

Diffusion of Sodium in Rubidium Chloride*

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The diffusion of Na^{22}Cl in RbCl was measured in the temperature range $377\text{--}707^\circ\text{C}$ by the tracer-sectioning technique. The activation energy is 2.06 ± 0.02 and 0.59 ± 0.01 eV in the intrinsic and extrinsic regions, respectively. The temperature dependence of the correlation factor, as deduced from isotope-effect measurements, is 0.19 eV in the intrinsic region and -0.05 eV in the extrinsic region. When a theoretical value for the Na^+ -vacancy binding energy is used, values of $\frac{1}{2}h_f = 1.22$ eV and $h_m = 0.55$ eV are obtained, where h_f is the energy of formation, and h_m the energy of motion, of a cation vacancy. These values are not in agreement with the calculation by Tosi and Doyama.

INTRODUCTION

THE aim of this study is to check experimentally the calculations of Tosi and Doyama¹ on the motion of impurities in alkali halides. The diffusion of Na^+ in RbCl was chosen for three reasons: (a) Tosi and Doyama predict a very low energy for the motion of Na^+ in RbCl ($h_m = 0.22$ eV); (b) the diffusion of small monovalent impurity ions in a lattice of large cations has not been studied experimentally, although the reverse case has been studied by Arai and Mullen²; and (c) the diffusion of a small impurity ion is a more severe test of the theoretical calculations.

The calculations of Tosi and Doyama give the energies of formation (h_f) and motion of cation vacancies in NaCl , KCl , and RbCl , as well as the energies of motion of Na^+ , K^+ , and Rb^+ in these chlorides. The activation energies Q for the diffusion of the various ions are obtained from these values with the additional assumptions that the correlation factor for diffusion f is independent of temperature, and that the impurity-vacancy binding energy h_b is zero.

The relations between these energies are the following: For impurity diffusion in the intrinsic region,

$$Q_{\text{int}} = \frac{1}{2}h_f + h_m - k \left(\frac{\partial(\ln f)}{\partial(1/T)} \right)_{\text{int}} + h_b, \quad (1)$$

where k is Boltzmann's constant. In the extrinsic region,

$$Q_{\text{ext}} = h_m - k \left(\frac{\partial(\ln f)}{\partial(1/T)} \right)_{\text{ext}} + h_b. \quad (2)$$

An experimental measurement of Q and the temperature dependence of the correlation factor in both the intrinsic and extrinsic regions will give $\frac{1}{2}h_f$ and $h_m + h_b$. A value of h_m can then be obtained by using the theoretical value of h_b from Ref. 1.

EXPERIMENTAL

The activation energies were determined from the temperature dependence of the diffusion coefficient D of Na^{22} in RbCl . Thin-layer geometry and microtome sectioning were used to determine D . The correlation factor was determined by the isotope-effect technique (the simultaneous diffusion of Na^{22} and Na^{24} in RbCl). The isotopic ratios were determined by a half-life separation.³

Materials

Three single-crystal ingots of RbCl were purchased from Isomet Corporation. The major impurities in all ingots, as detected by spectrochemical analysis, were 2000 ppm K, 1500 ppm Cs, 50 ppm Na, 6 ppm Ca, and 5 ppm Al. In addition to the above impurities, ingot 2 contained 20 ppm Ba and 2 ppm Sr. Seven or eight diffusion samples $1 \times 2 \times 0.4$ cm were cleaved from each ingot. The cleaved crystals were lightly ground on 4/0 emery paper to produce a flat surface, and then preannealed in an NH_4Cl atmosphere.

Diffusion Measurements

For the measurements of D , Na^{22}Cl was evaporated onto the flat surface of the RbCl crystals. The samples, with the active face placed against a quartz flat, were wrapped in Pt foil, encapsulated under vacuum, and annealed. The errors in the measurements of temperature were less than $\pm 1^\circ\text{C}$. Time corrections for heating and cooling of the specimen were applied to each diffusion anneal. After diffusion, the edges of the samples were cleaved off to avoid surface-diffusion effects. The samples were sectioned on a sledge-type Leitz microtome using a standard biological blade. The crystals were aligned on the microtome by means of a mirror with a 3-m optical arm. The first $3\text{-}\mu$ cut always cut the entire sample surface. The cuttings were brushed into tared bottles and the section thicknesses were determined from the section weights. Careful brushing kept the weight losses to less than 1%. The bottles were counted to 10^4 or more counts above background in a well-type scintillation counter.

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¹ M. P. Tosi and M. Doyama, Phys. Rev. **151**, 642 (1966).

² G. Arai and J. G. Mullen, Phys. Rev. **143**, 663 (1966).

³ S. J. Rothman and N. L. Peterson, Phys. Rev. **154**, 552 (1967).

Isotope-Effect Experiments

A mixture of Na^{22}Cl ($t_{1/2}=2.6$ yr) and Na^{24}Cl ($t_{1/2}=15.0$ h) was evaporated onto the sample surfaces. The same techniques were used for the diffusion anneals and sectioning as in the diffusion measurements; however, a different counting procedure was used.

After a preliminary count, the samples were dissolved in 1.00 ml of H_2O . Total γ radiation A above a lower-level discriminator was counted with a well-type scintillation counter. The initial activity of the sections ranged from 10^7 to 5×10^8 cpm. Hot sections were diluted to an activity of 5×10^5 cpm or less; the volume to be counted was kept constant. This procedure was used to avoid changes in the gain of the photomultiplier tube, and to keep the uncertainty of the dead-time correction to less than 0.1%. Each section was counted to 10^6 counts at least six times during a period of four days. The ratio of the activities of Na^{22} and Na^{24} was determined by fitting these counting data to the time

elapsed from an arbitrary zero time:

$$A = A_{22} \exp(-\lambda_{22}t) + A_{24} \exp(-\lambda_{24}t). \quad (3)$$

Here A_{22} and A_{24} are the activities due to Na^{22} and Na^{24} , respectively, at time zero, and λ_{22} and λ_{24} are the decay constants. The average of two measurements of the decay constant of Na^{24} gave $\lambda_{24} = (7.708 \pm 0.004) \times 10^{-4} \text{ min}^{-1}$, in agreement with the value in the literature.⁴ The literature value $5.112 \times 10^{-7} \text{ min}^{-1}$ was used for λ_{22} .⁴ A Cs^{137} source was counted before and after each section in order to correct for long-term counter drifts. Corrections accurate to 0.1% were made for counter dead time, background, and counter drift. A null experiment, in which aliquots of different activities taken from the same solution of Na^{22} and Na^{24} were counted in the same manner as the sections of a diffusion sample, showed that the isotopic ratios determined by this procedure were not count-rate-dependent.

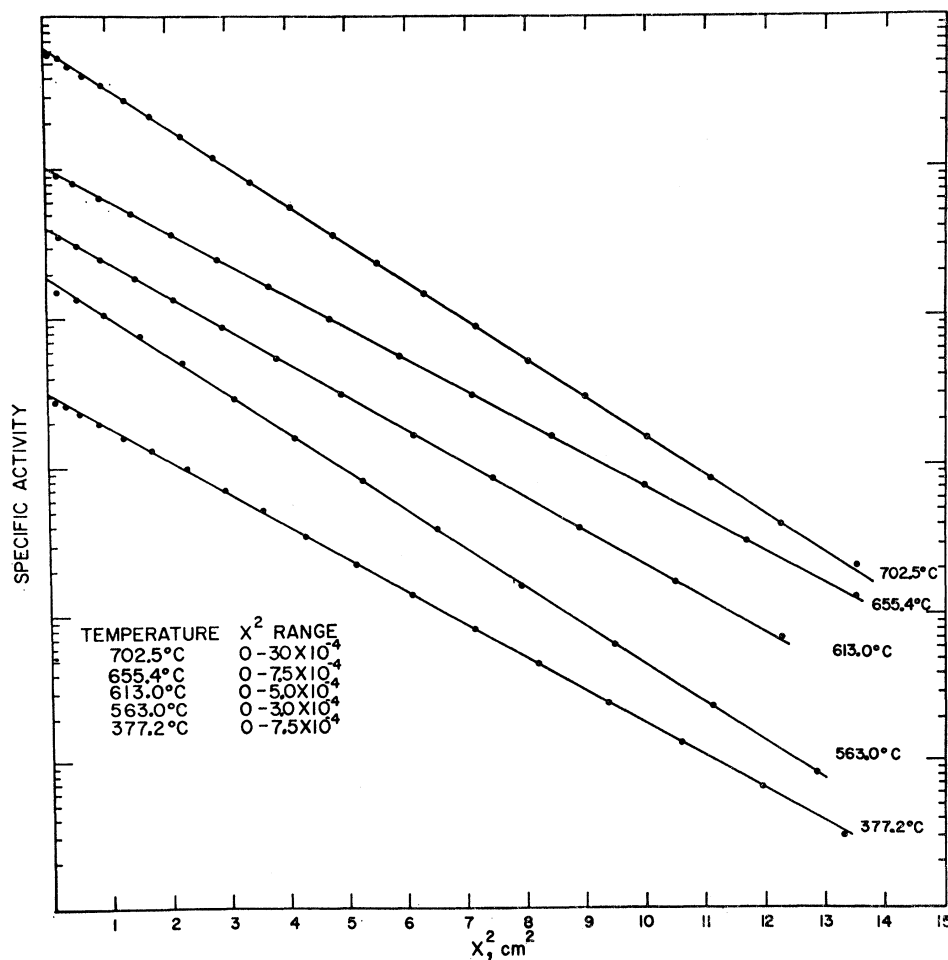


FIG. 1. \log_{10} specific activity of Na^{22} versus penetration distance squared for the diffusion of Na^{22}Cl in RbCl .

⁴ C. M. Lederer, J. M. Hollander, and I. Perlman, *Table of Isotopes* (John Wiley & Sons, Inc., New York, 1967).

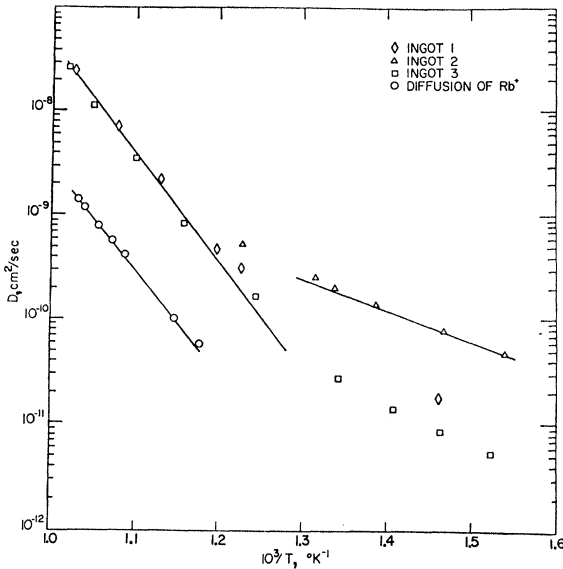


FIG. 2. $\text{Log}_{10} D$ versus reciprocal absolute temperature for the diffusion of Na^{22}Cl in RbCl . The data of Arai and Mullen (Ref. 2) for Rb^+ diffusion in RbCl are also shown.

RESULTS

The mathematical solution of the diffusion equation for the boundary conditions used in our experiments is

$$\ln C = \text{const} - X^2/4Dt, \quad (4)$$

where C is the specific activity of Na^{22} in a section whose center is X cm distant from the original surface, and t is the annealing time. Figure 1 shows five typical plots of $\log_{10} C_{22}$ versus X^2 . Their linearity, in agreement with Eq. (4), shows that volume diffusion is being measured. The values of D are shown as a function of $1/T$ in Fig. 2 and are listed in Table I. The values for Rb^+ diffusion in RbCl from the work of Arai and Mullen² are also shown in Fig. 2.

TABLE I. Diffusion of Na^{22} in RbCl .

Ingot	Temp. (°C)	D (cm ² /sec)
1	702.5	2.41×10^{-8}
	655.4	7.21×10^{-9}
	613.2	2.28×10^{-9}
	563.0	4.72×10^{-10}
	542.8	3.08×10^{-10}
2	411.8	1.80×10^{-11}
	541.9	5.38×10^{-10}
	488.0	2.53×10^{-10}
	473.9	1.96×10^{-10}
	448.2	1.39×10^{-10}
3	408.4	7.75×10^{-11}
	377.2	4.77×10^{-11}
	707.0	2.64×10^{-8}
	678.0	1.19×10^{-8}
	634.7	3.67×10^{-9}
	587.6	8.77×10^{-10}
	531.9	1.64×10^{-10}
	472.2	2.80×10^{-11}
	437.0	1.40×10^{-11}
	409.7	8.62×10^{-12}
382.8	5.40×10^{-12}	

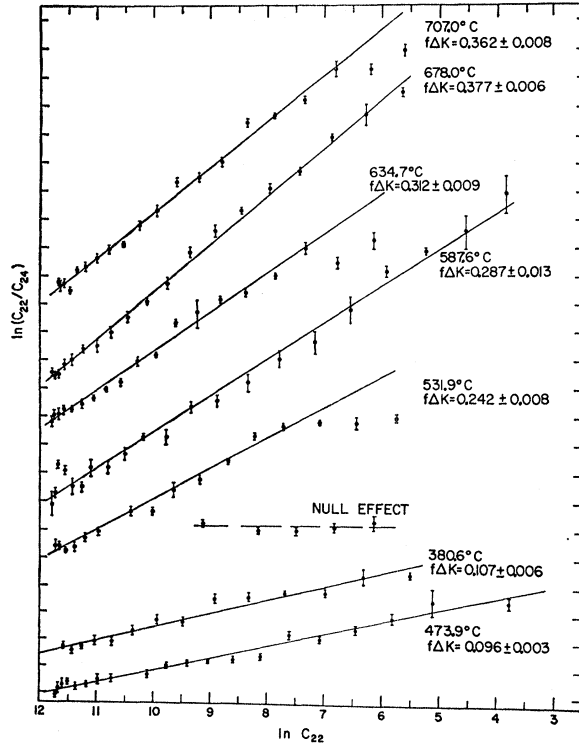


FIG. 3. $\ln(C_{22}/C_{24})$ versus $\ln C_{22}$ for the diffusion of Na^+ in RbCl . Each division on the ordinate is 0.01.

If Eq. (4) is written for Na^{22} and Na^{24} , one obtains⁵

$$\ln(C_{22}/C_{24}) = \ln(A_{22}/A_{24}) = \text{const} - \ln C_{22}(D_{22}/D_{24} - 1). \quad (5)$$

The plots of $\ln(C_{22}/C_{24})$ versus $\ln C_{22}$ (Fig. 3) obey Eq. (5), with the exception of some of the points at low concentration. This deviation is probably due to diffusion along dislocations and subboundaries.⁶ The error bars in Fig. 3 are the standard errors of $\ln(C_{22}/C_{24})$ calculated from a linear least-squares fit to Eq. (3). The results of the null experiment are also shown in Fig. 3. The values of $D_{22}/D_{24} - 1$ and their standard errors are listed in Table II.

TABLE II. Isotope effect for the diffusion of Na in RbCl .

Ingot	Temp. (°C)	$D_{22}/D_{24} - 1$	$f\Delta K$
3	707.0	0.0161 ± 0.0004	0.362 ± 0.008
	678.0	0.0168 ± 0.0003	0.377 ± 0.006
	634.7	0.0139 ± 0.0004	0.312 ± 0.009
	587.6	0.0128 ± 0.0006	0.287 ± 0.013
2	531.9	0.0108 ± 0.0004	0.242 ± 0.008
	473.9	0.0043 ± 0.0001	0.096 ± 0.003
	380.6	0.0047 ± 0.0003	0.107 ± 0.006

⁵ L. W. Barr and A. D. LeClaire, Proc. Brit. Ceram. Soc. 1, 109 (1964).

⁶ N. L. Peterson and S. J. Rothman, Phys. Rev. 163, 645 (1967).

DISCUSSION

Diffusion of Na²³ in RbCl

Diffusion measurements were made on three ingots that contained different concentrations of polyvalent impurities, because one ingot was too small to yield enough samples for a study of both the intrinsic and extrinsic regions. The data were treated by an iterative method in order to obtain Q_{int} and Q_{ext} . First, a straight line was drawn through the high-temperature data points from ingots 1 and 3. An extension of this line to low temperatures allowed a subtraction of the intrinsic part of D from the measured low-temperature D values from ingot 2. A straight line through the Arrhenius plot of these "extrinsic" values of D gave an approximate value of Q_{ext} . Straight lines with a slope of Q_{ext}/k were then drawn through the low-temperature D values from ingots 1 and 3. An extension of these lines to high temperatures allowed a subtraction of the extrinsic part of D from the measured high-temperature D values from ingots 1 and 3. A straight line through these "intrinsic" values of D gave an improved value of Q_{int} . The iteration procedure was continued with the improved value of Q_{int} until values of Q_{int} and Q_{ext} were consistent with the D values of all ingots. This procedure gave the following values: For the intrinsic region, $D_0 = (1.03 \pm 0.02) \times 10^8$ cm²/sec and $Q_{\text{int}} = 2.06 \pm 0.02$ eV; for the extrinsic region, $Q_{\text{ext}} = 0.593 \pm 0.007$ eV.⁷ The quoted error limits are the standard errors obtained from a least-squares fit of D_{int} and D_{ext} obtained by the iteration procedure to the Arrhenius equation.

Isotope Effect for the Diffusion of Na in RbCl

The isotope effect may be related to the correlation factor by the equation⁸⁻¹⁰

$$\frac{D_\alpha/D_\beta - 1}{(m_\beta/m_\alpha)^{1/2} - 1} = f\Delta K, \quad (6)$$

where D and m are the diffusion coefficients and masses, respectively, of two isotopes α and β of the same element, and ΔK is the fraction of the kinetic energy of the saddle-point configuration—associated with motion in the diffusion direction—that is possessed by the diffusing atom. The values of $f\Delta K$, calculated from the

⁷ The iteration procedure is essentially the same as fitting D to the equation $D = D_0 \exp(-Q_i/kT) + D_0 \exp(-Q_e/kT)$. As pointed out by Lidiard [*Handbuch der Physik* (Springer-Verlag, Berlin, 1957), Vol. XX, p. 286], D should be expressed by the equation $D = X_0 D_0 f \exp(g_0/kT)$, where the fraction of vacancies is $X_0 = \frac{1}{2} C [1 + (1 + 4X_0^2/C^2)^{1/2}]$. The term C is the fraction of divalent impurity ions and X_0^2 is the product of the fractions of anion and cation vacancies. The correct expression for D is measurably different from the sum of two exponentials only when X_0 and C are the same within an order of magnitude. The quoted values of D_0 and Q were determined only from experimental values of D when the intrinsic and extrinsic portions of D differed by at least a factor of 10.

⁸ A. H. Schoen, *Phys. Rev. Letters* **1**, 138 (1958).

⁹ J. G. Mullen, *Phys. Rev.* **121**, 1649 (1961).

¹⁰ A. D. LeClaire, *Phil. Mag.* **14**, 1271 (1966).

experimental values of $D_\alpha/D_\beta - 1$ by means of Eq. (6), are listed in Table II.

The correlation factor for impurity diffusion in the fcc lattice (Rb sublattice in RbCl) is¹¹

$$f = \frac{w_1 + \frac{7}{2} F w_3}{w_1 + w_2 + \frac{7}{2} F w_3}. \quad (7)$$

Here w_1 is the rate of exchange of a vacancy neighboring an impurity atom with any of the four solvent atoms that are also neighbors of the impurity; w_3 is the rate of exchange of a vacancy neighboring an impurity with any of the seven solvent atoms adjacent to the vacancy, but not neighbors of the impurity (dissociation jump); and w_2 is the impurity-vacancy exchange rate. The term F is a function of w_4/w_0 , where w_4 is the frequency of the association jump (reverse of a w_3 jump), and w_0 is the frequency of solvent-vacancy exchanges in the pure solvent crystal.

The jump frequencies depend on temperature exponentially

$$w_j = \nu_j \exp(-h_{mj}/kT),$$

where ν_j denotes the "vibration frequencies" and h_{mj} denotes the activation energies. In general, all h_{mj} values will not be equal, and f will not vary with temperature exponentially. ΔK is believed to be independent of temperature. (The temperature dependence of ΔK in zinc is zero.⁶)

Since the deviation from an exponential temperature dependence of f is small compared with experimental error, a plot of $\ln(f\Delta K)$ versus $1/T$ should give a straight line with a slope of $\partial(\ln f)/\partial(1/T)$. The data in Table II are plotted in this manner in Fig. 4. The data for the intrinsic region give $-k[\partial(\ln f)/\partial(1/T)]_{\text{int}} = 0.19$ eV with an estimated error of $\pm 10\%$.

The data in the lower right of Fig. 4 give $-k[\partial(\ln f)/\partial(1/T)]_{\text{ext}} = -0.05$ eV. Lines drawn through the extremes of the error bars of these two points allow $-k[\partial(\ln f)/\partial(1/T)]_{\text{ext}}$ to vary from -0.003 to -0.08 eV. The difficulty of making diffusion measurements with a short-lived isotope, when $D \approx 10^{-11}$ cm²/sec, prohibited further refinement of the -0.05 -eV value.

The reversal in sign of $\partial(\ln f)/\partial(1/T)$ between the intrinsic and extrinsic regions may be qualitatively explained. In the intrinsic region, Na⁺ exchanges with the vacancy much more rapidly than do any of the Rb⁺ neighbors. In fact, assuming that all Rb⁺ jumps occur with the same frequency (i.e., $w_1 = w_3 = w_4 = w_0$), and that $\Delta K = 1$ (Barr and LeClaire⁵ found $\Delta K = 0.93 \pm 0.07$ for Na⁺ diffusing in NaCl), the data in Table II and Eq. (7) show that at 575°C the Na⁺-vacancy exchange rate is 10 times larger than the Rb⁺-vacancy exchange rate. Thus w_2 is greater than all other jump frequencies and increases less rapidly with increasing temperature. This produces a small value of f that increases with increasing temperature.

¹¹ J. R. Manning, *Phys. Rev.* **128**, 2169 (1962).

In the extrinsic region, a number of the vacancies may be bound to polyvalent impurity ions. If the polyvalent impurity exchanges with the vacancy less frequently than does the Na^+ , the correlation factor will be much smaller than in the intrinsic region.¹² If h_m for the polyvalent impurity ions lies between h_m for Na^+ and h_m for Rb^+ , the correlation factor can be temperature-independent or even increase with decreasing temperature. This is consistent with the observed temperature dependence and small value of $f\Delta K$ in the extrinsic region.¹³ The increase of the degree of association with decreasing temperature may also be a factor.

From the experimental values of Q and $\partial(\ln f)/\partial(1/T)$ in both the intrinsic and extrinsic regions, one obtains $h_m+h_b=0.65$ eV and $\frac{1}{2}h_f=1.22$ eV [Eqs. (1) and (2)]. Tosi and Doyama¹⁴ calculated that Na^+ repels vacancies in RbCl with a repulsive energy of 0.1 eV. If the 0.1-eV value for h_b is used, we obtain $h_m=0.55$ eV. This value of h_m is appreciably larger than the theoretical value¹ of $h_m=0.22$ eV, but is much smaller than the theoretical h_m for Rb^+ (1.02 eV)¹ and the h_m obtained from our preliminary measurements of the electrical conductivity of the same RbCl ingots used in this investigation (0.78 eV).¹⁵ The motional energy for Na^+ must be smaller than the motional energy for Rb^+ to be consistent with the small values of f and the large values of D observed in this study.

The experimental value of $\frac{1}{2}h_f=1.22$ eV is in poor agreement with the theoretical values of Tosi and Doyama¹ (1.05 eV) and Boswarva and Lidiard¹⁶ (as large as 1.12 eV). Our preliminary measurements of electrical conductivity of RbCl give $h_f/2=1.18$ eV.¹⁵ The fact that the experimental value of $\frac{1}{2}h_f$ is larger than the theoretical value is in agreement with the divergence between experiment and calculations based on the usual ionic model in other alkali halides. Boswarva and Lidiard¹⁶ point out that the disagreements between theory and experiment are probably due to an overestimate of the polarization energy of the ions neighboring the vacancy. The difficulty in evaluating the polarization term had previously been noted by Mullen¹⁷

¹² R. E. Howard, Phys. Rev. **144**, 650 (1966).

¹³ Note that Eq. (6) is true only when the jump direction is an axis of at least twofold or threefold symmetry. This is not the case for diffusion by vacancies bound to an impurity. Howard (Ref. 12) calculated the correction to Eq. (6) for self-diffusion by bound impurity-vacancy pairs in a fcc lattice. This calculation suggests that the required correction for the present values of $f\Delta K$ is about 10%. This correction will not affect the experimental value of $\partial(\ln f)/\partial(1/T)$ because of the nearly temperature-independent values of f in the extrinsic region.

¹⁴ M. P. Tosi (private communication).

¹⁵ S. J. Rothman and N. L. Peterson, Bull. Am. Phys. Soc. **13**, 466 (1968).

¹⁶ I. M. Boswarva and A. B. Lidiard, Phil. Mag. **16**, 805 (1967).

¹⁷ J. G. Mullen, Phys. Rev. **143**, 658 (1966).

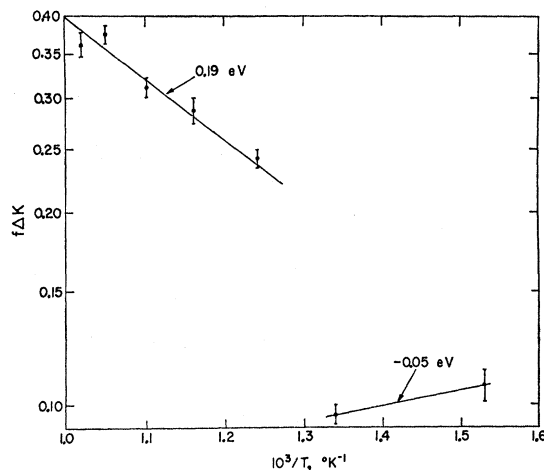


Fig. 4. $\ln f\Delta K$ versus reciprocal absolute temperature for the diffusion of Na^+ in RbCl in the intrinsic region (left) and the extrinsic region (right).

and prompted him¹⁷ to propose an alternative theory to evaluate h_f and h_m for the alkali halides. Although Mullen's theory contains far-reaching assumptions (and tends to overestimate h_f), it does predict a value of $\frac{1}{2}h_f$ (1.27 eV) that is in fair agreement with the present results for RbCl.

In deducing $\frac{1}{2}h_f$ from our experimental data, we assumed that h_m+h_b is the same in both the intrinsic and extrinsic regions; i.e., the energy required for a sodium ion-vacancy exchange plus the sodium ion-vacancy binding energy is the same for both vacancies that are bound to polyvalent impurity ions and for free vacancies. No direct measurement is available to verify the assumption.

CONCLUSION

The activation energy for Na^+ diffusion in RbCl is 2.06 ± 0.02 and 0.59 ± 0.01 eV in the intrinsic and extrinsic regions, respectively. The temperature dependence of the correlation factor, as deduced from isotope-effect measurements, is 0.19 eV in the intrinsic region and -0.05 eV in the extrinsic region. If a theoretical value for the Na^+ -vacancy binding energy is used, values of $\frac{1}{2}h_f=1.22$ eV and $h_m=0.55$ eV are obtained. These values are not in agreement with the calculations of Tosi and Doyama.¹

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