

## Pressure Dependence of Self-Diffusion of Na<sup>22</sup> in NaCl<sup>†</sup>

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The effect of hydrostatic pressure of 6.2 kbar on the rate of diffusion of Na<sup>22</sup> in NaCl has been studied at temperatures of 663 and 731 °C using a tracer-sectioning technique. The cation-diffusion process is characterized by a pressure-dependent activation volume varying between about 37 cm<sup>3</sup>/mole at low pressures to about 25 cm<sup>3</sup>/mole at high pressures. If possible divacancy contributions can be neglected, this result implies a volume of formation of Schottky defects of about 2.2 molar volumes. Diffusion profiles at high pressure show a marked deviation from the expected Gaussian dependence. This effect is shown to be due to the presence of trace amounts of polyvalent impurity co-diffusing with the "carrier-free" Na<sup>22</sup> tracer.

### I. INTRODUCTION

The alkali halides, and particularly NaCl, as prototype ionic crystals, have been studied exhaustively for more than 40 years. Still, considerable uncertainties remain in both precise specification and understanding of their defect properties. Mass transport at high temperatures is well known to occur predominantly by the presence of cation-anion vacancy pairs—Schottky defects—but unresolved problems persist in determination of the precise properties of these defects.

Measurements of tracer diffusion and ionic conductivity<sup>1,2</sup> in NaCl show that at atmospheric pressure in the intrinsic range—at temperatures above about 600 °C where impurity effects can usually be neglected—both charge transport and mass transport are dominated by motion of the cations, with an activation energy of  $2.00 \pm 0.04$  eV. The energy of formation for Schottky defects deduced from these diffusion data is in excellent agreement with that calculated from first principles.<sup>3</sup> There is, however, some evidence for a possibly major contribution due to motion of anions at temperatures very near to the melting point: Nelson and Friauf<sup>4</sup> estimate that cation-anion vacancy pairs contribute about 50% to mass transport near the melting point; Bénére *et al.*<sup>1</sup> estimate the pair contribution at only a few percent; recent isotope effect measurements by Rothman *et al.*<sup>2</sup> suggest a pair contribution of 30–45% close to the melting point. Theoretical calculations<sup>5</sup> favor a small pair contribution.

Differences also persist in both experimental and theoretical determinations of the activation volumes associated with the diffusion process in these materials.<sup>6</sup> Studies of the effect of pressure on ionic conductivity by Yoon and Lazarus<sup>7</sup> show evidence for a pressure-dependent activation volume in the intrinsic region, while the results of Beyeler and Lazarus<sup>8</sup> show the activation volume to be independent of pressure. Both studies indicate that the

formation volume for Schottky defects in NaCl is substantially larger than the molar volume,<sup>9</sup> while the theoretical calculations of Faux and Lidiard<sup>3</sup> predict that the formation volume should be substantially smaller than the molar volume. Clearly, major uncertainties remain both in precise experimental specification of the mechanism or mechanisms responsible for diffusion in these materials and in theoretical understanding of the detailed nature of the defects responsible.

The present experiment was undertaken with the modest aim of trying to resolve the discrepancy surrounding the pressure dependence of the activation volume, or lack of it, reported by the two groups who studied ionic conductivity in NaCl. To be certain that only cation motion was measured, the present experiment involved determination of the effect of high pressure on the motion of Na<sup>22</sup> tracer atoms, so that any possible effects due to anion motion would not complicate the interpretation. As discussed below, the present results substantiate the earlier conclusion that the formation volume of Schottky defects is considerably larger than the molar volume and indicate a significant pressure dependence for the activation volume, but, more importantly, indicate strongly that unanticipated effects associated with minute amounts of polyvalent impurity in the tracer may cast doubt on the accuracy of *all* tracer-diffusion measurements in insulators.

### II. EXPERIMENTAL TECHNIQUES

Diffusion specimens were prepared from Harshaw high-purity NaCl crystals by cleaving parallelepipeds of dimensions 8×8×3 mm, and polishing the cleaved surfaces with an American Optical Co. 860 microtome. The samples were then annealed for 2 h at 750 °C in an atmosphere of dried argon. Na<sup>22</sup> tracer, purchased in "carrier-free" form as NaCl in H<sub>2</sub>O from International Chemical and Nuclear Corporation, was deposited by vacuum evaporation

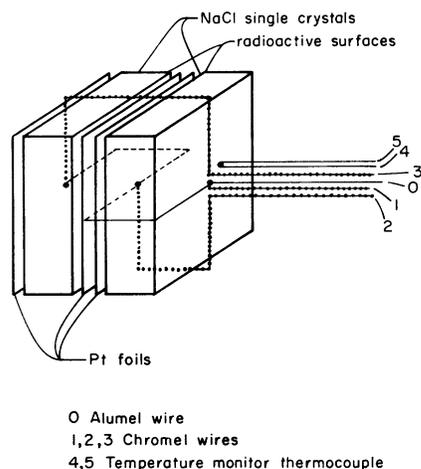


FIG. 1. Sample holder inside high-temperature furnace, showing thermocouple arrangement: 0—alumel wire; 1, 2, 3—chromel wires; 4, 5—temperature monitor thermocouple. The thermocouple readings of 2 and 3 agreed within 1°C.

onto one of the 8×8-mm surfaces of each sample to a total activity of about 0.1  $\mu$ Ci.

Diffusion anneals at high pressure were carried out in an atmosphere of dried and purified argon using the pressure bomb and internal furnace arrangement described previously.<sup>10</sup> Internal pressures were monitored to  $\pm 1\%$  using a Heise Bourdon gauge and a Harwood manganin gauge. Considerable precautions were taken in the determination of the temperature at the diffusion interface to ensure against potentially large errors inherent in such measurements.<sup>10</sup> Four chromel-alumel couples were used in the two-specimen arrangement shown in Fig. 1. The thermoelectric power of these couples is pressure independent below about 8 kbar and 750°C,<sup>11</sup> and the couples do not degrade rapidly below 800°C in argon. Temperature determination is thus presumed accurate to  $\pm 1^\circ\text{C}$ . After the high-pressure diffusion runs, some specimens showed a superficial surface contamination of a black substance which could be removed by light brushing with acetone. Mass spectrographic analysis of diffused specimens disclosed no change in impurity content between virgin bulk material and a 100- $\mu\text{m}$  thick surface region where diffusion had occurred.

Following the high-pressure diffusion anneal, the specimens were prepared for sectioning by first removing the lateral surfaces with a microtome to a depth considerably greater than the anticipated tracer-penetration distance. The specimens were then remounted with the initial interfaces accurately perpendicular to the microtome axis and sectioned normal to the diffusion direction. The first slice, of about 10- $\mu\text{m}$  thickness, was collected on a piece of

aluminum foil and weighed using a calibrated Cahn electrobalance. The subsequent sections, of about 8- $\mu\text{m}$  thickness each, were collected by pressing a small strip of Scotch tape to the surface of the sample<sup>12</sup> before passage of the microtome blade. The thicknesses of the individual slices were determined from the microtome-screw-dial readings, and the thickness of the first slice and total penetration distance were estimated by comparison to the total weight loss of the specimen. Because of constraints within the internal furnace of the pressure system, it was not possible to determine precise weights for the individual slices. The Na<sup>22</sup> activity was then measured for each slice with a conventional scintillation detector and pulse-height analyzer circuit.

Since two identical specimens were mounted and sectioned for each run, a comparison of their relative penetration curves gives an internal check on the accuracy and self-consistency of the sectioning procedure. On this basis, the over-all accuracy of the measurements, aside from temperature and timing errors (corrections were made for warm-up time), was about  $\pm 2\%$  at low pressures, increasing to discrepancies as large as  $\pm 15\%$  at the highest pressures.

### III. EXPERIMENTAL RESULTS

Diffusion anneals were performed for pressures up to 6.2 kbar for a large number of specimens at two different temperatures spanning the most accessible part of the "intrinsic" range for NaCl: 663 and 731°C. Lower temperatures would have required longer anneal times than were practicable with maintaining the pressure system leak free or, alternatively, shorter tracer-penetration distances than could be measured with the available microtome-sectioning technique. Higher temperatures would have required excessive warmup corrections for very short anneal times or tracer-penetration distances too large for the specimen size chosen. The two temperatures chosen should have shown a marked temperature dependence in the position of the "knee" found by Yoon and Lazarus<sup>7</sup> in their ionic-conductivity studies if that anomaly, as presumed, was due entirely to cation motion.

The tracer-penetration curves, four of which are shown in Fig. 2, indicate marked and systematic deviations from the Gaussian form expected for the planar geometry and  $\delta$ -function source used. As evident from the figures, the tracer concentration in some cases falls off more rapidly than exponentially with penetration distance squared, in a manner opposite to that expected if the anomaly were due to diffusion along surfaces or short-circuiting paths.<sup>13</sup> The curvature is evident for all runs except those at the highest temperatures and lowest pressures, and increases markedly with increasing

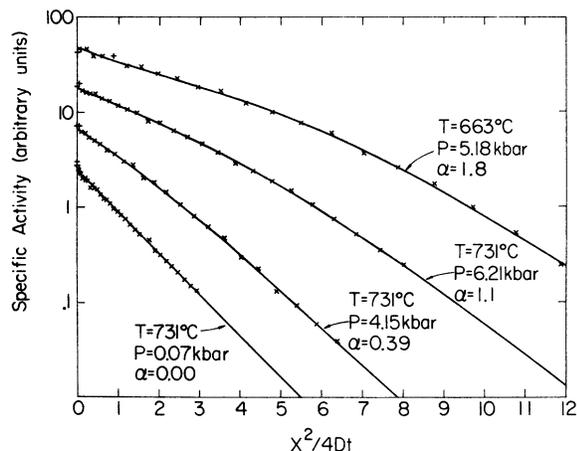


FIG. 2. Typical penetration profiles with computer fits. Points labeled + were excluded from fitting program.

pressure and decreasing temperature. Previous workers<sup>1,2</sup> have reported slight discrepancies in the near-surface region of their penetration profiles and have suggested that these may be due to extrinsic vacancies introduced by slight amounts of impurity in their tracers. In cases where such curvature was evident, the values of diffusion coefficients reported were based on the best Gaussian fit to their data with the exclusion of the first several points. The same procedure can be used for deriving values of diffusivity from the present data, but the curvature is so marked in most cases that it is

nearly impossible to identify the "wrong" points to be excluded.

This anomaly has prompted an attempt to find a general solution to the problem of diffusion of a monovalent tracer in the presence of a diffusing polyvalent impurity of comparable concentration. The results of this calculation, as shown in detail in the companion paper by Feit, Mitchell, and Lazarus,<sup>14</sup> indicate the ubiquitous nature of this problem for all cases of tracer diffusion in insulating solids. Even the experimental finding of a "proper" Gaussian solution to the diffusion equation is no guarantee that the slope thus calculated is, in fact, simply related to the diffusion coefficient of the monovalent tracer. The probability is high that there are at least divalent impurities present in the Na<sup>22</sup> "carrier-free" tracer used in this experiment, since it is made by cyclotron bombardment in a Mg<sup>24</sup>(*d*,  $\alpha$ ) reaction, and some residual trace of magnesium impurity is almost surely inevitable. Mass spectrographic examination of the Na<sup>22</sup> tracer disclosed no detectable amount of Mg<sup>24</sup> or other polyvalent impurity, so the amount present must be comparable in concentration to the tracer itself.<sup>15</sup> However, as shown in the detailed solution, even such a tiny concentration of polyvalent impurity is quite sufficient to cause the observed marked deviations from the Gaussian form for the Na<sup>22</sup> tracer.

To find an exact value for the true diffusivity of the tracer from a measured nonlinear penetration curve one must know precise values for both the concentration and diffusivity of the unknown impurity for the run, data which are not ordinarily avail-

TABLE I. Na<sup>22</sup> diffusion in NaCl: best-fit parameters.

Temperature (°C)	Pressure (kbar)	Time (10 <sup>4</sup> sec)	Estimate of Na <sup>22</sup> deposited (10 <sup>11</sup> atoms)	Diffusion coefficient best fit (10 <sup>-10</sup> cm <sup>2</sup> /sec)	$\alpha$	$r$
731	0.07	1.44	9.8	48.0	0.00	1.0
			18.0	46.0	0.06	0.4
	2.08	1.78	29.0	19.0	0.23	1.6
			16.0	18.0	0.26	2.0
	4.15	1.60	25.0	7.5	0.79	3.0
			15.0	9.2	0.39	1.4
	6.21	3.36	22.0	4.8	1.4	3.2
25.0			4.1	1.1	2.8	
663	0.00	1.96	6.7	7.0	0.22	0.7
			8.0	7.0	0.09	1.1
	0.12	2.00	4.9	8.1	0.00	0.6
			8.8	4.2	0.27	1.7
	1.38	2.13	9.2	3.7	0.51	1.5
			5.4	2.3	0.25	1.3
	3.45	4.46	6.1	2.4	0.10	0.5
			9.1	1.7	0.27	3.4
	5.17	3.84	6.1	1.3	0.58	3.1
			28.0	1.5	1.8	2.2
5.18	4.56	21.0	1.1	2.0	2.8	

able. Excellent approximate solutions, however, can be found by computer analysis using the iterative procedure described in detail in the companion paper. This method provides best-fit values for the tracer diffusivity together with a parameter  $\alpha$ , which varies directly with the concentration of polyvalent impurity and inversely with the  $\frac{3}{2}$  power of the diffusivity and the square root of the diffusion time, and a parameter  $r$ , equal to the ratio of the diffusivity of the unknown polyvalent impurity to that of the tracer. Values of the tracer diffusivity are deducible to within a precision of the order of magnitude of the scatter in the experimental data, while values of  $\alpha$  and  $r$  are deducible within roughly 50%.

The best-fit solutions using this procedure are shown, together with the experimental points, in Fig. 2. Values of the best-fit parameters are presented in Table I, along with measured values for the diffusion time for each run and an estimate of the initial tracer concentration—presumed proportional to the initial impurity concentration—as deduced from the initial activity and half-life of the tracer.

As evident from Fig. 2, the computer analysis provides an excellent fit to the data, with deviations not exceeding the random errors. Table I shows a reasonable consistency between calculated values of  $\alpha$  and  $r$  and physical expectations: there is a general trend for  $\alpha$  to increase with increasing tracer concentration and with decreasing diffusivity, in the expected manner;  $r$  generally increases with increasing pressure, and is never very different from unity, indicating that the diffusivity of the impurity

is suppressed less by pressure than that of the tracer.

The values of the best-fit tracer diffusivities are also presented in Table II together with those estimated by two previously used techniques: a Gaussian fit through all the points and the limiting slope technique of fitting by omission of the "wrong" points in the near-surface region. The differences are notable, particularly for the highest-pressure data which show the most marked curvature. The previous procedures are seen to overestimate the tracer diffusivity, sometimes by as much as a factor of 2.

Table II also shows the limits of the maximum and minimum values of the diffusion coefficient which could reasonably be considered as proper fits to the data within a least-squares criterion. These values generally lie within  $\pm 10\%$  of the best-fit values. Consideration of both the usual experimental errors and these possible fitting errors suggests an over-all precision of about  $\pm 15\%$  for the individual values of the diffusion coefficients.

Figure 3 shows the variation of the deduced Na<sup>22</sup> diffusivities with pressure at 731 and 663 °C. The activation volume for the process,  $\Delta V$ , is defined by

$$\Delta V = -RT \left( \frac{\partial \ln D}{\partial P} \right)_T,$$

where  $R$  is the gas constant,  $P$  the pressure, and  $T$  the absolute temperature. The correction to  $\Delta V$  resulting from the pressure dependence of the frequency factor terms<sup>6</sup> is presumed negligible.

The activation volumes are seen to be pressure

TABLE II. Na<sup>22</sup> diffusion in NaCl: various fits.

Temperature (°C)	Pressure (kbar)	Gaussian	Diffusion coefficient (10 <sup>-10</sup> cm <sup>2</sup> /sec)			
			Limiting slope	Best fit	Max.	Min.
731	0.07	49.0	49.0	48.0	49.0	47.0
		47.0	47.0	46.0	47.0	44.0
	2.08	23.0	22.0	19.0	21.0	17.0
		21.0	20.0	18.0	19.0	15.0
	4.15	12.0	11.0	7.5	8.9	6.0
		11.0	11.0	9.2	10.0	7.7
	6.21	7.7	6.6	4.8	5.5	2.9
7.9		6.6	4.1	5.1	3.6	
663	0.00	7.7	7.5	7.0	7.1	6.1
		7.3	7.3	7.0	7.2	6.4
	0.12	8.1	8.1	8.1	8.2	7.9
		5.0	4.8	4.2	4.5	3.8
	1.38	4.9	4.5	3.7	4.0	3.0
		2.7	2.5	2.3	2.5	2.1
	3.45	2.5	2.5	2.4	2.5	2.3
		2.0	1.9	1.7	1.8	1.5
	5.17	1.8	1.5	1.3	1.5	1.1
		3.5	2.7	1.5	1.7	1.3
5.18	2.9	2.1	1.1	1.4	1.0	

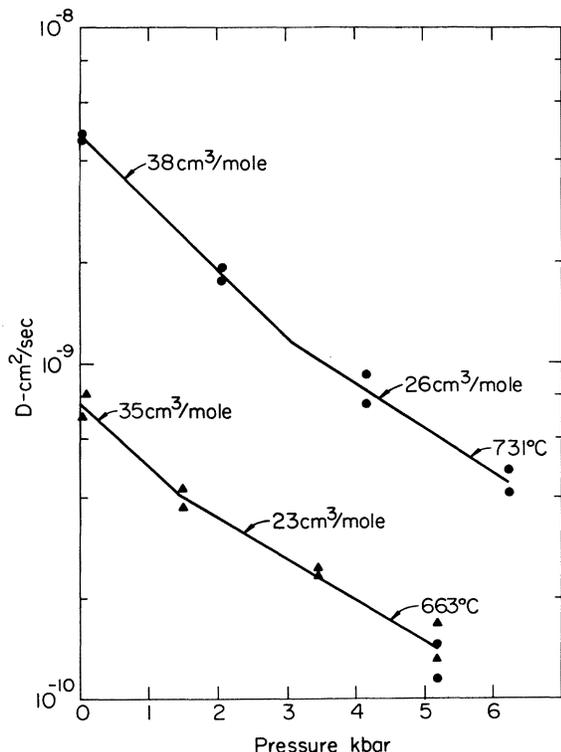


FIG. 3.  $\text{Na}^{22}$  diffusion coefficient in NaCl as a function of pressure at two temperatures. The activation volumes indicated are calculated from the initial and final slopes of the two curves.

dependent, decreasing from a value of 38 to 26  $\text{cm}^3/\text{mole}$  at 731  $^{\circ}\text{C}$ , and from 35 to 23  $\text{cm}^3/\text{mole}$  at 663  $^{\circ}\text{C}$ . This temperature difference is not significant within the  $\pm 10\%$  uncertainties in  $\Delta V$ . From this we may estimate the zero-pressure activation volume to be about  $37 \pm 4 \text{ cm}^3/\text{mole}$ .

#### IV. DISCUSSION

Cation diffusion can proceed via single cation vacancies and by vacancy pairs, as well as by other, much less probable, processes. The vacancy pair process is expected to be strongly temperature dependent and characterized by an activation volume considerably larger than that for the single vacancy process. Since our high-temperature value for  $\Delta V$  is only 10% larger than the low-temperature value, it appears unlikely that vacancy pairs are a major contributor to the tracer diffusion. In the absence of a detailed theory, we may simply ignore the possible contribution of vacancy pairs and deduce the defect formation volume from the measured value

of  $\Delta V$ . Using the measured value for the motion volume of cations of  $\Delta V_m = 7 \text{ cm}^3/\text{mole}$ ,<sup>6,7</sup> we thus deduce the formation volume of a Schottky defect to be  $2(37 - 7) = 60 \text{ cm}^3/\text{mole}$ , approximately 2.2 times the molar volume of  $27 \text{ cm}^3/\text{mole}$ .

In the present experiment, while there are slight uncertainties due to ignoring possible vacancy pair effects, there are none resulting from possible accompanying anion diffusion which complicated the interpretation of the earlier ionic-conductivity experiments. Indeed, the fact that the present value of  $\Delta V$  found for diffusion of the  $\text{Na}^{22}$  tracer is the same, within experimental errors, as that found from ionic conductivity by Yoon and Lazarus,<sup>7</sup> suggests that the ionic-conductivity experiments were not, in fact, complicated by any appreciable anion diffusion. The present value of about 2.2 molar volumes deduced for the formation volume of a Schottky defect is, therefore, completely at odds with the theoretical value of less than 1 molar volume calculated by Faux and Lidiard.<sup>3</sup>

The present result for the pressure dependence of the activation volume is not inconsistent with the behavior found by Yoon and Lazarus,<sup>7</sup> which showed a marked nonlinearity in the pressure dependence of the ionic conductivity for NaCl. In both cases, the "knee" in the curve apparently moves to lower pressures at lower temperatures. The present result is not completely consistent with the ionic-conductivity studies of Beyeler and Lazarus<sup>8</sup> which showed a pressure-independent, somewhat smaller, value of  $\Delta V$  (26  $\text{cm}^3/\text{mole}$ ). The reasons for this discrepancy are not well understood, but may result from small errors in temperature measurement or slight contamination in one of the experimental arrangements.

The marked curvatures found in the tracer-penetration plots, particularly those at high pressure and low temperature, give strong support to the notion that these complications arise from a co-diffusion of polyvalent impurities with the tracer. These results underscore the necessity for care in interpreting the results of tracer-diffusion measurements in *any* insulator where there is any possibility that impurities may be co-deposited with the tracer.

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<sup>15</sup>It seems clear that the trace impurity could be detected directly with an Auger spectrometer, but we were unable to find any friendly Auger specialists willing to contaminate their clean systems with Na<sup>22</sup>!

## Ca(OH)<sub>2</sub> Infrared Vibrational Spectra around 3600 cm<sup>-1</sup>: Experimental and Theoretical Study on Microcrystals and Single Crystals

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An experimental study of the high-frequency vibrational spectra around 3600 cm<sup>-1</sup> is presented here, and a theoretical model for the high-energy sidebands of the OH<sup>-</sup> stretching mode is given where we make the assumption that the OH<sup>-</sup> vibration is like a localized mode. Then these sidebands appear as a projected density of states and this quantity is obtained from theoretical dispersion curves which have been calculated using a point-ion electrostatic model. The adjustable parameters have been determined through the experimental low-energy-phonon frequencies. We discuss also the experimental and theoretical results on infrared absorption of microcrystalline samples and the shape of dispersion curves of phonons.

### I. INTRODUCTION

Ca(OH)<sub>2</sub> crystals present a complex infrared absorption spectrum in the 4000–3000-cm<sup>-1</sup> range as in hydroxides of other monovalent and divalent metals such as Mg(OH)<sub>2</sub> and Li(OH)<sup>1–6</sup> as well as in alkali halides doped with OH<sup>-</sup> impurities.<sup>7</sup> Such spectra generally exhibit a main and narrow absorption band and sidebands on both the low- and high-energy sides with approximately mirror symmetry. The narrow band is related to the stretching mode of the OH<sup>-</sup> ion and the sidebands to its coupling with librational modes or lattice modes.

The coupling with librational modes<sup>8–9</sup> is insufficient to explain the polarizations and intensities of certain bands in Li(OH)<sup>5</sup>; for instance, this model predicts that all frequency shifts from the stretching frequencies should be divided by a factor of 1.37 in the deuterated case, in contradiction to experimental results. The model using the coupling of the stretching mode with normal modes of the lattice is more successful in explaining the experimental results.<sup>10–12</sup> In the particular case of

Ca(OH)<sub>2</sub>, Oehler<sup>3</sup> calculated the dispersion curves in the rigid-ion approximation and found not too bad an agreement between maxima in the sidebands and points in the dispersion curves where the density of states should be high; however, this approach is very qualitative first because only those wave vectors of the form  $\vec{k} = (a, a, 0)$  were used and also because he did not give any microscopic model to describe the coupling between the stretching mode and normal modes of the lattice.

In this work we propose a model of coupling between the linear vibration of OH and the phonons of the crystal. One can calculate the form of the satellite spectrum (at low temperature) on the high-energy side using this model, which involves an anharmonic electrostatic interaction. To do this one needs the phonon dispersion curves, and since detailed neutron scattering information is unavailable, we needed the frequencies of the fundamental vibrations of Ca(OH)<sub>2</sub> which are either infrared or Raman active to obtain the parameters of the crystal dynamics model. Some infrared absorption measurements have been performed on