IONIC CONDUCTIVITY OF POTASSIUM BROMIDE

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Résumé. — La conductivité de quatre cristaux de KBr — un pur et trois dopés par SrBr_2 — a été ajustée au modèle classique. Les paramètres de migration de la lacune cationique déduits de l'analyse des résultats relatifs aux cristaux purs ne sont pas en accord avec ceux obtenus dans les cristaux dopés. De même les paramètres de la diffusion de l'anion trouvés dans le cristal pur sont trop élevés. Les effets de la contrainte uni-dimensionnelle ont été étudiés et il a été démontré que la contrainte accroît la conductivité des cristaux purs de KBr à haute température. Cet accroissement de la conductivité est attribué à une migration de l'anion par dislocations. L'effet demeure après léger recuit mais peut être supprimé par un recuit prolongé. La conductivité de KBr pur a donc été analysée avec un modèle incluant une contribution par dislocations : les paramètres de la migration cationique sont plus proches des valeurs déduites des données des cristaux dopés que celles qui étaient obtenues dans le modèle de Debye-Hückel mais l'accord n'est pas encore satisfaisant. Cependant, les paramètres de la migration de l'anion ont des valeurs plus raisonnables.

En raison de ces désaccords et en particulier la grande variation de l'entropie trouvée d'après les résultats des cristaux dopés, deux autres modèles pour les interactions à courte distance ont été examinés. L'un fait intervenir trois types de complexes et l'autre la formation d'agglomérations d'impuretés et lacunes cationiques. Aucun de ces modèles ne donne des résultats satisfaisants.

Abstract. — The conductivity of four crystals of KBr — one pure and three doped with SrBr_2 — have been fitted to the conventional model which allows for short range interactions between M^{2+} ions and cation vacancies via complex formation and long range defect interactions in the Debye-Hückel approximation. The cation vacancy migration parameters derived from the analysis of the pure crystal data do not agree with those derived from the data for doped crystals. Also the anion migration parameters found from the pure crystal data are too high. The effects of uniaxial stress have been investigated and it has been demonstrated that stress increases the conductivity of pure KBr crystals at high temperatures. This enhancement of the conductivity is attributed to anion migration down dislocations. The effect survives moderate annealing but can be removed by a prolonged anneal. The conductivity of pure KBr was therefore analyzed on a model which includes a dislocation contribution : the cation migration parameters are closer to the values deduced from the doped crystal data than were those from the Debye-Hückel model but the agreement is still not satisfactory. However, the anion migration parameters have more reasonable values.

In view of the discrepancies in the cation migration parameters and in particular the big variations in the entropy found from the doped crystal data, two other models for the short-range defect interactions were examined. One of these allowed for three different configurations of complexes and the other for the formation of clusters of impurity ions and cation vacancies. Neither of these models, however, gave satisfactory fits to the data.

1. Introduction. — Ionic conductivity measurements are generally interpreted in terms of a basic model described by Lidiard [1]. It is considered that the crystals contain point defects : vacancies and or interstitial ions, and that their electrical conductivity results from the migration of these defects in the applied electric field. At high temperatures the number of defects in the crystal is determined principally by the requirement of thermodynamic equilibrium. The type of defects present (Schottky, cation Frenkel, or anion Frenkel) depends on their Gibbs free energies

of formation. In the alkali halides the intrinsic defects are predominantly of the Schottky variety although the possibility of Frenkel defect formation on either the cation or the anion sub-lattice cannot be totally ignored. At lower temperatures the number and type of defects present will be determined by the purity of the crystals. The presence of M^{2+} ions incorporated substitutionally on the cation sub-lattice results in the existence of an equal number of cation vacancies.

Interactions between point defects in ionic crystals are primarily coulombic in nature. Cation and anion vacancies on nn sites constitute a vacancy pair. Such pairs being neutral do not contribute to ionic conductivity although they are important in the

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diffusion of both cations and anions. Vacancy interactions at longer range $R \geq R_0 = \sqrt{2} a$, where a is the anion cation distance, are generally handled via the Debye-Hückel approximation [1]. A more accurate theory has been developed by Allnatt and Loftus [2], [3], [4]. For crystals in the extrinsic range defined by $c_- < c$, where c denotes the site fraction of M^{2+} impurity ions and c_- that of anion vacancies, the dominant interactions are between M^{2+} ions and cation vacancies. A M^{2+} ion with a vacancy in a near neighbour position is considered to be in a complex with the result that the mobility of the vacancy is restricted to jumps between equivalent lattice sites until such time as it forms a complex with a different configuration or the complex dissociates completely. The configurations which constitute complexes are a matter of definition and require only a statement of the value of R_0 with the understanding that defects separated by a distance $R \geq R_0$ are subject to long range interactions, to be handled via the Debye-Hückel approximation, while those for which $R < R_0$ form separate thermodynamic species. Conductivity data are usually analyzed in terms of the Teltow nn model [5] for which $R_0 = 2 a$. This avoids proliferation of thermodynamic parameters, but evidence has been accumulating for some time [6] that other configurations may be equally or even more important.

The objectives of the present investigation were to investigate the adequacy of the Teltow-Lidiard model for KBr and to evaluate the thermodynamic parameters governing the formation, migration and interaction of defects in this material. Since other similar investigations on KCl [7], [8] and NaCl [9] had revealed possible inadequacies in this model various modifications of the basic model have been examined: these include (i) other charge transport mechanisms (Frenkel defects, conduction along dislocations) and (ii) more elaborate models for the defect interactions (up to three configurations of complexes and clusters of nn complexes).

Since the Dreyfus and Nowick review [10] in 1962 the ionic conductivity of KBr crystals has been measured by Maycock [11], Rolfe [12], [13], Gründig [14], Jain [15], Dawson and Barr [16], and Hoshino and Shimoji [17]. However, in only two of these investigations [13], [16] was a detailed analysis of the conductivity made. Moreover, several of these authors [14], [15], [17] used either dc or low frequency ac methods for measuring the conductivity so that their data are subject to possible errors through polarization. The only completely published, fully analyzed set of data on KBr is that of Chandra and Rolfe [14]. These authors used anion and cation doping to identify the transport parameters of anion and cation vacancies and employed a non-linear least squares procedure for fitting the experimental data to the theoretical equations but they investigated only the basic Teltow-Lidiard model.

2. Experimental procedure. — The experimental technique used was largely that developed by Allnatt and Jacobs [20] and Beaumont and Jacobs [21] except for these minor but important variations. The KBr was purified by extraction of an aqueous solution with oxine, recrystallization from conductivity water, and pre-treatment of the melt with HBr and Br_2 . The crystal cleaves were microtomed to give greater precision in the measurement of its geometrical parameters and electrodes of pure graphite were applied [9]. The conductivity was measured at 1592 Hz by means of a Wayne-Kerr Model B 221 transformer ratio arm bridge. Temperature control was effected with a Hallikainen temperature controller and at least one hour elapsed after re-setting the controller before measurements were made to ensure thermal equilibrium. Four successive readings of G (conductance) and $\mathcal{E}$ (thermocouple emf) were then made within one minute; these were accepted if they were identical, otherwise repeated measurements were made. The temperature was always constant to $< \pm 0.1$ K during a measurement of G . Thermocouples at the centre of each platinum electrode were used [20] and temperature gradients were removed in the obvious way by adjusting the current through the various furnace windings. The density of points was greater than that used by Beaumont and Jacobs [21], typically about every 3 K. The annealing procedure is important. Except in some special experiments the crystal was thermally cycled between 850 and 910 K until reproducible results were obtained, usually after two days.

The Sr^{2+} content in two of the doped crystals was determined colorimetrically by Johnson Matthey Chemicals Limited with a stated relative accuracy of $\pm 10\%$. Frequency-dependence of the conductivity due to polarization [22] was checked for but found to be negligible. To investigate the effect of dislocations on the conductivity of KBr several crystals were strained by uniaxial compression and the conductivity of the crystals was then measured.

3. Experimental results. — The conductivity of five crystals of KBr is shown in figure 1 in the form of the usual plot of $\log \sigma T$ against T^{-1} . The conductivity of the pure crystal grown from oxine-extracted OH-free KBr (1) is a factor of 2.5 lower than that of a crystal obtained from the Harshaw Chemical Company at low temperatures, but the data for the two crystals agree well in the intrinsic region. The lines for the three doped crystals show the expected curvature due to association. The effect of straining the crystals is shown in figures 2 and 3. Figure 2 shows the low temperature region for (1) a pure KBr crystal [(1) from Fig. 1], (6) a cleave from the same pure KBr crystal that had been strained to 3% decrease in length, and (7) a cleave again from the same crystal that had been strained to 5.5%. Crystal (6) was heated to 860 K, readings taken at increasing

FIG. 1. — Temperature dependence of the specific conductivity σ of KBr crystals (1) pure KBr; (2) a Harshaw KBr crystal; (3) KBr: Sr^{2+} , $c = 80 \times 10^{-6}$; (4) KBr: Sr^{2+} crystal, $c = 164 \times 10^{-6}$; (5) KBr: Sr^{2+} crystal, $c = 385 \times 10^{-6}$.

FIG. 2. — Effect of uniaxial stress on the low-temperature conductivity of pure KBr crystals. (1) unstrained; (6) strained to 3 % decrease in length; (7) strained to 5.5 % decrease in length.

temperatures to 980 K and then at decreasing temperatures from 855 K down to 580 K. The temperature was then raised to 913 K and measurements made once more in the high temperature region up to 991 K. Figure 2 shows that the extrinsic conductivity of a uniaxially strained crystal is less than that of the unstrained crystal even after a high temperature anneal lasting several days. (It took 13 days before the readings shown in figure 2 were made and for three days of this period the crystal was at 850 K or above.) Crystal (7) was treated differently: the conductivity was measured at steadily increasing temperatures from 590 to 980 K (50 points in 24 h) to ensure minimum anneal. The extrinsic conductivity

in this crystal that had been strained to 5.5 % is lower than that of the 3 % strained crystal (Fig. 2).

Figure 3 shows the conductivity in the high temperature region 895-996 K for the same three crystals. The intrinsic conductivity has clearly been increased by straining the crystals and it is perhaps remarkable that this effect is so pronounced even in the partially annealed, 3 % strained crystal. That these differences are not just due to irreproducibility is proved by figure 4 which shows the high temperature conductivity over a wider temperature range, 805-996 K. The three crystals clearly have the same conductivity

FIG. 3. — Effect of uniaxial stress on the high-temperature conductivity of pure KBr crystals ● crystal (1) unstrained; □ crystal (6) 3 % strained and partially annealed; ○ crystal (7) 5.5 % strained and conductivity measured without prior anneal.

FIG. 4. — This figure displays the intrinsic region of the conductivity of pure KBr crystals and shows that the effects of uniaxial stress occur at high temperatures only and not just above the knee ● unstrained; □ strained 3 % and partially annealed; ○ strained 5.5 % and conductivity measured without prior anneal; △ strained 5.5 % and annealed as described in the text.

just above the knee and it is in the high temperature region that differences appear. After the first heating up to 980 K crystal (7) was annealed for 10 days at 820 K. It was then given 4 h anneals at 950 K on three successive days and then finally measurements were made at temperatures down to 850 K. The intrinsic conductivity now reproduced that of an unstrained crystal — see the points in figure 4 that correspond to the annealed 5.5 % strained crystal.

A Harshaw crystal was strained to 2 % decrease in length and given the usual anneal (two days cycling between 850 and 910 K) and its conductivity was then measured in the usual manner for an unstrained crystal. The intrinsic conductivity was unchanged from that of an unstrained crystal but the extrinsic conductivity was lower than that for the unstrained Harshaw crystal shown in figure 1. This could be an example of the effect shown in figure 2 but might conceivably have been due simply to variations in impurity content. The crystal was therefore annealed for 3 days at 930 K and the conductivity again measured down to 580 K. The extrinsic conductivity had increased by 13.5 % following the final anneal.

4. Discussion. — The annealing procedure generally followed was designed to remove possible effects on the conductivity from strain in the crystal introduced during crystal growth, cleaving and microtoming. That this procedure is effective in removing a moderate amount of strain introduced by uniaxial compression is demonstrated by the experiment on the 2 % strained Harshaw crystal. It has not been proved that the anneal procedure removes the strain induced by microtoming and this point is currently being examined. The excellent reproducibility in the intrinsic region, however, inclines one to believe that any effects on the intrinsic conductivity due to strain are either very small ($< 1\%$) or common to virtually all conductivity measurements. Straining a crystal by a uniaxial stress to much larger extents results in damage that is not removed by the standard anneal (Fig. 3) but is removable by much longer anneals. Such damage results in an increase in the intrinsic conductivity in the high temperature portion of the intrinsic region *only*. This implies that the increased dislocation content of the strained crystals provides easy paths for the motion of *anions*, a conclusion reached previously by Dawson and Barr [23] from the existence of a low temperature structure sensitive component in the anion diffusion coefficient of KBr. Were there enhanced mobility of cations the conductivity of the heavily strained crystals would show an increase just above the knee, which it does not (Fig. 4). There is, however, no direct means of telling how important such a contribution might be to the intrinsic conductivity of an unstrained, annealed crystal.

Some investigators measure the conductivity at increasing temperatures only without prior anneal.

We feel that this procedure might conceivably introduce errors if the crystals have been strained, as they inevitably must have been to some extent during preparation. An example of this is shown by an analysis of the data for the 3 % strained crystal (Fig. 2, 3, 4) after the preliminary anneal and after the final anneal which removed the enhancement of the intrinsic conductivity. Parameters derived from non-linear least squares analysis are shown in table I. The model used allowed for nn complexes and ignored all long-range interactions; however since the same model was used for both sets of data the conclusion that the data for the strained crystal give high values of the Schottky defect formation parameters and the anion mobility parameters is a valid one. This is simply a consequence of ignoring the mechanism that gives the enhancement of conductivity in the strained crystal.

TABLE I

Schottky defect formation parameters and anion mobility parameters determined from analysis of the conductivity of a strained KBr crystal after a preliminary anneal (6a) and after a final anneal (6b).

	h/eV	s/k	$\Delta h_-/\text{eV}$	$\Delta s_-/k$
6a	2.472	8.15	1.694	14.49
6b	2.190	4.49	1.214	9.56

Uniaxial compression also reduces the conductivity in the extrinsic region and this effect too can be reversed by prolonged annealing. It demonstrates the removal of M^{2+} impurities at the dislocations introduced by straining the crystal.

COMPUTER ANALYSIS. — The results of the usual computer [8], [9], [21] analysis of these data are shown in tables II and III. For the pure KBr crystal three sets of runs were performed. In series 1.1 the association enthalpy h_a was fixed at -0.400 eV. This value was chosen after an extensive investigation showed that the sum of the squares of the deviations ϕ was independent of h_a for $h_a \leq 0.4$ eV but increased markedly for $h_a > 0.4$ eV. In series 1.2 both h_a and s_a were allowed to vary but the mean value for $h_a = -0.399$ eV is accidental since the actual values ranged from -0.296 to -0.530 eV. In series 1.3 the (non-configurational) entropy of association was fixed at zero. Each of the parameter sets in table II represent the mean of several runs with different starting values, a total of 16 runs in all. The agreement between the formation and migration parameters is generally good: c is higher for 1.3 than for the other two sets and this is compensated for by a lower Δs_+ . It is clearly impossible to fix the association parameters at all accurately for such a pure crystal because of the small amount of association and this leads to

TABLE II

Thermodynamic parameters governing the formation migration and association of defects in KBr determined from fitting the conductivity curve for pure KBr to the Debye-Hückel model. h , s are the enthalpy and entropy of formation of a Schottky defect pair; c is the site fraction of M^{2+} impurity; Δh_+ , Δs_+ are the enthalpy and entropy of migration of a cation vacancy; Δh_- , Δs_- are enthalpy and entropy of migration of an anion vacancy; h_a , s_a are the enthalpy and entropy of association of an M^{2+} ion and a cation vacancy.

	1.1	1.2	1.3
h/eV	2.036	2.011	2.023
s/k	4.11	3.83	4.88
$c \times 10^6$	0.93	0.98	1.54
$\Delta h_+/eV$	0.699	0.701	0.702
$\Delta s_+/k$	1.45	1.40	0.99
$\Delta h_-/eV$	1.251	1.253	1.240
$\Delta s_-/k$	8.74	8.78	8.08
$-h_a/eV$	0.400	0.399	0.069
$-s_a/k$	0.49	2.45	0

TABLE III

Defect parameters determined by fitting the conductivity curves for doped KBr to the Debye-Hückel model with $R_0 = 2a$ (nn complexes). Symbols are defined in the caption to table II.

Crystal	3	4	5
$c \times 10^6$	80.5	164	385
$\Delta h_+/eV$	0.591	0.577	0.608
$\Delta s_+/k$	0.058	0.087	0.634
$-h_a/eV$	0.622	0.676	0.629
$-s_a/k$	1.72	2.61	2.08

difficulties in separating c and Δs_+ , which would be perfectly correlated in the absence of association [8]. The only other remarkable features of the numerical values in table II are the high values for the anion diffusion parameters, a phenomenon encountered also with KCl [8].

In the analysis of the conductivity of the doped crystals the formation and anion migration parameters were fixed at the values obtained from the analysis for pure KBr. This left the five parameters h_a , s_a , c , Δh_+ , Δs_+ variable. In several runs the remaining four parameters were allowed to vary also but this inevitably resulted in wild variations in h which in turn affected c . It is not practicable to fix the formation parameters unless at least the knee of the conductivity curve is available. The results in table III show fair consistency for the association and cation migration enthalpy and entropy. The computed concentrations for (3) and (4) are -12% and $+7\%$ away from the analytically determined values. Both Δh_+ and

Δs_+ are much lower than the values found for the pure crystal in table II.

A test of the computed concentrations is to plot a σ vs $c(1-p)$ isotherm which should be linear. Such a plot, shown in figure 5, shows reasonable scatter about a straight line. Use of the analytically

FIG. 5. — Plot of specific conductance σ against $c(1-p)$ at $10^3/T = 1.550 \text{ K}^{-1}$. The plot should be linear if the concentrations determined by computer fitting are consistent.

determined concentrations would, however, have yielded points even further away from the line i. e. (3) would be shifted to the right and (4) to the left. If we select from the runs averaged to give table III the ones that yielded the most consistent values of $c(1-p)$, as judged by the criterion of lying closest to the best straight line, then the values of the association and migration parameters are not significantly altered. In particular, the big variation in the entropy Δs_+ is still present. In summary, then, the large values of Δh_- , Δs_- and the big differences in the values of Δh_+ and Δs_+ obtained from analyzing the data for the pure and the doped crystals leads us to suspect the adequacy of the model being employed.

The first adjustment made was to allow for three different configurations of complexes. A M^{2+} ion at $(0, 0, 0)$ has 12 nn cation positions at $(1, 1, 0)$, 6 nnn positions at $(2, 0, 0)$, 24 third nn positions at $(2, 1, 1)$ and so on. Vacancies at sites for which the separation distance $R \geq R_0 = \sqrt{8}a$ were treated via the Debye-Hückel approximation and those with $R < R_0$ were regarded as forming complexes with the equilibrium constants for the association process given by

$$K_{aj} = Z_j \exp(-\Delta g_{aj}/kT) \quad (1)$$

where $Z_j = 12, 6$ and 24 for $j = 1, 2, 3$ respectively. The model was tested with data from crystal (4). Formation and migration input parameters were taken from a converged run used in the averaging

that resulted in the appropriate column of table III and h , s , Δh_- , Δs_- were held constant as usual. Reasonable guesses for the input enthalpies and entropies of association were chosen and, these together with the converged values after 37 iterations, are shown in table IV. This experiment might be taken to imply that, at least in KBr : Sr^{2+} , the nn complex is favoured for the computer is effectively rejecting the nnn and third nn complexes. However, the data are clearly not very sensitive to this type of calculation for quite a good fit (row 3) could also be obtained with all parameters but Δh_- , Δs_- variable. This was achieved by continually resetting h_{a_2} and h_{a_3} to the values in the first row of table IV and thus biasing the calculation to give finite enthalpies. If left to run without interference the program ran h_{a_2} and h_{a_3} down to the values shown in the second row. However, the large negative entropy for a_3 and the small positive on for a_2 are not readily explicable and we feel that this calculation is not to be taken seriously. If one could input information on h_{a_1} and h_{a_2} obtained from other experiments then it might be possible to make it work. However, the difference plots for the doped crystals, a typical example of which is shown in figure 6 do not display any systematic variations for the nn model so that it would clearly be very difficult to improve on the model. In contrast, if we suppress the Debye-Hückel interactions and allow only for nn complexes then φ is roughly a factor of 10 larger than for minimizations that include the long range interactions in the Debye-Hückel approximation. Moreover φ increases with

impurity concentration for the three doped crystals when Debye-Hückel interactions are suppressed but is not concentration-dependent when they are included.

A cluster model was also investigated. In this model divalent impurity cation vacancy complexes are allowed to aggregate according to the equilibrium

$$n[\text{M}^{2+} \square] = [\text{M}^{2+} \square]_n \quad (2)$$

with equilibrium constant

$$K_n = c_n/(c_k)^n. \quad (3)$$

Because of evidence that the formation of trimers precedes precipitation only $n = 3$ was investigated. The computer fits were poor with generally a high φ and few sign changes in the deviations. In the few runs that gave a reasonable φ the program produced very low values for h_n and s_n the enthalpy and entropy changes associated with the equilibrium (2). At most the prediction of the total amount of impurity ion in clusters, for crystal (4), amounted to 0.01 to 0.1 % at the highest temperature up to perhaps 10 % at the lowest temperature. However, the non-random deviations led us to reject the cluster model for our system. It might, however, be worth considering for other systems particularly those close to precipitation.

The possibility of other charge transport mechanisms was investigated next. The assumption of the presence of a small number of Frenkel defects on the cation sub-lattice introduces four more disposable parameters and so would be expected to give noticeably better fits to the data [8]. However, φ is about the same as for the ordinary Debye-Hückel model and though a not unreasonable value was obtained for the enthalpy of Frenkel defect formation (Table V), the entropies of formation and migration are much higher than can reasonably be expected for interstitials and so we conclude that the presence of Frenkel

FIG. 6. — Plot of the difference between experimental (e) and calculated (c) values of $\log \sigma T$ against $10^3 K/T$ for the most heavily Sr^{2+} -doped crystal, $c = 385 \times 10^{-6}$. The dashed lines show a 1 % deviation in σT .

TABLE V

Frenkel defect parameters found from the best fit of the conductivity curve for pure KBr to a model which includes both Schottky defects and cation Frenkel defects. The entropies are unrealistically high.

h_F/eV	s_F/k	$\Delta h_i/\text{eV}$	$\Delta s_i/k$
2.81	6.4	0.86	10.9

TABLE IV

Input and converged values for the association model (crystal 4)

	$-h_{a_1}/\text{eV}$	$-s_{a_1}/k$	$-h_{a_2}/\text{eV}$	$-s_{a_2}/k$	$-h_{a_3}/\text{eV}$	$-s_{a_3}/k$
Input parameters	0.6	1.74	0.5	0.58	0.4	0
Converged values	0.677	2.38	0.049 6	-1.8×10^{-3}	1.5×10^{-4}	0
	0.694	2.84	0.382	-9.5×10^{-2}	0.199	1.68

defects is not the explanation of the high values of the anion parameters found with the Debye-Hückel model.

The uniaxial stress experiments have indicated the probability of additional charge transport (by anions) along dislocations. Further the diffusion experiments of Dawson and Barr have shown that this effect is present even in annealed crystals [24]. The total anion diffusion coefficient (after pair correction) can be written as $D_{Br-} = D_- + D_x$ where D_x is the dislocation contribution. Since we expect D_x to obey the Arrhenius equation for an activated process, we simply add to σ the term

$$\sigma_x = (B/T) \exp(-E/kT)$$

and treat B and E as disposable parameters. Three sets of calculations, comprising 23 runs in all from different starting values of parameters were performed. The mean converged parameters from each set are shown in table VI. In the calculations that resulted in the column headed 1.4 h_a and s_a were both set equal to zero; for that headed 1.5 they were started at $h_a = -0.4$ eV and $s_a = -1.16$ k, and in column 1.6, they were given initial values of $h_a = -0.4$ eV, $s_a = -0.116$ k.

TABLE VI

Parameters derived from the dislocation model. A term $\sigma_x = (B/T) \exp(-E/kT)$ has been included so that $\sigma = \sigma_+ + \sigma_- + \sigma_x$.

	1.4	1.5	1.6
h/eV	2.319	2.330	2.340
s/k	7.62	7.86	8.74
$c \times 10^6$	0.657	0.683	1.004
$\Delta h_+/\text{eV}$	0.660	0.659	0.664
$\Delta s_+/k$	0.987	0.951	0.632
$\Delta h_-/\text{eV}$	1.083	1.084	1.066
$\Delta s_-/k$	6.58	6.50	5.82
$10^{-6} B/\Omega^{-1} \text{ m}^{-1} \text{ K}$	1.447	2.654	4.656
E/eV	1.305	1.339	1.387
$-h_a/\text{eV}$	0	0.398	0.176
$-s_a/k$	0	0.137	0.162

The parameters in table VI have several interesting features. Firstly the values deduced for B and E are in very reasonable agreement with those derived by Barr and Dawson [24] from diffusion measurements namely $B \approx 5 \times 10^{-6} \Omega^{-1} \text{ m}^{-1} \text{ K}$, $E = 1.35 - 1.41$ eV. Variations of B over at least a power of 10 would be expected from the structure sensitive nature of the process. Next the inclusion of σ_x has the effect of raising both h and s (cf. Table II). It also reduces Δh_+ and Δs_+ so that the former is now in closer agreement with the analysis of the doped crystal data (Table III). Finally, the inclusion of a dislocation contribution has reduced the bulk anion migration

parameters to values much closer to those determined from diffusion [24] and anion doping [13]. It must be remarked that any other activated process contributing to σ would yield the same results; however, a dislocation contribution is the most reasonable suggestion.

PREDICTION OF DIFFUSION COEFFICIENTS. — The most severe test of the parameters derived from computer analysis of conductivity data is the prediction of diffusion coefficients and the comparison of these with values determined experimentally. The experimental anion and cation diffusion data should, of course, have been corrected for the contribution from vacancy pairs and for any extrinsic contribution. Figures 7a and 7b display the temperature dependence of D_+ and D_- and show lines

FIG. 7. — Logarithm of the single vacancy diffusion coefficients as functions of reciprocal temperature. The lines D have been calculated from experimental measurements of D after correction for diffusion by vacancy pairs. The dashed lines C were calculated from conductivity parameters, determined from the Debye-Hückel model. Lines A , B were calculated from conductivity parameters determined from the dislocation model. a) Cation diffusion coefficient, b) anion diffusion coefficient.

corresponding to the directly determined values and to values of D calculated from conductivity parameters. The lines C have been calculated from parameters determined from the Debye-Hückel model and data for pure KBr. The cation diffusion coefficients agree with the diffusion values D at low temperatures but the calculated line has a lower slope than the experimental one. The calculated anion diffusion coefficients are higher than the measured values at all temperatures and the calculated line has too high a slope (because of Δh_- , Δs_-). The lines A , B have been calculated from (two) different sets of parameters determined using the dislocation model. The anion line B lies closer to the experimental values

although A has the better slope. For the cation data B again lies closer and it has the better slope.

These discrepancies are much larger than can be regarded as satisfactory. They are, for example much larger, than were found in a recent study [25] of AgCl and when one considers the evidence steadily accumulating [8], [9] one must conclude that a completely satisfactory model for analyzing the conductivity data for alkali halide crystals has not yet been found.

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APPENDIX I

TABLE VII

Comparison of defect parameters for KBr deduced from the Debye-Hückel model and from the dislocation model, with those found from diffusion and by double doping experiments. Representative values of h from theoretical calculations are : 2.42 eV (Boswarva [26]) ; 2.15 eV (Simpson [27]) ; 2.12 eV (Schulze and Hardy [28]) ; and 2.24 eV (Faux and Lidiard [29]).

	Debye-Hückel model pure	Sr ²⁺ -doped	Dislocation model	Chandra and Rolfe [13]	Barr and Dawson (^a)
h/eV	2.02		2.33	2.53	2.37
s/k	4.3		8.1	10.3	7.2
$\Delta h_+/\text{eV}$	0.70	0.59	0.66	0.65	0.67
$\Delta s_+/k$	1.28	0.06-0.63	0.86	1.9	2.5
$\Delta h_-/\text{eV}$	1.25		1.08	1.22	0.9
$\Delta s_-/k$	8.5		6.3	7.3	3.8
$10^{-6} B/\Omega^{-1} \text{ m}^{-1} \text{ K}$			3		5
E/eV			1.35		1.39
$-h_a/\text{eV}$		0.64		0.61 (^b)	0.57 (^b)
$-s_a/k$		2.1		2.2 (^b)	1.8 (^b)

(^a) Quoted by Chandra and Rolfe [13] and [24].

(^b) Ca²⁺-doped KBr.

APPENDIX II

Remarks on computer fitting of conductivity data. —

It is not the purpose of this appendix to give a general account of the theory of methods available for estimating parameters in non-linear least squares problems (see, however, Appendix III). Rather we shall attempt to discuss some of the difficulties associated with fitting conductivity data. The first of these is the strong likelihood of convergence to a false minimum. The best method of discovering a false minimum is by taking different sets of initial parameters and such a procedure should be standard practice. However, initial guesses are usually arrived at as a result of some bias (known or even not realized) and consequently even many different sets of initial parameters may not disclose that the minimum is a false one. We have, therefore, recently adopted [30] a Monte

Carlo method of selecting initial guesses. Because no iteration is involved the method is rapid and although a good fit is unlikely it is an efficient method of selecting initial guesses from which one can proceed by a normal least squares refinement.

Two criteria exist for the goodness of fit. Most programs will print the sum of the squares of the residuals

$$\varphi = \sum_{i=1}^M (y_i - \hat{y}_i)^2 \quad (4)$$

where y_i is the experimental value of $\log \sigma T$ and $\hat{y}_i$ the estimated value, for a given set of parameters, at the i th data point. It should be superfluous to remark that one needs a high density of data points [25] and data of the highest quality obtainable (see [8] for some estimates of random errors in conductance

measurements). Clearly the smaller φ the better the fit. Because φ depends on the number of data points, for comparing different crystals or results of different workers, the standard deviation

$$\sigma_{sd} = (\varphi/M - 1)^{1/2} \quad (5)$$

should be used.

Typically in good fits φ [9] will be about 10^{-3} to 10^{-4} and σ_{sd} [25] about 2×10^{-3} . A better picture of the fit is obtained by plotting $y_i - \hat{y}_i$ against T^{-1} . Ideally the deviations should be small ($< 1\%$ in σT) and random. Non-random behaviour is generally taken to indicate deficiencies in the model but it may simply result from lack of convergence.

The original objective of computer-fitting [21] was to develop a satisfactory method for evaluating the defect parameters. The present trend seems to be to use it to evaluate models: that is, when one derives parameters that agree poorly with values derived from different experiments (e. g. diffusion coefficients) one suspects the model. Apart from comparing single parameters, the whole set may be tested by using them to compute other properties such as diffusion coefficients [8], [9], conductivity isotherms [25] and thermoelectric power [31]. Even if one had a perfect model there would still be difficulties because of the high correlation between certain parameters. The greatest difficulty arises from c and Δs_+ but correlations between c and s , between Δh_+ and h_a , and between each of the enthalpies and their corresponding entropies also cause difficulties. Analytical determination of c seems an obvious way out but early work [21] showed that treating c as an unknown was as reliable as X-ray fluorescence. The isotope dilution method of Allnatt and Chadwick [9], [32] is the best method of measuring the total concentration of impurity but one is still left with the doubts about whether it is all dissolved substitutionally. Checks on the computed values of c involve the linearity of isotherms in which σ is plotted against $c(1 - p)$ for temperatures in the structure sensitive region [8], [25] and the consistency of values of Δs_+ . The lack of consistency of the values found for Δs_+ is one of the main deficiencies in the analysis described in this paper.

APPENDIX III

The object of this appendix is to provide a few comments on non-linear least squares fitting to arbitrary functions. It contains nothing original but may be useful to those without previous experience in the field. For further details the reader is referred to [33]-[36]. The measure of goodness of fit is

$$\chi^2 = \sum_{i=1}^M \frac{1}{\sigma_i^2} (y_i - \hat{y}_i)^2 \quad (6)$$

where $\hat{y}_i \equiv \hat{y}(x = x_i; a_j)$ and $\hat{y}$ is a non-linear function of the independent variable x and parameters a_j , $j = 1, \dots, N$. σ_i is the uncertainty in the i th data point. Very often the fitting is performed without weighting in which case the weights σ_i^{-1} are all set equal to unity and χ^2 becomes equal to φ of eq. (4). We desire to find the values of a_j which minimize χ^2 . The most obvious approach would be to conduct a grid search, that is to divide the permissible range for each parameter a_j into $n - 1$ equal increments and evaluate χ^2 at each of the Nn sets of parameter values. This method is valuable for constructing a map of χ^2 in parameter space but is not a practical method of minimization for large numbers of parameters. To find a minimum we could simply increment each parameter in turn, until a minimum for $\chi^2(a_j)$ is found. However, as the parameters are not independent in the problem under consideration many successive iterations would be required and convergence would be prohibitively slow (see, however [37]).

A practical alternative is the gradient search method, which consists of incrementing all the parameters a_j simultaneously and adjusting their relative magnitudes such that the direction of motion of the representative point in the parameter space $\chi^2(a_j)$ is along the gradient, or direction of maximum variation, in χ^2 (but in the negative direction). This method is therefore called the method of steepest descent [38]. One difficulty is that as the minimum is approached the partial derivatives $\partial\chi^2/\partial a_j$ become very small and it becomes impossible to calculate the gradient. One can then conduct a version of the grid search by continuing along the last calculated gradient and employing parabolic interpolation to improve the location of the minimum. Alternatively, second partial derivatives can be computed.

The second main group of methods involve finding an analytical approximation to the χ^2 hypersurface. If χ^2 is expanded to first order in a Taylor series expansion in terms of the parameters (which is equivalent to approximating the hypersurface as a paraboloid),

$$\chi^2 = \chi_0^2 + \sum_{k=1}^N \left(\frac{\partial\chi^2}{\partial a_k} \right)_0 \delta a_k \quad (7)$$

where χ_0^2 denotes the value of χ^2 at some starting point, O. The desired values for the increments δa_j are those that make χ^2 a minimum. These conditions

$$\frac{\partial\chi^2}{\partial a_j} = 0, \quad j = 1, \dots, N \quad (8)$$

may be written in matrix form

$$\beta = \alpha \delta a \quad (9)$$

where

$$\beta_j \equiv -\frac{1}{2} \left(\frac{\partial\chi^2}{\partial a_j} \right)_0 \quad \text{and} \quad \alpha_{jk} \equiv \frac{1}{2} \left(\frac{\partial^2\chi^2}{\partial a_j \partial a_k} \right)_0 \quad (10)$$

so that the increments to locate the minimum are given by

$$\delta \mathbf{a} = \boldsymbol{\alpha}^{-1} \boldsymbol{\beta}. \quad (11)$$

The elements of the column vector $\boldsymbol{\beta}$ and the curvature matrix $\boldsymbol{\alpha}$ are evaluated by finite difference approximations. Clearly if O is far from the minimum then the analytical approximation will be a poor one but this may be rectified by successive applications of the method.

The third group of methods involves linearization of the function $y(x; a_j)$ by a first order Taylor expansion in the parameters a_j and using the method of linear least squares to minimize χ^2 [34]. This results in the same matrix problem (9) as the previous method. This method, therefore, like the previous one converges rapidly when close to the minimum but is unreliable far from the minimum where χ^2 may even have the wrong curvature. One may obviate these difficulties, for example by treating all curvatures as positive, but since the gradient search method is more suitable when far from the minimum an effective approach is to combine the best features of both methods.

The method of Marquardt [36] optimizes the search in a direction between the gradient search and analytical search vectors by replacing $\boldsymbol{\alpha}$ by $\boldsymbol{\alpha} + \lambda \mathbf{I}$. In

addition the elements of the curvature matrix are approximated by neglecting second partial derivatives so that

$$\alpha_{jk} \approx \alpha'_{jk} = \sum_{i=1}^M \frac{1}{\sigma_i^2} \left\{ \left[\frac{\partial \hat{y}(x_i; a_p)}{\partial a_j} \right]_0 \left[\frac{\partial \hat{y}(x_i; a_p)}{\partial a_k} \right]_0 \right\}. \quad (12)$$

For large λ the method approaches the gradient search and for small λ , the analytical approximation. At each iteration λ is optimized to ensure that χ^2 decreases. Strictly, this is the Levenberg [39] procedure,

$$\delta \mathbf{a} = [\boldsymbol{\alpha}' + \lambda \mathbf{I}]^{-1} \boldsymbol{\beta} \quad (13)$$

Marquardt [36] has an additional scaling factor γ which is $\boldsymbol{\alpha}'$ with its off-diagonal elements reduced to zero. This is equivalent to replacing the unit matrix $\mathbf{I}$ in eq. (13) by γ . Slightly more rapid convergence [40] can be achieved by determining the value of λ which gives the lowest χ^2 at each step instead of using the lowest value of λ that ensures a decrease in χ^2 [41]. The Marquardt algorithm is available as an IBM share program NLIN (No. 3094) and is currently being used by several groups [8], [9], [13] for fitting conductivity data.

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DISCUSSION

C. RAMASASTRY. — How is the lower value of the diffusion coefficient, D , obtained from tracer diffusion compared to that calculated from the conductivity data explained in KBr ?

P. W. M. JACOBS. — Either the models used to analyse the conductivity data are not quite correct or there is a fundamental discrepancy between the conductivity and diffusion data.

A. L. LASKAR. — Is there any simple explanation for the enhanced conductivity in strained crystals at high temperature and not at lower temperature ?

P. W. M. JACOBS. — I think the reason why the conductivity of the strained crystals is increased only

at high temperatures is that dislocations introduced by the stress have a compensating charge cloud of anion vacancies in KBr. Since anion vacancies are less mobile than cation vacancies the effect is most pronounced at higher temperatures.

F. GRANZER. — Can you give some more detailed information concerning the mechanism, which may be responsible for the additional anionic transport along dislocations ?

P. W. M. JACOBS. — The detailed mechanism is not known. Either the vacancies migrate in the dislocation core or in the space charge region. My preference is for the space charge region.