PHYSICAL REVIEW B VOLUME 4, NUMBER 10 15 NOVEMBER 1971

Ionic Conductivity of Potassium Chloride Crystals

P. W. M. Jacobs and P. Pantelis

Department of Chemistry, University of Western Ontario, London 72, Canada

(Received 19 April 1971)

The ionic conductivity of four relatively pure crystals of potassium chloride has been measured over a wide temperature range. Precautions were taken to minimize the effects of sublimation at temperatures close to the melting point. The data have been analyzed in terms of the conventional Schottky defect model allowing for transport on both sublattices and for both nearest-neighbor and long-range (Debye-Hückel) defect interactions. The defect parameters obtained are used to predict cation and anion diffusion coefficients. The cation diffusion coefficients are in excellent agreement with experiment, but both the enthalpy and entropy of activation for anion diffusion are higher than the values obtained from diffusion experiments by Fuller. Possible reasons for these discrepancies are discussed.

I. INTRODUCTION

The ionic conductivity of simple ionic solids like the alkali and silver halides has been studied intensively in recent years. Such measurements provide information concerning the number of defects present in a crystal, the mobility of these defects, and the interactions between them. This information is most conveniently summarized in terms of defect thermodynamic parameters: enthalpies and entropies of formation, migration, and interaction. Inasmuch as the ionic conductivity can be computed as a function of temperature from these parameters, agreement between calculated and measured conductivities provides tests both of the theoretical model employed and of *a priori* calculations of defect parameters using lattice theory.[1]

A method of calculating defect parameters from conductivity measurements was first given by Koch and Wagner.[2] This method is based on a very simple model in which only one kind of defect is supposed to be mobile at low temperatures in doped crystals and defect interactions are ignored completely. Improvements in this simple model were effected by Teltow,[3] by Etzel and Maurer,[4] who allowed for nearest-neighbor defect interactions between divalent cation impurities and cation vacancies, and by Lidiard,[5,6] who pointed out that long-range interactions could be included by utilizing the Debye-Hückel theory[7] originally developed for dilute ionic solutions. A technique for handling defect interactions which is based on Mayer cluster theory has been developed by Allnatt and Cohen.[8,9] Although this theory indicates the temperature at which the Debye-Hückel approximation is expected to break down, convergence problems prevent the development of a practical formula which could be used as a "next best" approximation.

On the Koch-Wagner model, plots of $\log_{10} \sigma T$ vs T^{-1} are expected to consist of two linear sections separated by a curved region generally referred to as the "knee." Association of divalent impurity cations and vacancies would cause the low-temperature (extrinsic) region to be concave downwards, while long-range interactions between defects would cause the high-temperature (intrinsic) region to become concave upwards. An additional cause of nonlinearity in the intrinsic region is the occurrence of mobile defects on both sublattices.[10] These perturbations reduce the effectiveness of the simple graphical methods which had been traditionally used to analyze conductance data. A better technique is to use a nonlinear least-squares computer program to calculate best-fit values of the defect parameters. This method was first applied by Beaumont and Jacobs,[11] who were able to predict anion migration parameters for KCl which were in reasonable agreement with those determined directly by Fuller,[12] the calculations having been performed[13] before Fuller's results were available to them. However, despite this initial success with computer fitting, their work contains some deficiencies. (i) Because of anticipated difficulties due to sublimation, Beaumont and Jacobs ceased their measurements about 90 °C below the melting point, so that the full temperature range was not explored. (ii) Although aware of the desirability of including long-range interactions, they allowed only for nearest-neighbor interactions (Teltow association model) as a first approximation. (iii) The residuals showed nonrandom dependence on temperature. This last effect could be due to inadequacies in the model used or in slow convergence of the least-squares routine, or to both causes. For these reasons we thought it desirable to reinvestigate the conductivity of KCl, including a thorough examination of the high-temperature region and a critical analysis both of the model used and of the computing techniques.

Recent work on the conductivity of alkali halides in which there has been extensive analysis of the data comprises the studies by Fuller *et al.*[14–16]

(RbCl and KCl), Allnatt *et al.*[17,18] (NaCl), Chandra and Rolfe[19,20] (KCl and KI), and Bauer and Whitmore[21] (NaF). In addition, a thorough investigation of self-diffusion in and conductivity of KBr has been made by Barr and Dawson.[22–24] Fuller and Reilly[14] analyzed data for RbCl above the knee in terms of an equation appropriate for "intrinsic" conductivity. Such an equation is only approximate, however, for even in relatively pure crystals the effects of the adventitious divalent cation impurities persist into what is generally termed the intrinsic region. Their experimental data showed the usual intrinsic curvature found for other alkali halides[10] but the difference between the anion and cation activation energies for RbCl came out to be anomalously high. Dawson and Barr[24] attribute this to the difficulties of computer fitting an "intrinsic-only" section of the complete conductivity curve. Fuller *et al.*[15] note that their parameters for KCl, which were determined by fitting the intrinsic-only section of the conductivity curve (> 560 °C) using the approximate four-parameter equation which neglects c, the concentration of divalent impurity, entirely, do not agree with those of Beaumont and Jacobs,[11] who analyzed the whole conductivity curve (370–690 °C) using equations that are exact within the framework of the simple association (Teltow) model employed. This in itself is not surprising, but what is significant is that they extrapolated the conductivity curve to high temperatures using the Beaumont and Jacobs parameters to give a line lying significantly below their own experimental points above 690 °C. However, this discrepancy refers to a single run on Harshaw KCl and no special precautions were apparently taken to deal with the problem of sublimation.

In a later paper, Fuller *et al.*[16] derive values for defect parameters for KCl by combining conductivity data (480–750 °C) with the earlier diffusion data.[12] The anion migration parameters were not allowed to vary in the conductivity analyses, while the parameters governing the formation and association of defects were not allowed to vary in the diffusion analyses. The results show the same nonrandom features in the temperature dependence of the residuals as was apparent in earlier work on KCl.[11] They also show that inclusion of Debye-Hückel interactions reduces the percent deviation, for example from about 4% to about 2% maximum deviation for KCl containing 375 ppm of $SrCl_2$. Perhaps the most striking feature of the results is the catastrophic increase in the magnitude of the percent deviation in σT, $100\times[(\text{calc} - \text{expt})/\text{expt}]$, for pure crystals between 700 and 760 °C.

This increase in the specific conductance at high temperatures has been noted also for NaCl,[17] for which it was found that the inclusion of a small Frenkel defect component reduced the nonrandom behavior of the σT deviations to a significant extent. Fuller and Reilly[25] have attempted to explain the anomalous increase in the specific conductance of pure KCl at high temperatures by ascribing this to a possible trivacancy contribution. However, to take the difference between the calculated "best-fit" σT and the experimental values as an estimate of the trivacancy concentration may not be a valid procedure, since these high-temperature points were presumably included in the original best-fit calculations.

An alternative approach to the problem of finding the values of the defect parameters from conductivity data has been devised by Rolfe.[26] This involves doping with divalent anion impurity ions, specifically $CO_3^=$, in addition to the more usual divalent cation impurities. Although attractive in principle, this method suffers from the disadvantage that anionic impurities tend to be rather insoluble and it is therefore difficult to be sure that all the measured impurity is in fact in solution. The same difficulty also in principle applies to cation-doped crystals, in that any analytical procedure gives the total amount of impurity, whereas it is only those impurity ions in solution on normal lattice sites that introduce compensating cation vacancies.

The present investigation was confined to pure (i.e., undoped) crystals of KCl for the above reason and also because it is not obvious that the same model, e.g., Schottky defects with association of cation vacancies and divalent impurity ions, will be equally valid for pure and doped crystals. For example, divalent cation doping would increase the trivacancy concentration but would decrease the concentration of interstitial cations, if Frenkel defects exist.

II. EXPERIMENTAL

The conductance cell and associated vacuum line were essentially the same as those used previously.[11] Conductance measurements were made with a transformer ratio arm bridge (Wayne Kerr, model B221) at a frequency of $10^4/2\pi$ Hz. Frequent checks were made to see if the measured conductance was frequency dependent, but as no frequency dependence was found it was concluded that polarization resistance was negligible. A Wayne Kerr AF Signal Generator S121 and Waveform Analyser A321 were used for these experiments. Various refinements in the experimental technique were made. The cleaved crystals were microtomed on their two larger faces to provide a roughened surface to which pure-graphite powder adheres rather readily. After the graphite had been applied, the other four faces were microtomed to remove any graphite powder which might be adhering to them. Microtoming provides more uniform dimensions and reduces significantly errors in the cell constant which is obtained by measuring the crystal with a micrometer both before and after the run. Post-run cell constants were also determined by weighing the crystals (see later). Pure-graphite discs were introduced between the crystal and the platinum electrodes. The combination of rubbed graphite and graphite discs provides excellent contact with the electrodes and eliminates the small distortion of the crystal (caused by the Pt/Rh thermocouple wire brazed to the back of the electrode) which occurs when graphite discs are not employed. Lead corrections were determined as a function of temperature and applied in all cases.

Sublimation is a problem and, if not corrected for, causes some irreproducibility in the measurements at the highest temperatures, i.e., in just the range where we particularly wished the accuracy to be maintained. The technique finally adopted was to anneal the crystal as usual at a temperature of ~ 600 °C until reproducible results were obtained on thermal cycling. The temperature was then raised to 690 °C and the conductance measured at approximately 5° intervals as the temperature was decreased until the bridge measurement could no longer be relied on to 0.1% ($G = 10^{-9}\ \Omega^{-1}$). Each time the temperature controller was reset, measurements of G were made periodically until a constant value indicated that thermal equilibrium had been established. The temperature and conductance were then each measured in rapid succession, the measurements (emf, G) were then repeated to ensure that no thermal drift had occurred. Each measurement, therefore, took about 30 min from the time that the controller was reset to a new temperature. Frequent checks were made for precipitation or other spurious effects, the criterion for acceptability being less than 1% change in G in 16 h at the same temperature. After completing the low-temperature measurements, the temperature was then raised again to 690 °C, periodic check points being taken on the way up, and the conductance measurements completed by taking readings as rapidly as possible up to 770 °C. In some runs, sublimation altered the cell constant slightly during the run. This is shown by a discontinuity in plots of $\log_{10}\sigma T$ vs T^{-1} (see Fig. 1) at places where there has been a long interval between points due to an anneal at too high a temperature or to taking measurements at high temperatures in the interim. In such cases the change in the cell constant g was determined from overlapping data and the appropriate value of g used in converting the measured conductance values G to specific conductance σ using the relation $\sigma = Gg$. The most reliable values of g were considered to be those obtained by measuring the thickness of the crystal with a micrometer and determining the area indirectly by weighing the crystal (ignoring the weight of carbon which is negligible). Figure 1 shows high-temperature data for two runs, one an incomplete run on a Harshaw crystal and the other a complete run (designated 102-2) on a zone-refined crystal. For both runs, σ has been calculated using a g factor determined by weighing the crystal after the run. The agreement is very satisfactory. Cell constants for the other three runs analyzed numerically were, therefore, determined by normalizing the data to run 102-2. This was done in the following way. The top points in each run were

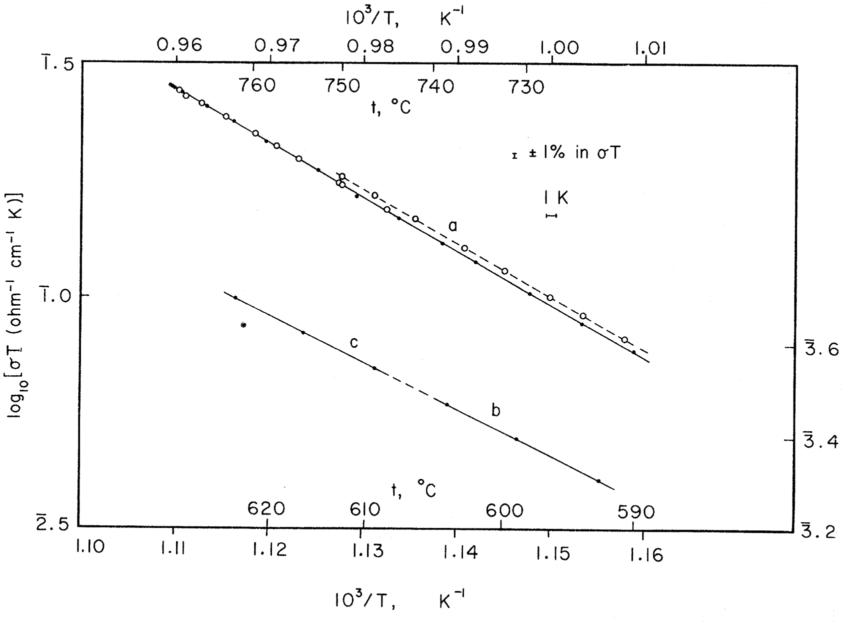

FIG. 1. Conductance of KCl at high temperatures. The closed circles are run 102-2; the continuous line is the least-squares fit to the top eight points for this run. The open circles are run H3. There was an interval of 16 h between the points on the dashed line and those which lie very close to the least-squares fit to 102-2, showing that an increase in geometric factor of rather less than 2% occurred during the 16-h anneal (at 672 °C) due to sublimation. No such change in g occurs on annealing at 600 °C, or on thermal cycling below that temperature, as shown by the lack of any significant discontinuity between the lines b and c.

fitted to linear equations by the method of least squares. Because of the small temperature range, this is a valid procedure (see, for example, Fig. 1). The necessary corrections to the constant term in these linear equations to make the conductivity agree with that of run 102-2 at 753 °C ($10^3/T = 0.975$) were found and $\log_{10}\sigma T$ then recalculated using the revised g factors. Figure 1 also shows that no change in g factor occurs even after a prolonged time interval at lower temperatures. The points in run 102-2 were taken in the following sequence: (a) 701–769 °C, (b) 605–361 °C, (c) 611–707 °C. The absence of any discontinuity between sections (b) and (c) shows the reproducibility of the measurements and specifically that no change in the g factor occurred during (b).

Four complete runs were made and analyzed, two on a KCl crystal zone refined in pure graphite in an atmosphere of HCl and two runs on a crystal grown from $5N$-purity KCl (from Koch Light Laboratories, Ltd.) *in vacuo* in a crucible of graphite after premelting under 1 atm of Cl_2. These runs are designated 102-1, 102-2 (for zone-refined KCl), and B4-5, B4-6 (for $5N$KCl). In addition to separate computer analyses of each run, a composite run was constructed by combining the 92 points from B4-6 with those data from the other three complete runs and the (intrinsic only) Harshaw run, which lay on a common curve. In practice, this amounted to only another 44 data points, showing how limited is the temperature region in which the conductivity can be described as intrinsic. The two B4-6 runs are later distinguished by the number of points analyzed, viz., 92 or 136.

III. ANALYSIS OF DATA

A. Debye-Hückel Model

Most of the calculations were based on the familiar model in which it is supposed that the principal defects are anion and cation vacancies, in concentrations determined by the Schottky defect equilibrium, and divalent cation impurity ions substituting for K^+ ions on normal lattice sites. The defect interactions allowed for are the formation of vacancy pairs (which contribute to diffusion but not to ionic conductivity), association of cation vacancies with divalent cation impurity ions on nearest-neighbor cation sites, and long-range Coulomb interactions through the Debye-Hückel approximation.[6] Expressing all concentrations as site fractions, the equations appropriate to this model are

$$f_1 c_1 f_2 c_2 = K_1' = e^{-g/kt}, \qquad (1)$$

$$c_k / f_1 c_1 f_M (c - c_k) = K_2' = 12\, e^{\zeta/kT}, \qquad (2)$$

$$c_1 - c_2 = c - c_k = c(1-p). \qquad (3)$$

Equation (1) expresses the Schottky defect equilibrium: c_1 and c_2 are the concentrations of (unassociated) cation and anion vacancies, respectively, and $g = h - Ts$ is the change in the Gibbs free energy accompanying the formation of a Schottky defect pair, apart from the configurational entropy contribution, h and s being the corresponding enthalpy and entropy. Equation (2) expresses the association of free-cation vacancies with unassociated divalent metal impurity ions to give complexes of concentration c_k. $-\zeta = -\chi + T\eta$ is the Gibbs free energy of association apart from the configurational entropy contribution, with χ and η the corresponding enthalpy and entropy. K_1' and K_2' are equilibrium constants for the formation and association of vacancies, respectively, p is the fraction of divalent impurity c which is in the associated state, and the f's are activity coefficients given by

$$f_1 = f_2 = f_M = \exp - e^2 k / 2\epsilon k T (1 + \kappa R). \qquad (4)$$

Here e is the charge on the proton, κ^{-1} the Debye length given by

$$\kappa^2 = 4\pi e^2 \textstyle\sum_j c_j / 2a^3 \epsilon k T, \qquad (5)$$

a being the nearest-neighbor anion-cation distance, and ϵ the permittivity of KCl. Values of the lattice parameter a were obtained by least-squares fitting the data of Enck *et al.*[27] for the thermal expansion coefficient. The equation used was

$$a = 314.66\,[1 + (34.94 + 0.01719\, t) \times 10^{-6} (t - 25)]\,\text{pm}, \qquad (6)$$

where t is the temperature in °C. Values of the permittivity were obtained by least-squares fitting the data of Smith[28] for the dielectric constant of KCl to the equation

$$\epsilon/\epsilon_0 = 4.753 + 0.14748 \times 10^{-2} t + 0.48287 \times 10^{-7} t^2 + 0.20109 \times 10^{-8} t^3, \qquad (7)$$

with ϵ_0 the permittivity of free space. $\sum_j c_j$ denotes a sum over the concentrations of the interacting species; in this model $\sum_j c_j = c_1 + c_2 + c - c_k = 2c_1$. In Eq. (4), R is the distance of closest approach.

The specific conductance σ is given by

$$\sigma = \textstyle\sum_r c_r e u_r / 2a^3, \qquad (8)$$

with the mobility u_1, u_2 of cation and anion vacancies

$$u_1 = g_0 (4e a^2 \nu_1 / kT)\, e^{-\Delta g_1/kT}, \qquad (9)$$

$$u_2 = g_0 (4e a^2 \nu_2 / kT)\, e^{-\Delta g_2/kT}, \qquad (10)$$

where Δg_1, Δg_2 are the Gibbs free-energy changes accompanying the motion of a cation, or anion, adjacent to a vacancy to the col of the energy barrier in the direction of the vacancy. For want of better information, the effective vibrational frequencies of the ions adjacent to their respective vacancies ν_1,

ν_2 have both been assumed equal to the lattice frequency $\nu = 4.5 \times 10^{12}$ sec^{-1}. Any differences will be incorporated in the migration entropies Δs_1, Δs_2. g_0 is the Onsager-Pitts mobility correction[29]

$$g_0 = 1 - [e^2\kappa/3\epsilon kT(1+\sqrt{2})(1+\kappa R)(\sqrt{2}+\kappa R)]. \quad (11)$$

In calculating the mobility correction, the values of R used were $R = \sqrt{3}a$ when $c_2 > c$, and $R = 2a$ when $c_2 < c$.

The method of calculation is essentially that devised by Beaumont and Jacobs.[11] Elimination of c_1 and c_k between Eqs. (1), (2), and (3) gives the cubic equation for c_2,

$$c_2^3 + c_2^2(c + K_1K_2) - K_1c_2 - K_2K_1^2 = 0. \quad (12)$$

Throughout this paper the omission of a prime on the symbol for an equilibrium constant denotes the corresponding concentration product, e.g., $K_1 = K_1'/f_1f_2 = c_1c_2$. In calculating K_1 from K_1', $R = \sqrt{3}a$ in formula (4), but in calculating K_2 from K_2', $R = 2a$. Equation (12) is solved by Newton's method for assumed values of the parameters and $\log_{10}\sigma T$ is calculated. The parameters are refined until

$$\varphi = \sum[(\log_{10}\sigma T)_{\text{calc}} - (\log_{10}\sigma T)_{\text{expt}}]^2 \quad (13)$$

is a minimum, the sum running over all the data points.

B. Frenkel Defect Model

It has been suggested by Allnatt and Pantelis[17] that NaCl might contain Frenkel defects at high temperatures. We considered that the occurrence of (cationic) Frenkel defects would be less likely in KCl, but felt that the possibility should be examined in view of the results of the calculations on model A. If Frenkel defects occur on the cation sublattice, then the additional equilibrium condition is

$$f_i\, c_i f_1 c_1 = K_F' = 2\, e^{-g_F/kT}, \quad (14)$$

with c_i the concentration of interstitial cations and g_F the Gibb free energy of formation of a Frenkel defect pair apart from the configurational contribution. The activity coefficient f_i of interstitial cations is evaluated from (4) with $R = \frac{1}{2}\sqrt{3}a$.

The conservation condition (3) is replaced by

$$c_1 - c_2 = c_i + c - c_k\,, \quad (15)$$

and Eqs. (1), (2), (14), and (15) yield the cubic equation

$$c_2^3 + c_2^2[K_1K_2 + cK_1(K_1+K_F)^{-1}] - c_2K_1^2(K_1+K_F)^{-1}$$
$$- K_1^3K_2(K_1+K_F)^{-1} = 0\,, \quad (16)$$

which replaces (12). A limited number of calculations were also performed using a model which included Frenkel defects on both sublattices.

C. Trivacancy Model

Only a linear trivacancy comprising two cation vacancies and one anion vacancy was considered since this was the type and configuration considered most probable by Fuller and Reilly.[25] The equations of equilibrium and conservation, with T denoting the trivacancy, are

$$c_T/c_2c_1^2 = 3\, e^{-g_T/kT} = K_T'\,, \quad (17)$$

$$c_1 + c_T - c_2 = c - c_k. \quad (18)$$

When these are combined with Eqs. (1) and (2), they lead to the cubic equation

$$c_2^3 + c_2^2(K_1K_2 + c - K_TK_1^2) - c_2(K_1^3K_2K_T + K_1)$$
$$- K_1^2K_2 = 0\,. \quad (19)$$

The binding Gibbs free energy of the trivacancy (apart from configurational contributions) is $-g_T$, so that g_T is expected to be negative, or at least very small if it is positive, if a significant number of trivacancies are formed.

D. Excess Conductance Model

As will soon be apparent, none of the models A through C is completely satisfactory. We therefore examined a very general model in which the sum over r in (8) includes an extra term $(B/T)\,e^{-E/kT}$. The carriers responsible for this term remain unidentified, but they are presumed to be responsible for any "excess conductivity" not included in model A. The implication is that the carriers responsible are completely decoupled from the other equilibria.

Barr and Dawson[22,23] have identified a dislocation component in anion diffusion in KBr. Such a component could be due to the diffusion of pairs or to single vacancies. If pairs, there will be no contribution to the conductivity; if single vacancies, then their contribution can be included approximately by a variant of model D in which B is made proportional to c_2. Actually, an integration is required with the argument equal to $c_d e u_d$, where both c_d and u_d are functions of the distance from the center of the dislocation. c_d could be evaluated,[30] but there is no good theory for the mobility u_d as a function of the distance from the center of the dislocation. Also, the surface potential and dislocation density are not known very precisely and would have to be treated as additional parameters. In view of the theoretical difficulties described above and because the preliminary calculations with $B \propto c_2$ did not look very promising, this dislocation model was not pursued further.

IV. RESULTS

A. Test of Method of Data Analysis

Since the determination of the conductance parameters as well as the tests made on the various models considered in Sec. III depend on the validity of the computing method, this was thoroughly

TABLE I. Results of feasibility tests of the computing method for analyzing conductance data. h and s are the enthalpy and vibrational entropy changes accompanying the formation of a Schottky defect pair. $-\chi$ is the enthalpy of formation of a divalent cation-cation vacancy complex. c is the site fraction of divalent impurity ions. Δh_1, Δs_1 (Δh_2, Δs_2) are the enthalpy and entropy of migration for cation (anion) vacancies. φ is the sum of the squares of the deviations between computed values of $\log_{10}\sigma T$ and "experimental" values which, in this calculation, were obtained by adding random errors to the values of σT calculated from the set of parameters designated II. 92 points were used in the calculations.

	Maximum random errors (%) in		Starting parameters	h (eV)	s (meV/K)	χ (eV)	10^6c	Δh_1 (eV)	Δs_1 (meV/K)	Δh_2 (eV)	Δs_2 (meV/K)	$10^3\varphi$
	σT	$10^3/T$										
1	...	...	I	2.0672	0.3666	0.4000	6.6806	0.7305	0.2000	1.2405	0.7239	
2	...	...	II	2.1884	0.2380	0.5627	0.9743	0.6670	0.2008	1.2942	0.8924	
3	0.5	0	II	2.2123	0.2792	0.5637	1.0392	0.6632	0.1906	1.2857	0.8740	0.1476
4	0.5	0	I	2.2052	0.2491	0.5672	0.9200	0.6653	0.2035	1.2867	0.8869	0.1451
5	1.0	0	II	2.2036	0.2411	0.5714	0.8919	0.6624	0.2024	1.2808	0.8848	0.5820
6	0.025	0.025	II	2.1794	0.2318	0.5590	1.0033	0.6694	0.2013	1.3002	0.8974	0.1582
7	0.05	0.025	I	2.2180	0.3556	0.5484	1.5404	0.6605	0.1540	1.2968	0.8490	0.1695
8	0.1	0.05	I	2.1957	0.3216	0.5472	1.4873	0.6631	0.1602	1.3044	0.8638	0.6383

checked at the outset. Basically, the method was that used by Beaumont and Jacobs,[11] except that a more powerful least-squares program was employed. However, a particular set of data was run on the IBM 7040 computer at the University of Western Ontario using the new program and the same set was also analyzed on the Atlas computer of Manchester University using the Beaumont and Jacobs program. Essentially identical results were obtained for the parameters. The cubic equation was generally solved for c_2 by Newton's method; however, as c_2 becomes very small at low temperatures, a check was made to see if rounding errors were affecting the accuracy of the results by solving the equivalent cubic equation for c_1. No differences in the results were found.

Tests were then made of the ability of the program to converge to a particular set of "perfect-fit" parameters . It is not a sufficient test (although this too was accomplished) to generate a set of conductivity data at specified temperatures from a set of starting parameters and then show that a new set of parameters will converge to the original set, because such data are artificially smooth. We therefore generated a set of conductivity data from a set of parameters (the ones actually used being shown on the second line of Table I) at values of $10^3/T$ that corresponded to the actual temperatures used in a particular run (B4-6). Random errors up to a specified maximum value were then generated and added to the calculated values of σT and the chosen values of $10^3/T$. The maximum random error need not be the same for σT and $10^3/T$. The convergence of two sets of starting parameters were studied using the generated data, including the random errors, as "experimental data." One of these sets, designated II, was the original set used to generate the data and so would correspond to a perfect fit to the data if no random errors had been introduced. The other set was chosen so as to correspond to a very different start in eight-parameter space. The largest change was in the concentration which was off by a factor of more than 6.

It is difficult to decide on a reasonable magnitude for the random errors. The temperature remained stable to 0.1 K during a conductance measurement. (This was checked at every point and if a greater variation was found, measurements were continued until this condition was satisfied.) This corresponds to an error of 0.01–0.02% in T and the same in $10^3/T$. Measurements of σ were made to four significant figures which means 0.01–0.1% error. Both these estimates apply to the expected random errors associated with the determination of any one point and not, of course, to the absolute accuracy.

The results of these tests are shown in Table I. The starting parameters are on the first two lines. Lines 3 and 4 show that with 0.5% random deviations in σT only, the parameters from set I converge to as good a minimum as do the perfect-fit set II, and that the converged sets show good recovery of the enthalpies but lower accuracy in s and also c (5–7%). This is to be expected from the form of the conductance equation. With 1% random errors in σT, the sum of the squares of the deviations φ was worse by a factor of 4. When random errors are introduced into both variables, the concentration is off by almost 50% with corresponding variations in s and Δs_1, with which parameter c is strongly correlated. The recovery of Δs_2 and the four enthalpies is still uniformly good, however. Probably variations in starting values should have been probed in more detail. The recovery of c from a value off by a factor of 6 to one only 50% away from the best-fit value is, in fact, impressive as is the accuracy in the enthalpies, particularly Δh_1 (0.5–1%) and h (<1%). Since c is an unknown parameter, the slowness of c to converge to its correct value while still giving a reasonable fit to the data, e.g., lines 7 and 8, is a worrying feature. But if one obtains closely similar values for the entropies s and Δs_1 from analyses on different crystals, then it may be concluded that the minima found are the correct ones. Reproducibility of converged values for the concentration, when a range of starting values is used, will also be a guide that a correct minimum has been obtained. Finally, there is clearly little point in expecting φ to be less than about 2×10^{-4} for a 92-point run if the above random errors are realistic.

B. Debye-Hückel Model

Because of the slow convergence of c when it is far from the correct value, the first analyses on each crystal involved finding the approximate concentration of adventitious divalent cation impurity by varying the initial value of c over a wide range. Final analyses were then made limiting c to a range around this approximate value. The first conductance run analyzed was 102-2. As this refers to a zone-refined crystal, c is low ($<1\times10^{-6}$) and consequently association is limited, resulting in a difficulty of separating Δh_1 and χ. However, converged values of the other parameters did not depend systematically on the values of these parameters. It was clear from the slopes of the extrinsic part of the plots of $\log_{10}\sigma T$ vs T^{-1} that Δh_1 was <0.7 eV. The technique adopted in the systematic analysis of this run was therefore to fix Δh_1 at a series of seven values increasing in equal increments from 0.670 to 0.705 eV. As Δh_1 was increased, χ at first remained constant but then decreased rapidly for $\Delta h_1 = 0.695$, 0.705 eV. The mean value of χ for the first five runs was 0.565 eV, which agrees well with the value found for the two less-pure crystals (Table II). φ was about 3×10^{-4} for this 77-point run. Means of other parameters are shown in the line I in Table II. All are means of the converged results from seven computer runs except χ, for which the two obviously low values have been dropped, as explained above. The range of c, for example, was from 0.1831 to 0.2278×10^{-6} with no systematic dependence on Δh_1. A further series of seven runs was performed in which Δh_1 was allowed to vary. In four of these, the starting value of h was the (rounded) mean from line I; in the last three the initial value of h was varied over a wide range, namely, 2.25, 2.35, and 2.40 eV. Means of converged parameters for the two sets appear on lines II and III of Table II. Note the insistence of a value close to 2.30 eV for h, the good internal consistency of the other parameters, the "high" values for the anion migration parameters (to be discussed later), and the difficulty in preventing Δh_1 from drifting upwards in this run (with consequent low values for χ) because of the small degree of association. Means of all the analyses for this crystal are given on the fourth line of the table except for χ and Δh_1, for which it is not justified to do so.

The next conductance run analyzed was 102-1, done on a cleave from the same zone-refined crystal. Initial tests in which c was varied by a factor of 5 from 0.1 to 0.5×10^{-6} gave a mean converged value of c of 0.237×10^{-6}. In the final set of six runs, initial values of c were varied only over the range $0.20–0.28\times10^{-6}$. Means of the results for these six runs are given in line IV of Table II. This run contained insufficient extrinsic data to produce a reliable value for χ because there is so little association in these pure crystals. Random errors were evidently greater in this run since φ was about 2.5

TABLE II. Summary of conductance parameters from Debye-Hückel model. The symbols are defined in the caption to Table I. The meaning of the numbers I–VII is explained in the text.

	h (eV)	s (meV/K)	χ (eV)	10^6c	Δh_1 (eV)	Δh_1 (meV/K)	Δh_2 (eV)	Δs_2 (meV/K)
I	2.303	0.427	0.565	0.208	[a]	0.215	1.533	1.063
II	2.294	0.435	0.440	0.212	0.697	0.222	1.552	1.072
III	2.294	0.416	0.413	0.212	0.699	0.235	1.557	1.079
102-2 mean	2.296	0.427	[b]	0.210	[b]	0.222	1.543	1.070
IV	2.302	0.391	0.435[c]	0.256	0.677	0.220	1.420	0.981
V	2.301	0.374	0.594	0.587	0.679	0.231	1.340	0.913
VI	2.299	0.352	0.567	0.912	0.674	0.232	1.230	0.816
VII	2.302	0.358	0.577	0.850	0.665	0.226	1.303	0.884
DH mean	2.299	0.383	0.580	···	0.676	0.230	1.387	0.947

[a] Δh_1 held fixed at a series of values from 0.670 to 0.705 eV.

[b] When Δh_1 is allowed to vary, a high value for Δh_1, and a correspondingly low value for χ, are produced for this crystal because c is so small.

[c] Insufficient extrinsic data to produce a reliable value of χ because there is so little association in the pure crystals: not included in final means.

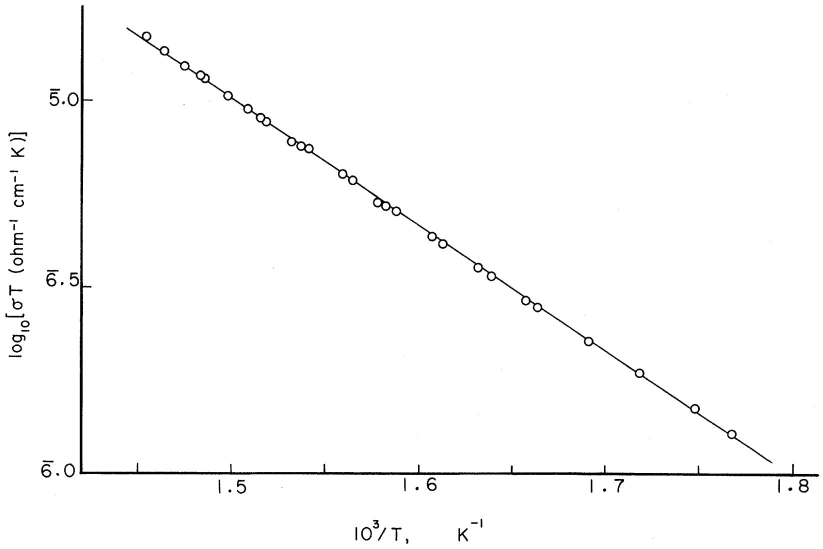

FIG. 2. $\log_{10}\sigma T$ vs $10^3/T$ for a relatively pure KCl crystal ($c \sim 2 \times 10^{-7}$) in the extrinsic region. The points scatter about a straight line because association is so small: p varies from 4×10^{-4} to 1.2×10^{-3} over the temperature range shown. The slope of this line corresponds to $\Delta h_1 = 0.668$ eV. Data are from run B4-1, which was not analyzed in detail because there were too few points taken at high temperatures. Some preliminary computer analyses gave $\Delta h_1 = 0.667$ eV, in agreement with the graphical value and the result from the 136-point composite run (line VII, Table II).

$\times 10^{-3}$ for 62 points.

Results of analyses for the two conductance runs B4-5 and B4-6 on KCl grown in pure carbon are given in the lines designated V and VI. Each is the mean of three computer runs in which c was varied over a small range, $\pm 11\%$ in B4-6 and $\pm 18\%$ in B4-5. For B4-5, φ was 9.5×10^{-4} for 53 points and, for B4-6, φ was 4.9×10^{-4} for 92 points. In line VIII appear the means from six computer analyses of the 136-point composite run. φ was 2.1×10^{-3}. These runs consist of two sets of three each, each one of the three having a different input concentration. The other input parameters were the means of results from runs other than B4-6, for the first set, and from the 92-point B4-6 analyses, for the second set. As there were no systematic differences in the final parameters the results for all six runs were averaged.

The parameters from the four individual conductance runs given in Table II show a high degree of concordance with one another. Greatest variations are in the anion migration parameters, which are all high. A check on the cation migration enthalpy is provided by plots of $\log_{10}\sigma T$ vs T^{-1} for pure crystals at low temperatures. Such a plot is shown in Fig. 2. The slope of the line yields a value for Δh_1 of 0.668 eV, showing that the computed values are satisfactory. The consistency of the results for c may be tested by plotting σ at a temperature safely in the extrinsic region vs $c(1-p)$, where p is the degree of association when a straight line is expected. Such an isotherm for $10^3/T = 1.500$ K^{-1} is shown in Fig. 3. The computed concentrations for the three highest concentrations lie on a straight line while the lowest concentration (run 102-2) lies below this line. Because of the strong correlation of s with c, a high value of c means a high value of s, which is borne out by the mean value for 102-2 of 0.427 meV K^{-1} compared with the means for the other three individual runs which range from 0.352 to 0.391 meV K^{-1}. The concordance in values for Δs_1 is an added indication that the values for c are at least consistent and, because four different runs are involved, likely to be close to the actual values for the site fraction of dissolved impurity. The means of the means for the four individual runs are given in the last line of the table so that they may be compared with VII, the means for the composite 136-point run.

In all the above analyses, the entropy of association was neglected. This is justifiable because of the small concentrations involved. However,

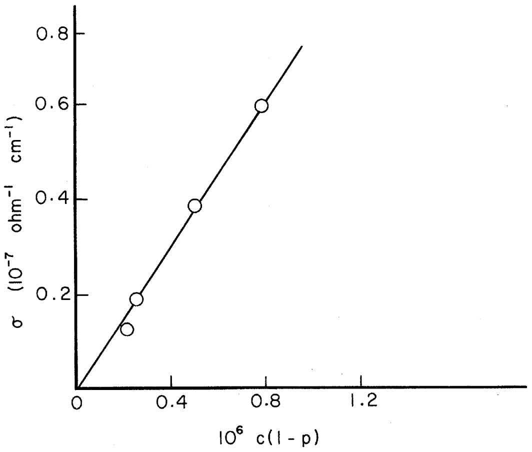

FIG. 3. Specific conductance σ at 393.6 °C ($10^3/T = 1.500$ K^{-1}) as a function of the concentration of free vacancies $c(1-p)$. The linear relation found shows that the values of c found from the computer analyses are mutually consistent.

TABLE III. Comparison of conductance parameters from various models. $-\eta$ is the vibrational entropy change accompanying the formation of a complex. h_F, s_F are the enthalpy and vibrational entropy of formation of a Frenkel defect pair. Δh_i, Δs_i refer to the enthalpy and entropy of migration of interstitial ions. The first time they appear in the list they refer to cations, the second time to anions. B and E are the parameters defining the unknown contribution to σT, $B\,e^{-E/kT}$. Remaining symbols are defined in the caption to Table I.

Parameter	VIII Debye-Hückel model with nonzero entropy of association	IX Debye-Hückel interactions suppressed	X Frenkel defects, cation sublattice	XIII Frenkel defects on both sublattices	XIV Excess conductance model
h(eV)	2.302	2.302	2.226	2.157	2.222
s(meV/K)	0.379	0.350	0.244	0.202	0.231
χ(eV)	0.590	0.571	0.563	0.560	0.561
η(meV/K)	0.048				
c	0.965	0.764	0.976	1.033	1.002
Δh_1(eV)	0.673	0.668	0.675	0.667	0.676
Δs_1(meV/K)	0.225	0.238	0.228	0.196	0.226
Δh_2(eV)	1.305	1.334	0.978	1.251	0.943
Δs_2(meV/K)	0.873	0.933	0.570	0.850	0.544
h_F(eV)			3.614	3.655	
s_F(meV/K)			0.094	0.256	
Δh_i(eV)			0.530	0.303	
Δs_i(meV/K)			1.574	1.213	
h_F(eV)				3.808	
s_F(meV/K)				0.235	
Δh_i(eV)				0.567	
Δs_i(meV/K)				0.704	
B(Ω^{-1} cm^{-1} K)					1.94×10^{15}
E(eV)					3.184

to check that this was not distorting the parameter values, an analysis of the composite run was performed with a finite η. Results are given in column VIII of Table III. The converged value of η was 0.048 meV K^{-1} and any improvement in the fit marginal and probably due merely to the increase in the number of parameters from eight to nine.

The effect of including long-range interactions through the Debye-Hückel model was also tested by suppressing that part of the calculation. The results of this test are shown in column IX of Table III. The results of this test are frankly disappointing since they show no significant changes either in the parameters or in φ (2.14×10^{-3}). The improved fit generally attributed to the inclusion of Debye-Hückel interactions may be due simply to prolonged computing leading to a better minimum.

C. Frenkel-Defect Model

The cation migration parameters determined from the Debye-Hückel model are reasonable, but the anion migration parameters seem too high. It may be argued that the presence of the extrinsic region will help to fix the cation parameters and that any discrepancies between the experimental and theoretical conductivities at high temperatures will therefore be forced into the anion parameters. In order to test whether KCl at high temperatures contained a small number of Frenkel defects in addition to the predominant Schottky defects, the data for the 136-point composite run was reanalyzed allowing for the presence of Frenkel defects. Debye-Hückel interactions were again included. These calculations showed that it is unlikely that the anomalous high-temperature conductivity of KCl (as evidenced by the values obtained for the anion migration parameters from the Schottky defect model) can be explained by the presence of Frenkel defects. It is true that good fits to the composite-run data can be obtained, $\varphi = 1.6$ to 2.2×10^{-3}, and that the anion migration parameters are now closer to diffusion values but the Frenkel parameters show unacceptable behavior. In column X of Table III, h_F is 3.6 eV (close to a calculated value[31] of 3.53 eV) and s_F is small as would be expected, but Δs_i is far too large. If attempts are made to reduce Δs_i by varying starting values, then an alternative minimum can be obtained with $\Delta s_i = 0.6$ meV K^{-1}, which is still rather high, but only at the cost of either a substantial decrease in the migration enthalpy Δh_i coupled with either a big increase in the formation entropy s_F, or a substantial decrease in the enthalpy of formation, h_F. The wide disparity in these sets of parameters and their unacceptable character lead us to the conclusion that cationic Frenkel defects are not the explanation.

A few calculations were also done on the B4-6 data assuming Frenkel defects on both sublattices.

The results are given in column XIII of Table III. Strangely, the anion vacancy migration parameters are not lowered as much as for the single-Frenkel-defect model. The anion Frenkel defect parameters do not seem too unreasonable although the migration entropy is rather high and the formation enthalpy more than 1 eV lower than the calculated value[31] of 5.40 eV. However, the extremely high cationic interstitial mobility which results from these calculations, coupled with the failure to reduce significantly the anion vacancy migration parameters, lead us to reject this model. We also feel that because 16 parameters were used and because the calculations were not pursued in great detail, the results for the double-Frenkel-defect model should not be used quantitatively, although the qualitative conclusions drawn about the model are probably valid.

D. Trivacancy Model

Calculation based on Eq. (19) were unsuccessful. A poor fit to the data for the composite run can be obtained but g_T comes out to be positive, i.e., the binding energy of the trivacancy is negative, which is physically absurd. Also, the trivacancy migration enthalpy seems too low at 0.20 eV. If h_T and s_T are set equal initially to -0.8 eV and -0.1 meV K^{-1}, the program makes them small and positive, 0.014 eV and 0.004 meV K^{-1}, with a corresponding migration enthalpy Δh_T of 2.26 eV. This kind of erratic behavior, the physical unacceptability of the parameters, and the poor fit to the data lead us to reject the trivacancy model.

E. Excess Conductance Model

This model was tested using the data for the composite run. Convergence was slow; but a reasonable fit, $\varphi = 1.68\times10^{-3}$ for 136 points, was obtained with the parameters designated XIV in Table III. The anion mobility enthalpy Δh_2 is 0.943 eV, more in line with diffusion values. If the initial values of B and E are decreased to correspond more closely with those found by Dawson and Barr[23] for extrinsic diffusion in KBr, then the calculation becomes ill behaved: With initial values for $B \geqslant 5\times10^5\ \Omega^{-1}\ \mathrm{cm}^{-1}$ K and $E > 1.46$ eV, Δh_2 and h increase as the calculation progresses, but if initial parameters are set so that $B = 1\times10^4\ \Omega^{-1}\ \mathrm{cm}^{-1}$ K, $E = 1.2$ eV, then B is driven negative. We conclude that a fit to the conductivity data for KCl cannot be obtained with parameters similar to those appropriate for extrinsic diffusion in KBr, although a reasonable fit can be obtained with the parameters cited in Table III, column XIV. A few calculations were also done making the preexponential factor B proportional to c_2 in a crude attempt to check if the migration of anion vacancies down dislocations or grain boundaries was responsible for the extra conductance. The fits were very poor. Convergence was not obtained and as the anion migration parameters drifted slowly upwards the calculations were not continued. One may conclude, though, that including a term $B'c_2\,e^{-E/kT}$ does not allow a good fit to the KCl data with reasonable anion migration parameters.

V. DISCUSSION

A. Comparison with Diffusion Data

The primary advantage of the method of analysis employed is that the parameters obtained from fitting the conductance data to various models can be used to predict anion and cation diffusion coefficients as functions of temperature. Diffusion coefficients D_r for species r were calculated from the modified Nernst-Einstein relation

$$D_r = 2a^3 f_r\,(kT/e^2)\,\sigma_r. \tag{20}$$

The value 0.7815 was used for the correlation factor f_r for both cation vacancies and anion vacancies. When this work was first analyzed, the only cation diffusion data available were that of Aschner.[32] When the calculations had been completed, two further investigations appeared in the literature.[33,34] Excellent anion diffusion data are available from the work of Fuller,[12] who also separated the vacancy-pair contribution so that we have $D_- = D_a - D_p$ where D_- is the contribution to the total anion diffusion coefficient due to single vacancies and D_p is that due to pairs. The cation diffusion data of Aschner were vacancy pair corrected using the equation for D_p given by Fuller.[12] This is not quite correct if the jump frequencies of anion and cation vacancies in a pair are unequal, making the ratio of the correlation coefficients different from unity and temperature dependent. Figure 4 shows the plot of Aschner's pair-corrected data as well as the least-squares fits to $\log_{10} D_+$, for corrected and uncorrected data, using only the points at temperatures such that $10^3/T < 1.17$ K^{-1}. Aschner's crystals were rather impure and there is a danger of impurity effects on the three low-temperature points. Also shown are predicted lines corresponding to the parameters from lines VII (Debye-Hückel model with $\eta = 0$), X (best fit to the Frenkel model), and from the work of Fuller *et al.*[16] and Chandra and Rolfe.[19] The latter two lines pass acceptably close to Aschner's data points, particularly if one neglects the three at the lowest temperatures, although the slope of both lines is greater than our least-squares fit to the Aschner data. The line X represents a total cation diffusion coefficient due to single cation jumps, i.e., vacancies plus interstitials, and, hence, it is not a straight line. The line marked XIV is that calculated from the parameters obtained from the excess conductance model. When our calculations were complete, two further papers on diffusion in KCl

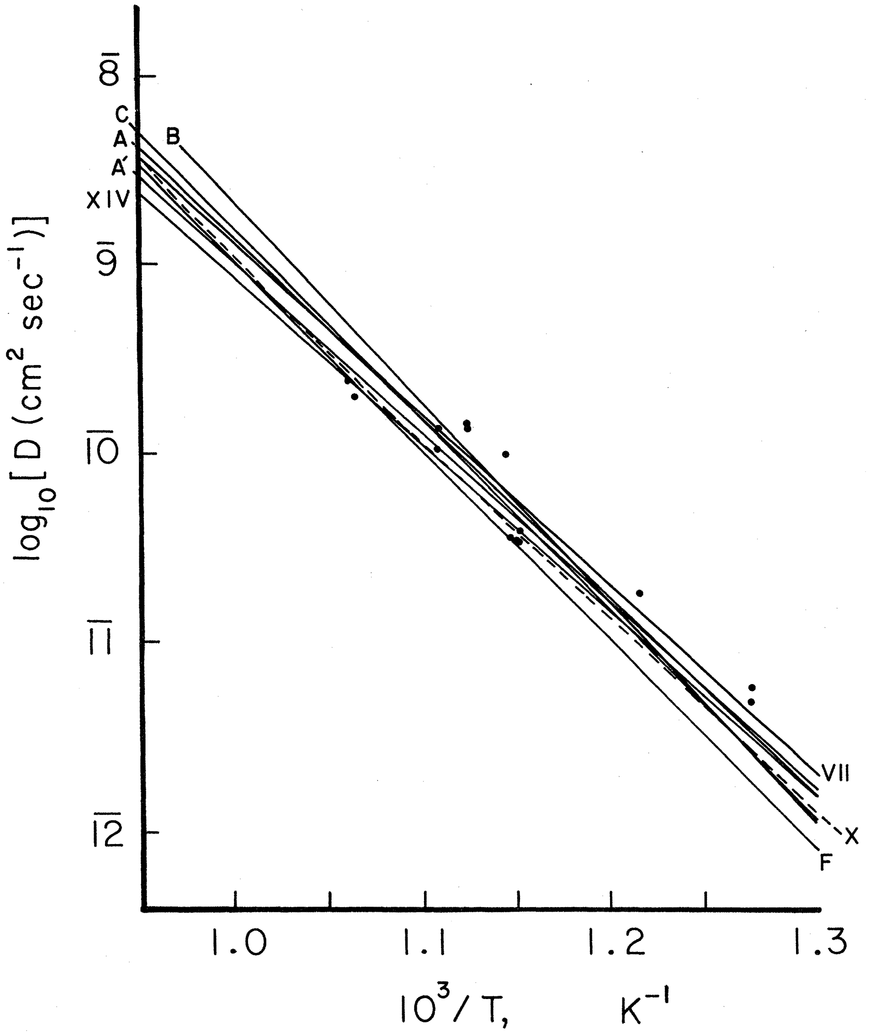

FIG. 4. Logarithm of the cation diffusion coefficient for KCl as a function of reciprocal temperature. The points are Aschner's (Ref. 32) experimental data vacancy-pair corrected using the equation of Fuller (Ref. 12). The line A′ is least-squares fit to Aschner's pair-corrected data. The line A is a least-squares fit to Aschner's uncorrected data. Line B is from the data of Bénière *et al.* (Ref. 34). Lines C and F have been calculated from defect parameters given by Chandra and Rolfe (Ref. 19) and by Fuller *et al.* (Ref. 16). Lines VII, X, and XIV have been calculated from the parameters so designated in Tables II and III.

were published. Parashar's crystals are clearly very impure and show a good deal of association.[33] Because of the limited intrinsic region (perhaps two points), no meaningful comparisons can be made. The data of Bénière *et al.*[34] are remarkably self-consistent, and although they agree quite well with Aschner for $1.07 < 10^3/T < 1.17$, their line has a much higher slope than the least-squares fit to Aschner's data. The Bénière line B in Fig. 4 has not been corrected for vacancy pairs, and in their paper they state that the excellent linearity found in plotting $\log_{10}D_c$ vs T^{-1} shows that the pair contribution is negligible. Bénière's method of analysis rests heavily on the agreement between their values for the extrinsic activation energy for conductance of pure KCl, KCl + 6.1×10^{-5} $SrCl_2$ and cation diffusion in the $SrCl_2$-doped KCl. However, this value, 0.79 eV, is much too high. The slope of the (approximately) linear portion of the conductance curve gives an upper bound to Δh_1. In Fig. 2, we show the relevant portion of the conductivity curve for one of our pure crystals. The straight line corresponds to an enthalpy of migration of 0.668 eV. In general, the extrinsic slope of the conductance curve when multiplied by k is $\Delta h_1 + \chi p/(1+p)$ and we conclude that the neglect of association by Bénière *et al.* is not justified. Even in KCl containing 0.9 $\times 10^{-6}$ divalent impurity, the degree of association p is 0.104 at 418.4 °C ($10^3/T = 1.446\ \mathrm{K}^{-1}$) rising to 0.508 at 260 °C ($10^3/T = 1.876\ \mathrm{K}^{-1}$).

Plots for the anion diffusion coefficient are shown in Fig. 5. The points are Fuller's experimental data including his estimated experimental error for the primary data, D_a. The points plotted have been vacancy pair corrected and so the experimental uncertainty is actually larger than that for D_a, depending on the accuracy with which the pair contribution has been estimated. The line marked B is that due to Bénière *et al.*[34] after their own vacancy-pair corrections have been applied. The line F is calculated from the parameters obtained by Fuller *et al.*[16] from fitting their conductance and anion diffusion data and its agreement with the data points does not, of course, constitute an independent check on the parameters but merely confirms that the fitting was carried out correctly. The line C shows the diffusion coefficient predicted from the parameters of Chandra and Rolfe[19] while lines VII, X, and XIV again show the predictions from the conductance parameters obtained using the Debye-Hückel, Frenkel, and excess conductance models, respectively. The best fit to the Fuller data is given by X, but we regard this as fortuitous since the cation interstitial parameters appear unreasonable; in particular, the migration entropy is much too high. A definitive check on Frenkel disorder could be obtained if very precise cation diffusion coefficients were available up to the melting point, but such data would be extremely difficult to acquire. The parameters from the excess conductance model, line XIV, correspond to values of D_- that agree quite well with the experimental data of Fuller *et al.* The Debye-Hückel line VII intersects the center of the D_- experimental data but has too high a slope.

B. Reliability of Calculations

Apart from the reproducibility of final values for parameters achieved from different starting points in parameter space and in different calculations on different crystals (Table II), one should obviously seek to confirm that the experimental data have been adequately fitted by the particular model used. This may be gauged by φ or, in more detail, by difference plots of $\log_{10}(\sigma T)_e - \log_{10}(\sigma T)_c$ against T^{-1}, where e denotes the experimental value and c the calculated value. The program tests described in IV show that a value of $\varphi < \sim 2\times 10^{-4}$ cannot be expected when realistic random errors are included in synthetic values of $\log_{10}\sigma T$ and T^{-1}. For comparison of runs involving different numbers of points L, the variance $\sigma = [\varphi/(L-1)]^{1/2}$ is a more useful quantity. For the four runs analyzed separately, $\sigma \times 10^3$ was 2.0, 6.4, 4.3, and 5.4; for the

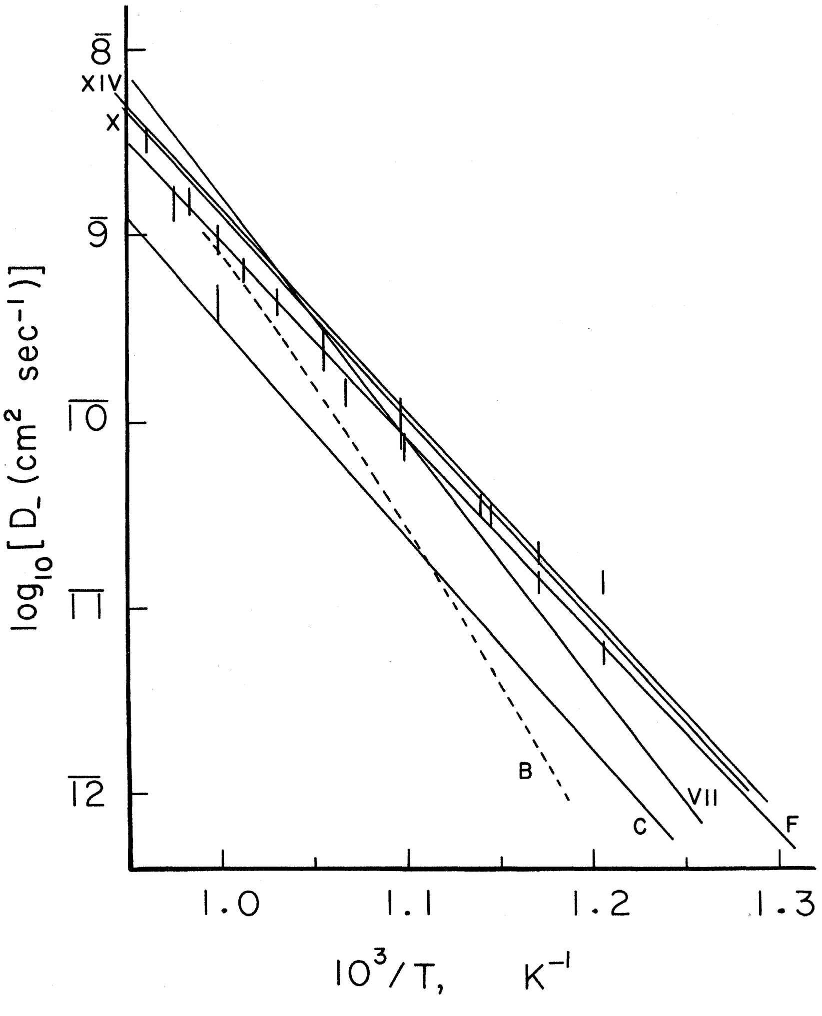

FIG. 5. Logarithm of the anion vacnacy diffusion coefficient for KCl as a function of reciprocal temperature. The vertical lines show Fuller's (Ref. 12) experimental data, vacancy pair corrected using Fuller's equation; the experimental uncertainty is that quoted for the primary data D_a. Line B is from Bénière *et al.* (Ref. 34) and has also been vacancy pair corrected. Lines C and F have been calculated from defect parameters given by Chandra and Rolfe (Ref. 19) and by Fuller *et al.* (Ref. 16). Lines VII, X, and XIV have been calculated from the parameters so designated in Tables II and III.

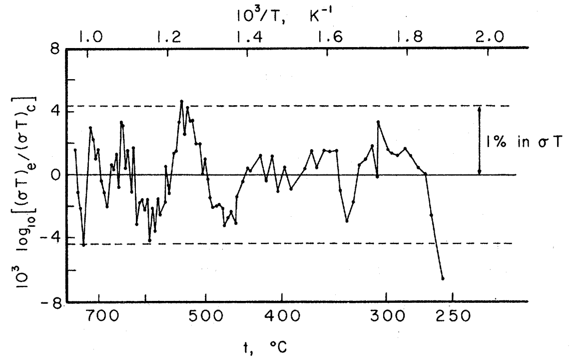

FIG. 6. Plots of $10^3 [\log_{10}(\sigma T)_e - \log_{10}(\sigma T)_c]$ vs $10^3/T$ for the computer fit to B4-6 (92 points), using the Debye-Hückel model. The dashed lines show the deviations to be expected for a 1% discrepancy in σT.

composite run, $\sigma = 3.9 \times 10^{-3}$. These values may be compared with $\sigma \times 10^3 = 1.3$, 1.4, and 2.6 for lines 6, 7, and 8 in Table I, and show that the fits obtained are realistic. A plot of $\log_{10}(\sigma T)_e - \log_{10}(\sigma T)_c$ vs T^{-1} is shown in Fig. 6 for a typical run. The behavior of the deviations approaches that expected for random behavior (cf. Refs. 11 and 16), although there is some indication of a low-period oscillation which might point to either inadequacies in the model or to incomplete convergence, or to both these factors. Figure 7 shows the high-temperature portion alone on a larger scale and illustrates the fit to the 136-point composite run obtained with the Debye-Hückel model and the excess conductance model. The deviations are smaller for the latter but the trends are similar.

C. Reconcilation with Diffusion Data

There appear to be three possible explanations to the relatively poor agreement of the experimental values of D_- with those predicted from the Debye-Hückel parameters if we accept the validity of the computing method, as seems quite justifiable from the above considerations. First we may be underestimating the long-range defect interactions. Whereas the Debye-Hückel formula is extremely simple to apply, it is by no means obvious what the next-best approximation should be. Certainly, a simple numerical formula is lacking. However, the effect on the parameters of including the Debye-Hückel corrections is small, so that it is doubtful if a more sophisticated approximation for the long-range interactions would improve matters. Second, there may be an additional contributor to the current at high temperatures. This species is unlikely to be trivacancies, nor is it likely to be cation interstitials because of the unrealistic entropy of migration that results from the best fit to the Frenkel model. The values of B and E from the excess conductance model are not much help in identifying such a species since quite widely different pairs of values for B and E give almost as good fits. This is not too surprising in view of the small temperature range over which this contribution is effective. For instance, for the fit XIV the transference number of the unknown species t_x goes from 0.01 at 560 °C to 0.28 at 770 °C, while over the same range t_- goes from 0.23 to 0.47. The one thing that does seem tolerably certain is that parameters similar to those which characterize Barr and Dawson's[23] extrinsic acion diffusion in KBr will not fit the high-temperature conductivity of KCl.

The third possibility is simply that the contribu-

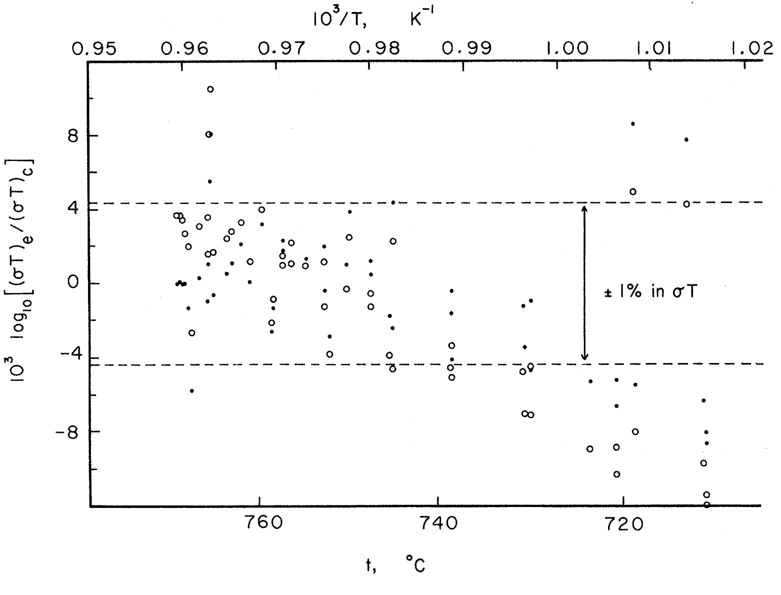

FIG. 7. Plots of $[\log_{10}(\sigma T)_e - \log_{10}(\sigma T)_c] \times 10^3$ vs $10^3/T$, for the high-temperature portion of the 136-point composite run. The dashed lines show the deviations expected for ±1% discrepancy in σT. Open circles, Debye-Hückel model; filled circles, excess conductance model.

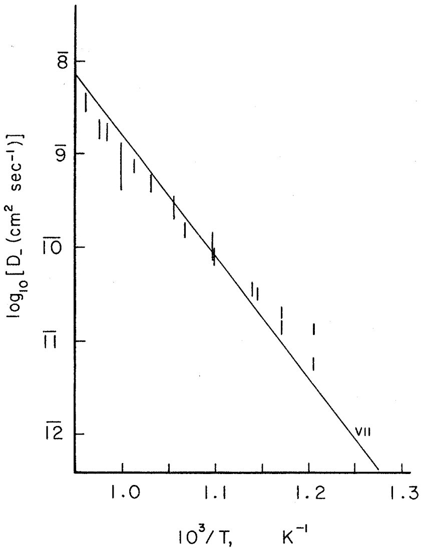

FIG. 8. Logarithm of the anion vacancy diffusion coefficient for KCl as a function of reciprocal temperature. VII represents diffusion coefficients calculated from parameters derived from fitting the conductance data to the Debye-Hückel model. (Numerical values are in Table II.) The vertical lines show the uncertainties in D_-; these have been calculated from the quoted uncertainties in D_a (Ref. 12) and in D_p (Ref. 16).

tion of vacancy pairs to anion (and cation) diffusion in KCl may not be well known and thus the error bars on the anion vacancy diffusion coefficients in Fig. 5 too conservative if we employ only the uncertainty in D_a. The three equations that have been given for the pair contribution D_p in $\mathrm{cm}^2\,\mathrm{sec}^{-1}$, are

$$D_p = 8560 \exp(-2.654\ \mathrm{eV}/kt), \qquad (21)$$

$$D_p = 5150 \exp(-2.62\ \mathrm{eV}/kt), \qquad (22)$$

$$D_p = 987 \exp(-2.49\ \mathrm{eV}/kt). \qquad (23)$$

The same data are involved in the first two equations; they differ because (21) is from a fit to diffusion data only while (22) results from a combined fit of conductivity and diffusion data. Equation (21) was the one used to calculate the values of D_- in Fig. 5. No error limits were available for the pair correction so that the error bars in Fig. 5 are simply Fuller's own estimates of the error in D_a. However, if we calculate new uncertainty limits for D_- based on the published uncertainties for D_p in Eq. (22),[16] and the original error limits for D_a, then Fig. 8 shows that the predicted diffusion coefficients from the Debye-Hückel model are rather more compatible with the experimental data if the revised, and more realistic, uncertainties in D_- are used. It will thus not be possible to decide unequivocally between the Debye-Hückel model and one which involves a further transport mechanism until more precise values of D_- and D_+ are available.

D. Summary of Defect Parameters

The best-fit parameters from the Frenkel calculation and the excess conductance calculation are summarized in Table IV, where they may be compared with the Debye-Hückel results VII and also those published by Fuller *et al.*,[16] Chandra and Rolfe,[19] and Bénière *et al.*[34] There are obvious discrepancies. The Schottky parameters obtained when an additional conduction mechanism is allowed for are consistent with one another; in particular, the anion migration energy, 0.94–0.98 eV, agrees with the diffusion value of Fuller and with conductance value found by anion doping (0.99 eV) but is still higher than the two values found from a combined analysis of conductance and diffusion data. The value of 0.85 eV is, however, not to be relied

TABLE IV. Summary of Schottky defect parameters for KCl. Symbols are defined in the caption to Table I.

Source	h(eV)	s/k	Δh_1(eV)	$\Delta s_1/k$	Δh_2(eV)	$\Delta s_2/k$
X	2.226 ±0.039	2.83 ±0.43	0.675 ±0.006	2.65 ±0.21	0.978 ±0.073	6.65 ±0.92
XIV	2.222 ±0.034	2.68 ±0.42	0.676 ±0.006	2.62 ±0.19	0.943 ±0.032	6.31 ±0.38
VII	2.302 ±0.020	4.16 ±0.29	0.665 ±0.006	2.62 ±0.20	1.303 ±0.012	10.26 ±0.19
Ref. 11	2.26	5.37	0.705	1.89	1.04	6.28
Ref. 12	2.31	7.56	...	...	0.95	4.19
Ref. 16	2.49 $^{+0.03}_{-0.02}$	7.64 $^{+0.24}_{-0.11}$	0.76 $^{+0.02}_{-0.01}$	2.56 $^{+0.11}_{-0.04}$	0.89 $^{+0.01}_{-0.05}$	3.95 $^{+0.71}_{-0.57}$
Ref. 19	2.59	9.61	0.73	2.70	0.99	4.14
Ref. 34	2.64	10.90	0.79	2.84	0.85	2.47

on because of the approximate method of analysis used. The anion migration entropies come out higher from the analysis of conductance data on pure crystals alone (this work) than from analyses based on anion and cation doping[19] or on a combination of diffusion and conductance data,[16] and this is particularly marked for the Schottky model with Debye-Hückel interactions. As pointed out in Sec. V C, there is a good deal of uncertainty in the anion parameters due to doubts about the exact vacancy-pair correction. The best comparison is, therefore, that in which a predicted diffusion coefficient is compared with experimental values including realistic uncertainty bars (Figs. 5 and 8). This comparison is, of course, precluded if the diffusion data have been utilized in the analysis. One might expect that an analysis based on anion doping would give the best results. In fact, the agreement is rather worse than that obtained from the present analysis of pure-crystal data using either the Debye-Hückel or the other carrier models. The main reason for this is probably the small temperature range over which the $CO_3^=$ ion is soluble in KCl. In addition, the method of analysis was approximate since the cubic equation was not solved.[19]

The discrepancies in the formation and cation migration parameters can be explained as follows. The use of any information other than the intrinsic conductivity of a pure crystal tends to peg the parameters most concerned. If the information is reliable this is, of course, a good thing since it eases (even makes possible) the analysis for the other parameters. We avoided cation doping since it is not clear that the same model holds for pure and doped crystals. The inclusion of a small amount of cation extrinsic conductivity is unavoidable except in very specially purified crystals, is desirable to aid data fitting, and should be unobjectionable theoretically. However, in such analyses the cation parameters tend to be fixed by the extrinsic portion so that any uncertainties go into the anion parameters (cf. Table II). We conclude that, as far as numerical values of parameters are concerned, the cation migration and formation parameters in line VII are to be preferred. If subsequent work confirms an additional transport mechanism, then the formation parameters will be somewhat high. No precise values can be given for anion parameters at present; although the anion diffusion coefficients calculated from the parameters in Ref. 16 (given in line 6 of Table IV) naturally agree best with the experimental diffusion coefficients, the parameters form a self-consistent set and we doubt that the cation migration and the formation parameters are correct. Because anion diffusion data were used in the fitting, these parameters get to be pegged and discrepancies go into the cation migration and the formation parameters. The same is true for using anion-doping data. If the Schottky defect model were completely adequate for KCl, then one should expect to get better agreement between the results from the three different approaches and this is perhaps the most convincing argument for the inadequacy of the model: Schottky defects, nearest-neighbor M^{2+}-cation-vacancy and anion-vacancy–cation-vacancy pairs, and long-range interactions via the Debye-Hückel approximation.

ACKNOWLEDGMENT

We wish to thank the National Research Council of Canada for financial support of this work.

---

*Present address: P. O. Research, Martlesham Heath, Ipswich, IP57RE, Suffolk, England.

[1] L. W. Barr and A. B. Lidiard, in *Physical Chemistry, an Advanced Treatise*, edited by H. Eyring, D. Henderson, and W. Jost (Academic, New York, 1970), Vol. X, Chap. 3.

[2] E. Koch and C. Wagner, Z. Physik. Chem. (Frankfurt) B38, 295 (1937).

[3] J. Teltow, Ann. Physik 5, 63 (1949); 5, 71 (1949).

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

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

[6] A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1957), Vol. XX, Part 2, pp. 246–349.

[7] R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd ed. (Butterworths, London, 1965).

[8] A. R. Allnatt and M. H. Cohen, J. Chem. Phys. 40, 1860 (1964).

[9] A. R. Allnatt and M. H. Cohen, J. Chem. Phys. 40, 1871 (1964).

[10] A. R. Allnatt and P. W. M. Jacobs, Trans. Faraday Soc. 58, 116 (1962).

[11] J. H. Beaumont and P. W. M. Jacobs, J. Chem. Phys. 45, 1496 (1966).

[12] R. G. Fuller, thesis (University of Illinois, Urbana, Illinois, 1965) (unpublished); see also R. G. Fuller, Phys. Rev. 142, 524 (1966).

[13] J. H. Beaumont, thesis (University of London, England, 1965) (unpublished).

[14] R. G. Fuller and M. H. Reilly, Phys. Rev. Letters 19, 113 (1967).

[15] R. G. Fuller, M. H. Reilly, C. L. Marquardt, and J. C. Wells, Jr., Phys. Rev. Letters 20, 662 (1968).

[16] R. G. Fuller, C. L. Marquardt, M. H. Reilly, and J. C. Wells, Jr., Phys. Rev. 176, 1036 (1968).

[17] A. R. Allnatt and P. Pantelis, Solid State Commun. 6, 309 (1968).

[18] A. R. Allnatt, P. Pantelis, and J. Sime, J. Phys. C (to be published).

[19] S. Chandra and J. Rolfe, Can. J. Phys. 48, 412 (1970).

[20] S. Chandra and J. Rolfe, Can. J. Phys. 48, 397 (1970).

[21] C. F. Bauer and D. H. Whitmore, Phys. Status Solidi 37, 585 (1970).

[22] D. K. Dawson and L. W. Barr, Proc. Brit. Ceram. Soc. 9, 171 (1967).

[23] L. W. Barr and D. K. Dawson, Atomic Energy Research Establishment Report No. R 6234, Harwell, England, 1969 (unpublished).

[24] D. K. Dawson and L. W. Barr, Phys. Rev. Letters 19, 844 (1967).

[25] R. G. Fuller and M. H. Reilly, J. Phys. Chem. Solids 30, 457 (1969).

[26] J. Rolfe, Can. J. Phys. 42, 2195 (1964).

[27] F. D. Enck, D. G. Engle, and K. I. Marks, J. Appl. Phys. 33, 2070 (1962).

[28] G. C. Smith, Materials Science Center Report No. 51, Cornell, 1962 (unpublished).

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

[30] J. D. Eshelby, C. W. A. Newey, P. L. Pratt, and A. B. Lidiard, Phil. Mag. 3, 75 (1958).

[31] By combining results from K. Tharmalingam, J. Phys. Chem. Solids, 25, 255 (1964) and I. M. Boswarva and A. B. Lidiard, Phil. Mag. 16, 805 (1967).

[32] J. F. Aschner, thesis (University of Illinois, Urbana, Illinois, 1954) (unpublished). We are indebted to Professor for R. J. Maurer for a copy of Dr. Aschner's thesis.

[33] D. C. Parashar, J. Phys. Chem. Solids 31, 2795 (1970).

[34] M. Bénière, F. Bénière, and M. Chemla, J. Chem. Phys. 67, 1312 (1970).