the Gibbs energy for the motion of the cation over the diffusion barrier. The activation volume for cation motion ΔV_m is obtained in the usual way,

$$\Delta V_m = \left(\frac{\partial \Delta G_m}{\partial P}\right)_T = kT\left[\left(\frac{\partial \ln n_f}{\partial P}\right)_T + 2\left(\frac{\partial \ln a}{\partial P}\right)_T + \left(\frac{\partial \ln \nu_0}{\partial P}\right)_T - \left(\frac{\partial \ln \sigma T}{\partial P}\right)_T\right], \tag{4}$$

where the last term, the apparent activation volume, is measured experimentally. Pierce was able to show that the pressure variation of the lattice constant and vibrational frequencies were negligible. By empirically evaluating the vacancy term from his extensive data, he deduced an essentially constant motional volume ΔV_m of 7.0 ± 0.5 cm^3/mole, which was in good agreement with the theoretical prediction of 5 cm^3/mole obtained from the strain-energy model of Keyes.[9] The strain-energy model relates the activation volume to the appropriate activation energy and elastic parameters to obtain

$$\Delta V_m = \left[\left(\frac{\partial \ln C}{\partial P}\right) - K_T\right]\Delta G_m, \tag{5}$$

where C is the effective shear modulus and K_T is the isothermal compressibility. Pierce used both the Grüneisen model of a solid and an expression for the average shear modulus due to Brooks[10] to evaluate (5).

Several authors have extended the pressure measurements in the temperature region above 800 °K finding apparent activation volumes approaching 36 cm^3/mole near 1000 °K.[11–13] Using an empirical analysis similar to Pierce's technique to evaluate Eq. (4), Biermann[11] found ΔV_m to be 9.5 cm^3/mole while Beyeler and Lazarus[12] found ΔV_m to be 6.6 ± 0.6 cm^3/mole for temperatures up to 950 °K. Yoon and Lazarus[13] using a similar technique found ΔV_m to be 7.0 ± 1.0 cm^3/mole at 993 °K, by application of a 10% correction to their data. In order to account for the large apparent activation volumes in the high-temperature "intrinsic" region, a large activation volume of formation of Schottky defects approaching 60 cm^3/mole near 1000 °K was inferred.[11–13] This result is in sharp disagreement with the recent calculation by Faux and Lidiard[14] indicating a smaller volume of about 15 cm^3/mole at room temperature.

The possibility that anion diffusion contributes to the measured as discussed by several authors[15,16] was effectively eliminated by the tracer diffusion measurements of Martin *et al.*[17] They found the zero-pressure activation volume for the self-diffusion of ^{22}Na in NaCl to be 37 ± 4 cm^3/mole from which they deduce the formation volume of Schottky defects to be 60 cm^3/mole in good agreement with the experimental conductivity results.[11–13] Thus, motion of the Na ion is confirmed as the principal conduction species and Martin *et al.*[17] suggest vacancy pair processes as being the more probable process at high temperatures.

Recently, Kost and Hultsch[18] measured the pressure effect on the nuclear magnetic resonance (NMR) rotating frame relaxation time in doped NaCl at low temperature. Assuming the association reaction complete and including the pressure effect on Schottky defects, they concluded that ΔV_m was about 7.4 ± 1.0 cm^3/mole at 385 °K.

Better agreement occurs between Faux and Lidiard's value of 2.2 eV for the activation energy of formation of Schottky defects and the measured values ranging between 2.0 to 2.5 eV.[19–21]

Several calculations[5,22] and measurements[23,24] indicate that the association energy $\Delta\xi$ is near 0.4 eV/atom rather than 0.3 eV/atom predicted by the Stasiw-Teltow analysis neglecting Debye-Hückel effects. It appears that the Debye-Hückel charge-cloud variation due to interacting defects makes an important contribution to the binding energy in NaCl crystals.

It is the purpose of this paper to report on a measurement of the pressure effect on the conductivity of polycrystalline NaCl at ambient temperatures, to incorporate the Lidiard association model into the calculation of activation volumes, and to compare the results of this calculation with existing data.

EXPERIMENTAL TECHNIQUE AND RESULTS

Reagent-grade NaCl crystals from Matheson, Coleman, and Bell, Chemists, Los Angeles, having total impurity content less than 0.4% of which the divalent impurities levels were Ba 0.001%, Ca 0.005%, and Mg 0.005% by weight were used in this experiment.

Cylindrical sample pellets were compacted with a pressure near 6 kbar to a diameter of 0.43 cm and height of 0.115 cm in a clean die and piston jig. These samples were placed in the sample holder of a high-pressure cell described elsewhere by Kendall *et al.*[25] and given a preliminary cycle to 100 kbar. Examining a typical sample indicated that further compaction had occurred in this preliminary cycle such that the sample height was now reduced to about 0.090 cm. Density was determined by the gravimetric technique of Voronov *et al.*[26] to be within 50 ppm of the density as determined by x-ray analysis. Further cycling of the samples yielded small additional hysteretic thinning of less than 1% per cycle, which was attributed to sample spreading. No correction has been made for this small hysteresis effect which occurred during the measurement.

Sample resistance was measured using the system described in Fig. 1 where a motor-driven switch reversed the current through the sample every 30 sec to avoid saturation due to the charge polarization described in the earlier work.[2] The specimen resistance was determined at the end of each cycle for both current directions, and an averaging technique indicated that the polarization voltage was less than 1% of the voltage drop across the sample.

Simultaneous ultrasonic measurements were made of the shear and longitudinal velocities using a resonance technique to be described elsewhere.[27] The ultrasonic measurements permitted the monitoring of sample dimensions at pressure and yielded a pressure calibration based on the ratio of longitudinal velocity to shear velocity from previously available data.[26,28]

In order to reach pressures in excess of 10 kbar, a solid high-pressure cell was used,[28] which necessitated several important changes in experimental procedures from those normally used in lower-pressure gas hydrostatic systems. First of all, the ultrasonic technique used to determine pressures[27] required the elastic isotropy of polycrystalline samples. Also, the nonhydrostatic pressing of samples inherent in solid systems increased the possibility of introduction of excess vacancies and dislocation into the samples during pressurization. Since repeated runs were made on each sample and *in situ* heating is not presently available on our cell, post-pressing annealing was not performed before runs. However, the measured resistance ratios were recoverable from run to run, within a random scatter of about 20%, whereas the larger random scatter at high pressures may be attributable to either the difficulty in measuring large resistances or the difficulty in obtaining "equilibrium" owing to reduced mobility of defects or both.

Figure 2 represents the resistivity ratio ρ_0/ρ (or conductivity ratio σ/σ_0) where the subscript 0 refers to the room-pressure value, as a function of pressure at 300 °K. The data shown are one of the pressure runs made on several of our samples which fairly indicate the larger scatter inherent in our technique. A straight-line fit to our *total* body of data yields an apparent activation volume of 4.5 ± 1.5 cm^3/mole for polycrystalline NaCl with reasonable accuracy, although there appears to be a trend to a slightly lower volume for pressures less than 15 kbar. Because of the somewhat larger random scatter of our data, curvilinear fits suggested by other investigators were not made. Typical sample resistances were 13 MΩ and a rough estimate of resistivity of 9.7 MΩ cm was in good agreement with literature values at 300 °K.[25]

THEORETICAL

The key step in the calculation of activation volumes from the measured conductivities lies in

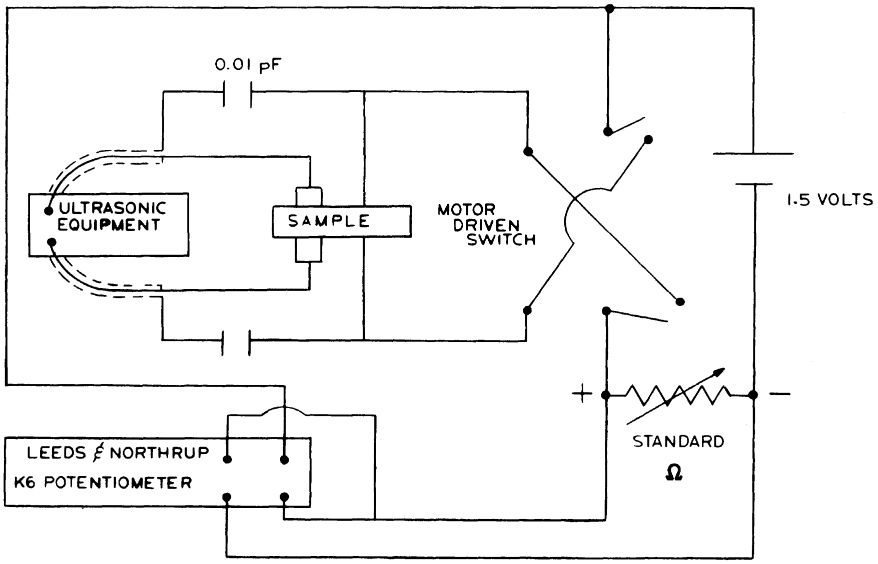

FIG. 1. Schematic of resistance and ultrasonic measuring system.

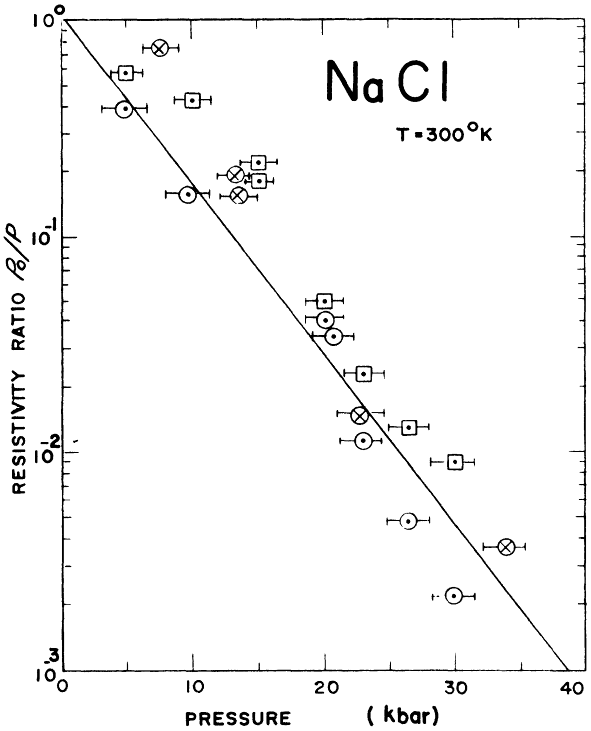

FIG. 2. Pressure effect on the resistivity ratio ρ_0/ρ (or the conductivity ratio σ/σ_0) for several samples.

the accurate estimation of the pressure variation of the total free vacancy concentration, since the bound impurity-vacancy complexes do not contribute to the measured conductivity.

Let us examine the thermal-disorder contribution to the free vacancy concentration first, since we have already determined that each contribution may be evaluated as a separate species. These defects are introduced in ionic crystals, such as NaCl, as a condition of thermodynamic equilibrium, i.e., the free energy contains a well-defined configurational entropy term. Furthermore, to establish electroneutrality, it is required that these thermal vacancies be formed in anionic-cationic pairs. In "pure" crystals, this is the only contribution to the free vacancy concentration n_f. The pressure effect on a "pure" crystal's conductivity would then contain an activation volume of formation of thermal defects, ΔV_{fV}, of

$$\Delta V_{fV} = \left(\frac{\partial \Delta G_{fV}}{\partial P}\right)_T , \tag{6}$$

where ΔG_{fV} is that portion of the Gibbs free energy required to form anionic-cationic vacancy pairs.

In "doped" crystals, the concentration of unassociated or "free" extrinsic cationic vacancies introduced by n_i cationic impurities is $n_i(1-p)$. The value of the degree of association p is determined from Eq. (2). Thus the total free cation vacancy concentration n_f is

$$n_f = n_i(1-p) + n_{fV}, \tag{7}$$

where n_{fV} is the concentration of thermal cation vacancies defined by

$$n_{fV} = e^{-(\Delta G_{fV}/2kT)}. \tag{8}$$

Using Eqs. (2), (7), and (8), one can obtain

$$kT\left(\frac{\partial \ln n_f}{\partial P}\right)_{T,n_i} = -\frac{n_{f'}}{n_f}\,\frac{p}{p+1}\,\Delta V_B - \frac{n_{fV}}{n_f}\,\frac{\Delta V_{fV}}{2} , \tag{9}$$

where the activation volume of reaction ΔV_B is defined by

$$\Delta V_B \equiv \left(\frac{\partial \Delta \xi}{\partial P}\right)_{T,n_i} \quad \text{and} \quad n_{f'} = n_i(1-p).$$

Normally, one assumes that the activation volume of motion[29] and formation[30] are temperature independent.[31] However, the activation volume of reaction requires a more careful evaluation. It is important to note that electroneutrality requires that the total number of "extrinsic" vacancies be independent of temperature and pressure and be determined solely by the concentration of multivalent impurities. Hence, the activation volume of reaction is the pressure effect on the reaction equilibrium in which the total number of reactants are constant. This reaction differs from the vacancy-impurity reaction in a metal, where the number of vacancy reactants is pressure and temperature sensitive.

The Gibbs-free-energy change $\Delta\xi$ obtained from the statistical-mechanical analysis of the equilibrium constant does not contain a term for the configurational entropy *per se*; it is "the work gained under conditions of constant temperature and pressure in bringing a vacancy from a particular distant position to a particular nearest-neighboring position of the impurity ion."[5] We may decompose this free energy into a heat of association and an entropy of association in the normal manner. Then, using the fact that entropy is an extensive thermodynamic property, we may separate those entropy-of-association terms we relate to the movement of the distant vacancy to a particular nearest-neighbor site ΔS_1 and assume that the pressure variation of all other enthalpy and entropy terms in $\Delta\xi$ cancel, then the activation volume of reaction is

$$\Delta V_B = \left(\frac{\partial \Delta \xi}{\partial P}\right)_{T,n_i} = -T\left(\frac{\partial \Delta S_1}{\partial P}\right)_{T,n_i} = T\left(\frac{\partial \Delta V_1}{\partial T}\right)_{P,n_i} , \tag{10}$$

where ΔV_1 is the change in the volume of the crystal due to a change in reaction equilibrium.

The volume of the crystal may be expressed as

$$V = p n_i V_p + n_i(1-p)V_v + (1-p)\, n_i V_i + V',$$

where V_p is the molar volume of a pair, V_v is the molar volume of a free extrinsic vacancy, V_i is the volume of a free impurity, and V' comprises all other volume terms. Thus, the volume change of the reaction ΔV_1 may be written

$$\Delta V_1 = \Delta\overline{V}(1-p) + V_p; \tag{11}$$

and using (10) we obtain

$$\Delta V_B = -T\left(\frac{\partial p}{\partial T}\right)_{P,n_i} \Delta\overline{V}\,, \tag{12}$$

where the reaction volume $\Delta\overline{V}$ is equal to $(V_v + V_i - V_p)$, i.e., "reactant's volume minus product's volume."

Using Eqs. (4), (9), and (12), we obtain

$$kT\left(\frac{\partial \ln\sigma T}{\partial P}\right)_{T,n_i} = \frac{n_{f'}}{n_f}\,\frac{p}{p+1}\,T\left(\frac{\partial p}{\partial T}\right)_{P,n_i}\Delta\overline{V} - \frac{n_{fV}}{n_f}\,\frac{\Delta V_{fV}}{2} - \Delta V_m, \tag{13}$$

from which ΔV_m may be determined, parametrized by the binding energy $\Delta\xi$, the reaction volume $\Delta\overline{V}$, and the activation volume of formation of thermal vacancies ΔV_{fV}. It is important to note that this analysis does not include either electrolytic interactions (Debye-Hückel) or impurity precipitation effects.

Debye-Hückel correction

The analysis leading to Eq. (13) ignored the existence of Coulombic interactions between the unassociated defects. These interactions will affect not only the free energy of association $\Delta\xi$ in the mass action [Eq. (2)], but will affect the mobility of the conduction defect. Following Lidiard,[5] the corrected free energy $\Delta\xi$ is

$$\frac{\Delta\xi}{kT} = \frac{T_0}{T} - \frac{2(2\pi\sqrt{2}\,)^{1/2}(T_0/T)^{3/2}[(1-p)\,n_i]^{1/2}}{1+2(2\pi\sqrt{2}\,)^{1/2}[(1-p)\,n_i\,T_0/T]^{1/2}} \tag{14}$$

assuming negligible thermal disorder and nearest-neighbor interactions between an impurity and a vacancy at a distance of $\sqrt{2}a$, where a is the normal anion-cation separation. Using pure Coulombic interactions in the simple Stasiw-Teltow theory yields a free energy $\Delta\xi = e^2/\sqrt{2}\,\epsilon a$ where ϵ is the dielectric strength.

Lidiard also applied the Onsager-Pitts correction to the limiting mobility and obtained the multiplicative correction factor g:

$$g = 1 - \frac{2(2\pi\sqrt{2})^{1/2}}{3(\sqrt{2}+1)}\;\frac{[n_i(1-p)]^{1/2}\,(T_0/T)^{3/2}}{(1+a\kappa)\,(\sqrt{2}+2a\kappa)} \tag{15}$$

in which κ is the Debye-Hückel screening constant defined by

$$a\kappa = 2[\pi\sqrt{2}\;n_i(1-p)\;T_0/T\,]^{1/2}. \tag{16}$$

It is interesting to note that this term suggests a hindrance to the mobility due to the Debye-Hückel charge cloud; however, increasing the pressure increases p due to the decrease in the concentration of unassociated defects. Thereby, the effective activation volume of motion is reduced. Using the above relations we may modify Eq. (13) to include the Debye-Hückel mobility correction and obtain,

$$kT\left(\frac{\partial \ln\sigma T}{\partial P}\right)_{T,n_i} = \left(\frac{n_{f'}}{n_f} - \frac{AE\,(1-\sqrt{2}\,E^2)}{2[(1+\sqrt{2}E)\,(1+E) - AE]}\right) \times \frac{p}{p+1}\,T\left(\frac{\partial p}{\partial T}\right)_{P,n_i}\Delta\overline{V} - \frac{n_{fV}}{n_f}\,\frac{\Delta V_{fV}}{2} - \Delta V_m, \tag{17}$$

where

$$A = T_0/3(\sqrt{2}+1)\,T$$

and

$$E = 2[\sqrt{2}\pi n_i(1-p)\;T_0/T]^{1/2} = \kappa a.$$

The Debye-Hückel theory is complete when the free energy [Eq. (14)] is used in Eq. (2) to calculate the degree of association p. The latter correction is more important in dilute solutions of NaCl which were investigated here.

ANALYSIS

The careful experimental measurements on monocrystalline NaCl by Dreyfus and Nowick[32] suggest that the dominant conduction defect is the extrinsic "free" vacancy defect introduced by polyvalent cationic impurities contained in even the most pure crystals at ambient temperatures. They also concluded that precipitation effects are negligible in samples containing less than 100 ppm impurities regardless of heat treatment. Below 273 °K, Dreyfus and Nowick found enhanced conductivity owing to quenched-in "free" vacancies and in heavily doped samples they observed annealing out of this excess conductivity within 2 h at 267 °K. Using their value of the annealing activation energy indicates that excess vacancies should be eliminated in less than the time interval (~ 30 min) between each pressure increment in our experiment.

At ambient temperatures, the reaction equilibrium is relatively insensitive to both temperature and pressure; therefore, the pressure effect on the conductivity is primarily owing to the pressure effect on vacancy motion for "pure" materials according to this model. Yoon and Lazarus[13] have recently reevaluated the motional volume calculated from the Keyes continuum model[9] and the Brooks expression for the average shear stress[10] obtaining a value of 5 cm^3/mole for ΔV_m. Since our measurement suggests that ΔV_m is 4.5 ± 1.5 cm^3/mole for polycrystalline NaCl in our system, we will use a value of $\Delta V_m = 5$ cm/mole for all temperatures in this analysis.

A proper value of the free energy $\Delta\xi$ for the evaluation of the association parameter must be selected. It is immediately apparent that the maximum near 550 °K observed in the experimental data for NaCl crystals doped with 10^{-4} mole fraction $CaCl_2$ by Lazarus[6] is primarily due to the impurity effect in Eq. (13), since any reasonable estimate of the thermal vacancies contribution is negligible at these temperatures. It is also noted that the position of the maximum is very sensitive to the impurity level and the free energy selected.

Using the pure Coulombic interaction in the simple Stasiw-Teltow theory yields a free energy $\Delta\xi = e^2/\sqrt{2}\,\epsilon a = 0.27$ eV, where ϵ is the dielectric strength. Using this energy yields a maximum near 400 °K in poor agreement with the Lazarus data. Instead, the Debye-Hückel correction to the association energy [Eq. (14)] is used in Eq. (2). For an impurity level of 10^{-4} mole fraction, values of T_0 near 5000 °K yield maxima near 550 °K for the first term, the "extrinsic" term, on the right-hand side of Eq. (13). Throughout this procedure, the ratio $n_{f'}/n_f$ was assumed to be unity. The value of the reaction volume is determined by varying its value to fit the available experimental data up to 650 °K assuming a negligible thermal vacancy effect. The best fit to the data is obtained for a value of $T_0 = 5000$ °K corresponding to an energy of association of 0.43 eV and a reaction volume $\Delta\overline{V}$ of 14 cm^3/mole. A fit to the peak in the Lazarus-Pierce data for $n_i = 2\times10^{-4}$ yields a value of $T_0 = 4600$ °K.

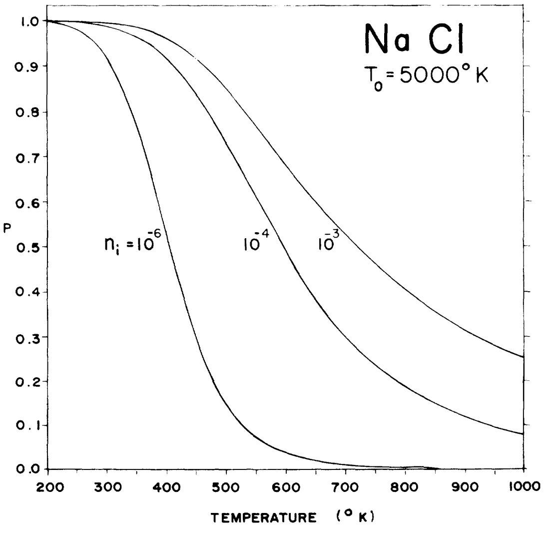

FIG. 3. Curves showing the degree of association p as a function of temperature for four different divalent impurity concentrations. The association energy $\Delta\xi = kT_0$ has been determined from Eq. (14).

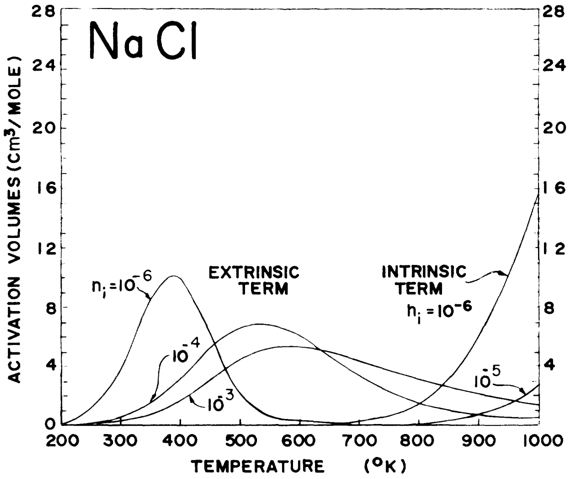

FIG. 4. Curves showing the contribution to the "apparent" activation volume $(\partial \ln\sigma T/\partial P)_T$ due to the "extrinsic" term $(n_{f'}/n_f)\,T(\partial p/\partial T)_{P,n_i}\Delta\overline{V}$, and the "intrinsic" term, $(n_{fV}/n_f)\,(\frac{1}{2}\Delta V_{fV})$, for several different divalent impurity concentrations. Parameters used in this figure are $T_0 = 5000$ °K, $\Delta\overline{V} = 14$ cm^3/mole, and $\Delta V_{fV} = 67$ cm^3/mole.

A plot of p versus temperature is shown in Fig. 3 for various impurity concentrations and $T_0 = 5000$ °K.

Figure 4 illustrates the effect of the variation of the impurity term in Eq. (13) for $T_0 = 5000$ °K and $\Delta\overline{V} = 14$ cm^3/mole for several impurity levels. Clearly the maximum is shifting to lower temperatures and to a larger value as the impurity concentration decreases in contrast to previous data.[6-8]

The data above 650 °K can now be analyzed to evaluate the "intrinsic" vacancy term $(n_{fV}/n_f)\times\frac{1}{2}\Delta V_{fV}$. The surprising result of our analysis is that impurity effects played an important role in the conductivity at temperatures above 650 °K even when the impurity level was less than 10^{-4}. This is primarily due to the competition of "extrinsic" and "intrinsic" vacancies to play the role of diffusion mechanism; i.e., the "extrinsic" term is non-negligible at high temperatures.

Using the parameters ($T_0 = 5000$ °K and $\Delta\overline{V} = 14$ cm^3/mole) obtained from fitting Eq. (13) to the maximum in the Lazarus data near 550 °K for crystals having 10^{-4} impurity levels, curves of apparent activation volumes were calculated for different impurity levels from this model. In this analysis, both the activation volume of formation and the concentration of Schottky defects were varied in an attempt to fit published experimental data. This fit yielded an absurd value of $\frac{1}{2}\Delta V_{fV} > 100$ cm^3/mole; however, the concentration parameters were in reasonable agreement with published values.

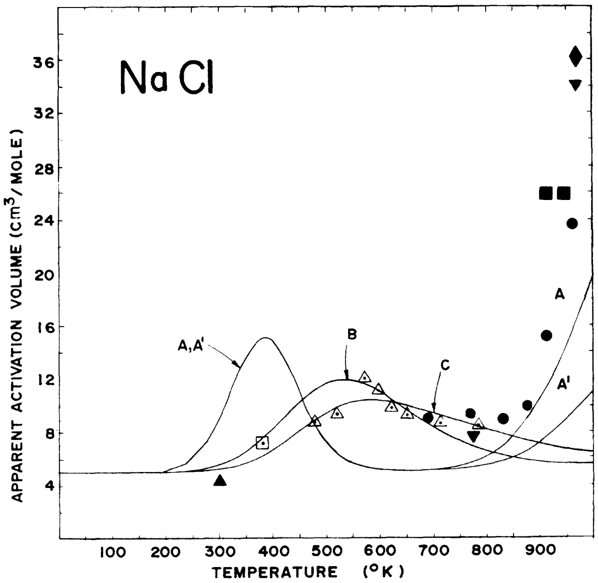

FIG. 5. Curves showing the temperature dependence of the "apparent" activation volume $(\partial \ln\sigma T/\partial P)_T$ for several different divalent impurity concentrations; A, 10^{-6}; B, 10^{-4}; C, 10^{-3} mole fraction with $T_0 = 5000\,°\mathrm{K}$, $\Delta\overline{V} = 14$ cm³/mole, and $\Delta V_{fv} = 67$ cm³/mole. Curve A' is shown for an impurity concentration of 10^{-6} mole fraction and $\Delta V_{fv} = 28$ cm³/mole. Data points are Δ (Refs. 6 and 8); ● (Ref. 11); ■ (Ref. 12); ▼ (Ref. 13b), ◆ (Ref. 13a); □ (Ref. 14), and ▲ (present). Solid symbols represent "pure" samples $(n_i \approx 10^{-6})$ whereas the open symbols represent "doped" samples $(n_i \approx 10^{-4})$.

In an attempt to determine the possible range of validity of our model, the experimental data in the highest temperature range were systematically excluded in the analysis. This procedure suggests that a reasonable fit to the data below 950 °K could be obtained with $\frac{1}{2}\Delta V_{fv} = 33.5$ cm³/mole and a concentration of thermal cationic vacancies n_{fv} given by

$$n_{fv} = 0.2\, e^{-(12\,500/T)}, \tag{18}$$

which is shown in Fig. 5 as curve A. Curve A' was calculated using Eq. (18) and with $\frac{1}{2}\Delta V_{fv} = 14$ cm³/mole for comparison, whereas curves B and C were calculated to show the effect of impurity levels on apparent activation volumes according to this model.

DISCUSSION

The value obtained for the free energy of association is in good agreement with previous measurements[22,23] and calculations[5,21] once the Debye-Hückel corrections due to interactions among unassociated "extrinsic" defects have been made.

There are no previous measurements or calculations of the reaction volume $\Delta\overline{V}$ to compare with our results. Essentially, this quantity is the change in volume due to the formation of impurity-vacancy pairs in our model. If one makes the crude assumption that the impurity radius is unchanged in either the "free" or "bound" state, then this volume represents the change in the vacancy's volume going from an environment of singly-charged Na nearest neighbors to the bound state in which one of its nearest neighbors is a divalent impurity. One cannot infer absolute volumes for either state of the extrinsic Na vacancy, since the activation volume of formation ΔV_{fv} deduced below may contain nonvolumnic terms.

Although this model predicts a maximum in the activation volume for the 10^{-4} impurity level at the proper temperature, the predicted apparent activation volume exhibits a broader peak than the Lazarus - Pierce data suggest.[6–8] If this is a real effect, there are several possible causes: the first problem may be the neglect of higher-order interactions in the Debye-Hückel theory, especially for higher concentration limits. The second problem may be the temperature variation of $\Delta\overline{V}$ which is difficult to evaluate. Finally, second-order effects on ΔV_B could occur through a pressure variation in the neglected enthalpy and entropy terms in Eq. (10).

The shift to higher temperatures for the apparent activation volume maximum with increasing impurity content is contrary to the reported data for NaCl.[6–8] Careful evaluation of the theory of association has indicated that the maximum in the zero-pressure activation volume should occur where ΔV_B or $T(\partial p/\partial T)_{p,n_i}$ is a maximum. This discrepancy is puzzling since the experimental data of KCl appear to support the prediction of this model.[33] In any event, a clear test of this model can be made by measuring the apparent activation volume for NaCl crystals having a 10^{-6} divalent impurity level which should show a clear maximum near 400 °K. Care must be taken in this measurement since the peak may be extremely sharp. Unfortunately, the temperature range above room temperature required to test this hypothesis, is not presently obtainable in our device.

The proposed model involving a simple impurity-vacancy interaction clearly does not agree with the measured activation volumes from conductivity[11–13] and self-diffusion[17] experiments above 950 °K. Thus, the contribution of single vacancies as described by this model cannot account for the large experimental apparent activation volumes unless unrealistic values for ΔV_{fv} are assumed. It appears that some other mechanism for the diffusion of Na ions is contributing to the conductivity above 950 °K. Since Martin *et al.*[17] have clearly eliminated anionic motion as a possible mechanism, our analysis supports their conclusion that vacancy pairs may be the most probable conduction mechanism. However, detailed experimental and theoretical work seems necessary in order to discriminate between the possible candidate mechanisms.[34]

Also shown in Fig. 5 are the calculated apparent activation volumes for less-pure crystals assuming a formation volume $\frac{1}{2}\Delta V_{fv} = 33.5$ cm^3/mole, which shows the marked decrease of over an order of magnitude in the "intrinsic" vacancy term due to a change in impurity level from 10^{-6} to 10^{-4} according to our model. If a volume $\frac{1}{2}\Delta V_{fv} = 14$ cm^3/mole is assumed, this decrease is less marked. Thus, an investigation of the effect of cationic impurities on the conductivity above 950 °K may yield qualitative data on the value of the formation volume of cationic vacancies.

In comparing our value of ΔV_m deduced from polycrystalline samples with published experimental results,[6,8,9,11,17] it is necessary to compare the Pierce analysis[8] with the predictions of this model. The critical assumption of the Pierce analysis was that the cationic vacancies in crystals containing 10^{-4} mole fraction of impurities would be completely dissociated at 773 °K, i.e., there would be no large changes in n_f with pressure at these temperatures. Although the prediction of our model is in qualitative agreement with this assumption, we find $(\partial \ln n_f/\partial P)_{T,n_i}$ to be approximately twice as large as that deduced in the Pierce analysis. Our result is dependent on the fit to the maximum in the Lazarus data; thus it appears that our experimental results and those deduced from other experiments using the Pierce analysis differ due to analysis rather than experimental technique. If the above speculations are valid and the value deduced from our model for $(\partial \ln n_f/\partial P)_{T,n_i}$ is used in the Pierce analysis then the values of ΔV_m, from all presently available data, are within stated experimental uncertainties. Furthermore, the lower value of ΔV_m suggested by our experiments is in excellent agreement with the Keyes model[9] as previously mentioned.

The concentration of Schottky defects deduced from our fit to the experimental data to 900 °K is in good agreement with earlier measurements[19,21] and the recent calculation of Faux and Lidiard.[14]

Above that temperature, the "intrinsic" vacancy term of this model for "pure" crystals becomes dominant and predicts an increasing apparent activation volume with increasing temperature for any reasonable value of $\frac{1}{2}\Delta V_{fv}$. This increased volume is unable to explain the measured values, thus our model supports the conclusion of Martin *et al.* that another conduction mechanism is operable in this high-temperature region. This component may be responsible for the pressure "knee" observed in the conductivity[13] and diffusion[17] measurements above 936 °K.

CONCLUSIONS

From our measurements of the pressure effect on the ionic conductivity of polycrystalline NaCl at 300 °K, a value of 4.5 ± 1.5 cm^3/mole for the activation volume of motion is obtained. Good agreement with measured apparent activation volumes up to 900 °K has been obtained using a theoretical treatment which includes our measurement of ΔV_m, an "extrinsic" vacancy term including Debye-Hückel effects [Eqs. (14) and (15)], and the "intrinsic" vacancy term [Eq. (18)]. From this analysis, values of the free energy of association and activation volume of reaction of 0.43 eV/atom and 14 cm^3/mole, respectively, are obtained. The prediction of this analysis above 900 °K is in poor agreement with measured apparent activation volumes and supports the conclusion of Martin *et al.* that an additional defect may be contributing to the conductivity in this high-temperature region.

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