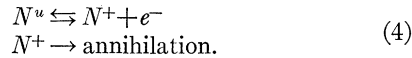


Willardson, the experimental assistance of P. W. Heindelman and A. M. Rosen, and helpful discussions with several of his colleagues at Atomics International.

APPENDIX

To derive Eq. (3) in the text, let N be the total concentration of close pairs, N^+ the concentration of close pairs with the interstitial ionized, and N^u the concentration with the interstitial unionized. We have the reactions



The rate of decay of the defects is given by

$$dN/dt = -K'N^+. \quad (5)$$

It is assumed, in Eqs. (4) and (5), that the decay of the pairs with ionized interstitials is the only mode of decay of the close pairs and that this decay is proportional to the number of pairs N^+ with rate constant K' . From statistical considerations, if the electron redistribution is rapid compared to the decay of close pairs,

$$(N - N^+)/N^+ n = \lambda^{-1} N_c^{-1} e^{\epsilon/kT}, \quad (6)$$

where n is the carrier concentration, $N_c = 2(2\pi kTm_n/h^2)^{3/2}$ is the standard expression for the density of states in

the conduction band, ϵ is the ionization energy of the interstitial, and λ is a statistical weighting factor which depends on the degeneracies of the ionized and unionized states of the interstitial.¹⁸ The carrier concentration is given by

$$n = n_f - \alpha N + N^+, \quad (7)$$

where n_f is the value of n on completion of recovery and α is the number of electrons removed from the conduction band per close pair. From Aukerman's^{4,19} work, it seems likely that ϵ is not less than 0.04 eV, and it is reasonable to assume that $N^+ \ll N$. Making this assumption and substituting (5) and (6) in (7), we have

$$dN/dt = -K n_f N / (n_f - \alpha N),$$

where $K = \lambda n_f^{-1} K' N_c e^{-\epsilon/kT}$. This is easily integrated to give

$$\ln(N/N_0) = (\alpha N_0/n_f)(N/N_0 - 1) - Kt,$$

in which N_0 is the value of N at $t=0$. This can be written in the form

$$\phi = e^{A(\phi-1)} e^{-Kt},$$

with $A = \alpha N_0/n_f$.

¹⁸ W. Ehrenberg, *Electric Conduction in Semiconductors and Metals* (Oxford University Press, New York, 1958), p. 42.

¹⁹ L. W. Aukerman, *J. Appl. Phys.* **30**, 1239 (1959).

Effect of Hydrostatic Pressure on Ionic Conductivity in Doped Single Crystals of Sodium Chloride, Potassium Chloride, and Rubidium Chloride†*

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The effect of hydrostatic pressure up to 9000 kg/cm² on ionic conductivity in NaCl, KCl, and RbCl single crystals doped with divalent impurities has been studied over the temperature range 200° to 500°C. The conductivity in this temperature range is due almost entirely to the motion of extrinsic cation vacancies. The activation volume ΔV_m for motion of the cation vacancies is 7.7 ± 0.5 cc/mole in NaCl doped with CaCl₂ and 7.0 ± 0.5 cc/mole in KCl doped with SrCl₂. The results are in fair agreement with values predicted on the basis of Keyes's empirical expression relating activation volume to activation energy and isothermal compressibility. Sample materials were chosen with the view of testing for a correlation between activation energy and shear modulus. The small shear modulus in KCl and RbCl decreases with increasing pressure, while the reverse is true for NaCl. However, the data are not adequate to draw definite conclusions about such a correlation. The conductivity of RbCl doped with BaCl₂ increases by an order of magnitude at the phase transition from the NaCl to the CsCl structure. At 300°C, the transition occurs at 6100 kg/cm².

I. INTRODUCTION

IN spite of the large amount of effort that has been devoted to the study of point defects, vacancies and interstitials, in recent years, there are still several aspects of their properties and nature which are not

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well understood. In particular, the extent of such a defect in a crystalline lattice, including relaxation and distortion of atoms or ions in the vicinity of a defect, is quite uncertain. Similarly, very little is known about the amount of lattice distortion necessary for diffusive motion of these defects in a solid. Experimentally, it is impossible at the present time to obtain a perfectly direct measure of this distortion. Theoretical calculations of necessity involve many approximations because of lack of detailed knowledge of interatomic forces.

The defect structure of the simplest ionic crystals, the alkali and silver halides, is probably better understood than that of any other type of solid.¹⁻³ The present experiment is concerned with alkali halides doped with divalent impurities. It is well established⁴⁻¹¹ that the dominant point defects present in alkali halides in the temperature range (200°–500°C) and impurity concentration range (10⁻³–10⁻⁴ mole fraction) of this experiment are positive-ion vacancies introduced into the crystal with the divalent impurities to maintain charge neutrality. Measurements of the transport number¹² in alkali halides in this temperature range show that charge transport occurs almost entirely by positive ion motion. Ionic conductivity and dielectric loss^{13,14} measurements on alkali halides made as a function of temperature allow the determination of several significant properties of the defects present. These include the energy of formation of Schottky pairs, the energy of motion of cation vacancies, the binding energy and degree of association of the cation vacancies with divalent impurities, and the jump frequency of such a bound vacancy in the vicinity of a divalent impurity.

It would be of considerable interest to know the effective volume of a lattice defect and the lattice expansion necessary to allow a defect to move. These quantities can be determined in principle from measurements of the effect of hydrostatic pressure on defect-limited processes, and when determined in this manner are known as activation volumes. The total activation volume ΔV_t consists of two parts. The volume of formation ΔV_f is the volume change of the lattice due to the formation of the defect. For the case of a simple vacancy, ΔV_f differs from the atomic volume by the amount of relaxation of the atoms surrounding the vacancy. The activation volume of motion ΔV_m may be defined as the expansion of the crystal due to the presence of a diffusing atom in the saddle-point configuration half-way between its former position and the site to which it is migrating. A hard-spheres model predicts that ΔV_m should be about equal to the volume of the diffusing atom for a vacancy mechanism and somewhat larger for an interstitial process.

It may be noted that the results of most of the previous pressure experiments on metals indicate a ΔV_t considerably less than one atomic volume.¹⁵⁻¹⁸ In marked contrast, the measurements of ΔV_t ¹⁹ and ΔV_f ²⁰ for Schottky defects in AgBr indicate that these volumes are considerably larger than the molecular volume in this material. A similar comparison may be made between ΔV_m for vacancies in metals and in ionic crystals. Emrick²¹ has found that ΔV_m for vacancies in gold is only 15% of the atomic volume. Kurnick,²⁰ on the other hand, found that ΔV_m for silver vacancies in AgBr is comparable to the volume available to the silver ion in its normal lattice site.

The apparent anomalies in relative sizes of the activation volumes between metals and ionic crystals furnish the primary motivation for the present experiment in the alkali halides. No experiments allowing a calculation of the activation volumes for defect processes in ionic crystals other than AgBr have been done previously. Thus, it was felt to be of some importance to furnish corroborative evidence for pressure effects in ionic crystals of a different type. Results for the alkali halides should perhaps be more easily interpretable than those for the silver halides, as the Schottky defect is firmly established as the only mobile point defect present in measurable quantities.

Three alkali halides, NaCl, KCl, and RbCl, are included in the study, furnishing an opportunity to test the validity of an empirically observed correlation between activation energy for defect motion and bulk shear modulus.²² Lazarus found that the small shear modulus C_{44} decreases with increasing pressure in KCl²³ and RbCl,²⁴ but increases in NaCl.²³ Atmospheric pressure ionic conductivity measurements on NaCl and KCl indicate that they behave quite similarly, and it was hoped that the high pressure measurements might serve as a test of the validity of this correlation.

Assuming that electrical conductivity in doped alkali halides is due entirely to motion of the positive ion vacancies, the following expression can be written on the basis of reaction rate theory,²⁵

$$\sigma = n_f e^2 a^2 \nu_0 k^{-1} T^{-1} \exp(-\Delta G_m/kT), \quad (1)$$

where n_f is the concentration of free vacancies, e is the electronic charge, a the lattice parameter, ν_0 is an

¹ F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954).
² A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, Germany, 1957), Vol. 22.
³ N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.* **34**, 485 (1938).
⁴ J. Teltow, *Ann. Physik* (6) **5**, 63, 71 (1949); *Z. physik. Chem.* **195**, 197 (1950).
⁵ E. Koch and C. Wagner, *Z. physik. Chem.* **B38**, 295 (1937).
⁶ O. Stasiw and J. Teltow, *Ann. Physik* (6) **1**, 26 (1947).
⁷ H. Kelting and H. Witt, *Z. Physik* **126**, 697 (1949).
⁸ H. W. Etzel and R. J. Maurer, *J. Chem. Phys.* **18**, 1003 (1950).
⁹ C. Beam, thesis, University of Illinois, Urbana, Illinois, 1952 (unpublished).
¹⁰ Y. Haven, *Rec. trav. chim.* **69**, 1259, 1471, 1505 (1950).
¹¹ H. Pick and H. Weber, *Z. Physik* **128**, 409 (1950).
¹² F. Kerkhoff, *Z. Physik* **130**, 449 (1951).
¹³ R. G. Breckenridge, *J. Chem. Phys.* **16**, 959 (1948); **18**, 913 (1950).
¹⁴ Y. Haven, in *Report of the Bristol Conference on Defects in Crystalline Solids, July, 1954* (The Physical Society, London, 1955); *J. Chem. Phys.* **21**, 171 (1953).

¹⁵ N. H. Nachtrieb, J. A. Weil, E. Catalano, and A. W. Lawson, *J. Chem. Phys.* **20**, 1189 (1952).
¹⁶ N. H. Nachtrieb, H. A. Resing, and S. A. Rice, *J. Chem. Phys.* **31**, 135 (1959).
¹⁷ G. W. Tichelaar and D. Lazarus, *Phys. Rev.* **113**, 438 (1959).
¹⁸ C. T. Tomizuka, in *Report of Lake George Conference on Very High Pressure* (John Wiley & Sons, Inc., New York, 1960).
¹⁹ D. S. Tannhauser, *J. Phys. Chem. Solids* **5**, 224 (1958).
²⁰ S. W. Kurnick, *J. Chem. Phys.* **20**, 219 (1952).
²¹ R. M. Emrick, *Phys. Rev.* **122**, 1720 (1961).
²² D. Lazarus, in *Impurities and Imperfections* (American Society for Metals, Cleveland, Ohio, 1955), p. 111.
²³ D. Lazarus, *Phys. Rev.* **76**, 545 (1949).
²⁴ D. Lazarus (unpublished).
²⁵ S. Glasstone, K. J. Laidler, and H. Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

atomic vibration frequency of the order of the Debye frequency, k is Boltzmann's constant, T the absolute temperature, and ΔG_m is the change in Gibbs free energy associated with the passage of a cation over the energy barrier for diffusion.

In the reaction rate model, it is assumed that the energy in the expression for ionic mobility is a free energy. It is then possible to express the pressure dependence of the ionic conductivity in well-defined physical terms. From the familiar expression for the Gibbs free energy,

$$dG = VdP - SdT, \quad (2)$$

we can write immediately, for the isothermal process under discussion,

$$\Delta V_m = \left(\frac{\partial \Delta G_m}{\partial P} \right)_T. \quad (3)$$

In terms of the parameters of Eq. (1),

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

The last term on the right in Eq. (4) is measured experimentally. It is possible to make reasonably good empirical corrections for the pressure dependence of the other terms. These corrections will be discussed later in connection with the interpretation of the data.

The foregoing treatment is based on the assumption that the basic transport process occurs in equilibrium, the lifetime of the excited state being sufficiently long that it is meaningful to ascribe thermodynamic properties to the activated complex.²⁵ This model has proven extremely successful in studies of the diffusion process,²⁶ but has frequently been questioned because of the equilibrium assumptions involved.²⁷ Rice²⁸⁻³² has recently proposed a dynamical theory of diffusion which apparently overcomes some of these objections, by considering the dynamics of the diffusion process in a harmonic crystal. However, the introduction of irreversibility into the dynamical model indicates that this theory may eventually yield the same dependence on free energies as the equilibrium model.³²

²⁶ See, e.g., C. Zener, in *Imperfections in Nearly Perfect Crystals* (John Wiley & Sons, Inc., New York, 1952).

²⁷ See, e.g., D. Lazarus, in *Advances in Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1960), Vol. 10.

²⁸ S. A. Rice, *Phys. Rev.* **112**, 804 (1958).

²⁹ S. A. Rice and N. H. Nachtrieb, *J. Chem. Phys.* **31**, 139 (1959).

³⁰ A. W. Lawson, S. A. Rice, R. D. Corneliussen, and N. H. Nachtrieb, *J. Chem. Phys.* **32**, 447 (1960).

³¹ O. P. Manley and S. A. Rice, *Phys. Rev.* **117**, 632 (1960).

³² S. A. Rice and H. L. Frisch, *J. Chem. Phys.* **32**, 1027 (1960).

II. EXPERIMENTAL EQUIPMENT AND PROCEDURES

The high-pressure system has been described in detail by Emrick²¹ and is fairly typical³³ for hydrostatic pressure measurements in the range to 10^4 kg/cm². The pressure vessel is made from Carpenter 883 steel and can be heated externally to 400°C. Dow Corning 200 fluid of one to three centistoke viscosity was used as the pressure fluid. Pressure measurements were made by observing the change in resistance of a coil of manganin wire and are accurate to considerably better than 1%. During the early part of the experiment the pressure vessel was heated by immersing it in a steel drum containing a molten eutectic salt mixture. The salt bath was later replaced by a simpler air furnace.

The specimen temperature was precisely controlled with an internal furnace, with the external furnace set to maintain the temperature of the pressure vessel slightly below the temperature of the sample and internal furnace. The internal furnace consisted of resistance wire wound on a Vycor tube and sealed inside a Lavite cylinder. The sample, coated with Aquadag on two surfaces, was mounted between stainless steel electrodes near the center of the furnace. The remainder of the space in the furnace was filled with brass, quartz, and Lavite spacers to serve as thermal reservoirs and to cut down on convection currents in the pressure fluid. Sample temperature was measured with a chromel-alumel thermocouple mounted within 2 mm of the sample position. Electrical leads were brought out of the pressure vessel through standard pipestone cone seals in the apparatus plug. The chromel and alumel thermocouple leads were hard soldered to cones machined from chromel and alumel stock. Pressure has been found to introduce a negligible correction to the thermal emf of chromel and alumel over this pressure range.³⁴

Measurements were made by a standard ac bridge technique, with a 1000 cps input into a General Radio 706 capacitance bridge. The greatest single complication in making measurements arises from leakage resistance to ground through the pipestone pressure seals and the lead insulation. The leakage resistance of the cones drops approximately exponentially with temperature, from about 100 megohms at 200°C to about one megohm at 500°C. The application of 10^4 kg/cm² pressure serves to increase the resistance by about a factor of 1.5. The resistance of the cones deteriorates with exposure to the pressure fluid at high temperature. It was found that this process can be at least partially reversed by baking the plug and cones in air for several hours at about 350°C. Quartz tubing was found to be the best high-temperature insulation for the leads, but it still contributed a measurable amount to the leakage resistance.

³³ See P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, England, 1949), for a general discussion of high-pressure equipment and techniques.

³⁴ F. Birch, *Rev. Sci. Instr.* **10**, 137 (1939).

The sample resistance decreases more rapidly than the leakage resistance with increasing temperatures. At 500°C the sample resistance is 10–100 times smaller than the leakage resistance, and corrections are small. With the measurements made it is possible to calculate two values for the sample resistance. Above about 300°C, the two calculations generally agree to better than 1%. The low-temperature limit of the measurements is determined by the high resistance limit of the bridge (about 200 megohms) and by the sample resistance becoming larger than the leakage resistance. This limit is usually in the vicinity of 200°C, and at this point the two calculated values of the sample resistance sometimes differ by about 10%.

The Dow Corning 200 fluid used as a pressure medium has the best temperature characteristics of any available liquid. The manufacturers claim that its volume resistivity is approximately 10^{14} ohm-cm up to at least 200°C. Pressure inhibits decomposition of the fluid, but it does occur at the temperatures achieved in this experiment, even under at least 3000-kg/cm² pressure. However, dummy runs showed that the electrical characteristics were not impaired sufficiently to contribute measurably to the leakage conductivity.

All of the crystals used in the course of this experiment were obtained from Dr. Karl Korth in Kiel, Germany. They were grown from the melt by the Kyropoulos method. The NaCl crystals were doped with CaCl₂; SrCl₂ was used to dope the KCl crystals, and BaCl₂ was the doping agent in the RbCl crystals. The divalent ions were selected to have an ionic radius as close as possible to that of the monovalent cation, so as to minimize elastic strain in the crystal. Also, in the case of NaCl and KCl, the impurity ions were chosen to correspond to systems which had been extensively studied at atmospheric pressure.

The crystals have not been analyzed chemically. However, it is possible to obtain a good estimate of the amount of impurity present by comparing the conductivity data with previous atmospheric pressure studies of the same systems. Such studies have been done in NaCl doped with CaCl₂,⁹ and on KCl doped with SrCl₂,⁷ but not on RbCl doped with BaCl₂.

Samples were prepared from the boules by the usual cleaving techniques. Samples used for pressure measurements are usually 0.5–1.0 mm thick. The specimens are painted with several layers of Aquadag, after which the edges are cleaved off, leaving a rectangle usually a little less than one cm² in area.

III. EXPERIMENTAL RESULTS

Before starting work with the pressure system, a series of atmospheric pressure measurements was made on each of the NaCl and KCl crystals in another apparatus. These measurements were made for several reasons. Accurate atmospheric pressure data were required to obtain information about the impurity con-

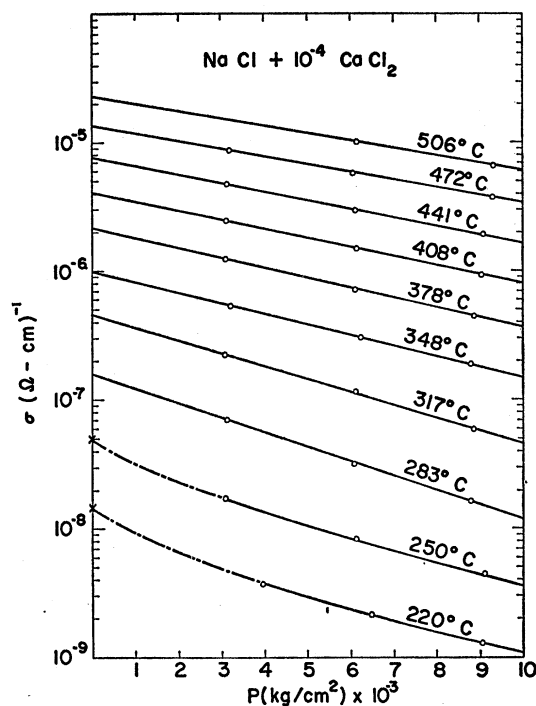


Fig. 1. Isotherms of conductivity vs pressure from sample of NaCl+ 10^{-4} mole fraction CaCl₂.

tent. Since it was not possible to reduce the pressure in the pressure system to very low values at elevated temperatures without undue decomposition of the pressure fluid, these data were needed for completeness. Finally, these data served as a check against systematic errors in the pressure measurements.

A. Sodium Chloride Doped with Calcium Chloride

All of the runs were made by measuring isotherms as a function of pressure. This procedure was employed primarily as a matter of convenience, since it is easier to maintain a constant temperature and to correct for small deviations in temperature than in pressure. Also, since the activation volume [containing the term $(\partial \ln \sigma T / \partial P)_T$] is the primary parameter to be obtained from the data, it was felt that this quantity should be measured directly.

Measurements were made on three crystals of NaCl grown from melts containing the following mole fractions of CaCl₂: 10^{-4} , 5×10^{-4} , and 2×10^{-3} . By comparison with Bean's⁹ data, the actual impurity content of the crystals was found to be 10^{-4} , 2×10^{-4} , and 9×10^{-4} mole fraction CaCl₂, respectively, within about 10%.

Semilogarithmic plots of conductivity vs pressure for samples from the three crystals are shown in Figs. 1–3.

The high-temperature isotherms indicate that the conductivity varies exponentially with pressure, within experimental accuracy, down to a temperature depending on the impurity content, approximately as listed:

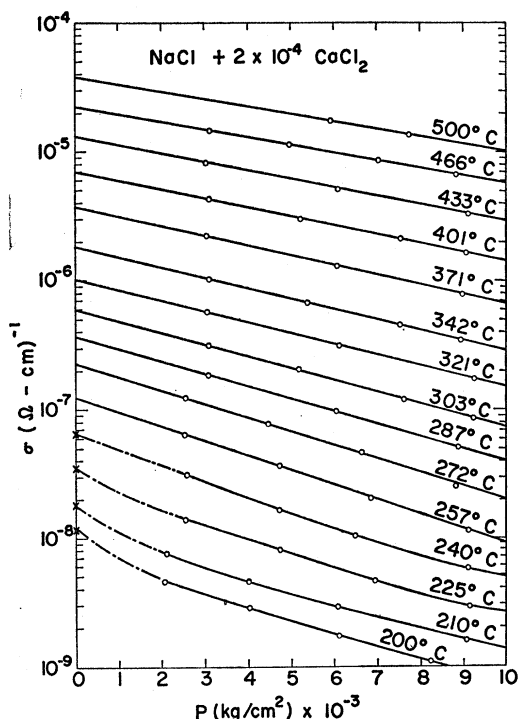


Fig. 2. Isotherms of conductivity vs pressure from sample of $\text{NaCl} + 2 \times 10^{-4}$ mole fraction CaCl_2 .

10^{-4} , 275°C; 2×10^{-4} , 255°C; 9×10^{-4} , 235°C. The slope consistently increases with decreasing temperature. For a given run, the high-temperature isotherms extrapolate either quite well to the atmospheric-pressure data at the measured temperatures or to approximately a constant difference from them. This difference varied rather systematically during the course of the experiment, indicating a small changing absolute error inherent in the internal thermocouple, possibly arising when the thermocouple was occasionally unsoldered from the chromel and alumel cones. The temperature indicated on the figures for each straight line isotherm which is plotted as a solid line all the way to atmospheric pressure is determined from the intersection of the extrapolated pressure data with the atmospheric pressure measurements and is probably accurate to $\pm 2^\circ\text{C}$. Temperature control during the course of measurements along a single isotherm is at least as good as $\pm 0.2^\circ\text{C}$ above 400°C and $\pm 0.1^\circ\text{C}$ below, as measured with the internal thermocouple. Temperature differences between successive isotherms are accurate to at least $\pm 1^\circ\text{C}$.

At approximately the temperature indicated above for each crystal, the isotherms begin to show distinct curvature. The curvature usually appears first at high pressures and progresses toward lower pressures at lower temperatures. At the lowest temperatures many of the isotherms are approximately straight lines on the semilogarithmic plot over most of the pressure range, but the slopes are considerably less than those found at temperatures just above the region where curvature

first appears. The low-temperature isotherms in general appear to extrapolate to the atmospheric pressure data at a temperature as much as 10°C below that indicated by the internal thermocouple. The reason for this is not completely understood, but it is not felt that the internal thermocouple could reasonably be in error by this amount. Thus, the temperature indicated on the curved isotherms is that measured with the internal thermocouple. The points at atmospheric pressure indicated by an X, to which the pressure data are extrapolated by an alternately dotted and dashed line, are taken from the earlier atmospheric pressure data for the temperature measured by the pressure system thermocouple. From comparisons made between this thermocouple and another calibrated thermocouple outside the pressure vessel when the vessel was in thermal equilibrium, it is felt that the indicated temperatures below 250°C are accurate to at least $\pm 2^\circ\text{C}$.

The high-temperature atmospheric pressure measurements give the necessary information for calculation of the activation energy of motion. There is a relatively short temperature range over which a plot of $\ln \sigma T$ vs T^{-1} is a straight line of minimum slope. In this region it is assumed that the concentration of free vacancies is a constant equal to the concentration of divalent impurity. In the crystal with 10^{-4} mole fraction of impurity this region extends from 635°C – 500°C . For the crystal with 2×10^{-4} mole fraction CaCl_2 , the temperature range extends from 635°C down to only about

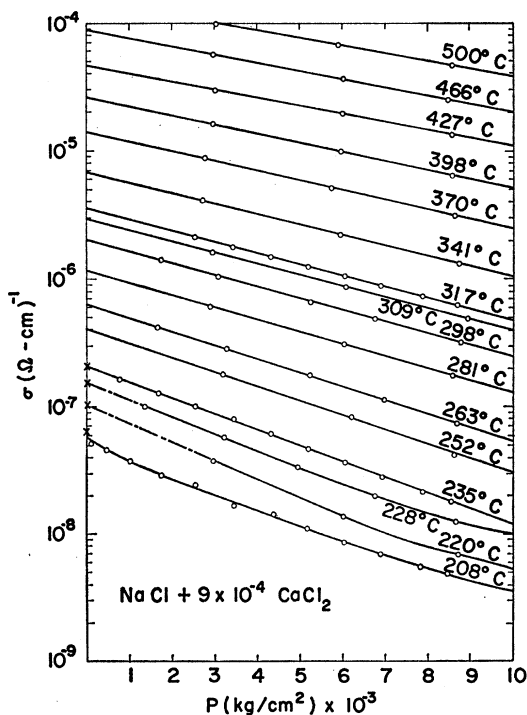


Fig. 3. Isotherms of conductivity vs pressure from sample of $\text{NaCl} + 9 \times 10^{-4}$ mole fraction CaCl_2 .

TABLE I. Effective activation energies (in electron-volts) for NaCl-CaCl₂ and KCl-SrCl₂ at various temperatures and pressures.

Mole fraction impurity Pressure (kg/cm ²)	NaCl				KCl
	10 ⁻⁴	2 × 10 ⁻⁴	9 × 10 ⁻⁴	10 ⁻⁴	
Completely dissociated range					
1	0.74 500°-635°C	0.76 560°-635°C	0.61 (?) >600°C	0.76 490°-630°C	
400°-500°C					
1	0.88	0.84	0.82	0.84	
3000	0.94	0.86	0.88	0.87	
6000	0.98	0.90	0.90	0.89	
9000	1.02	0.95	0.94	0.92	
250°-300°C					
1	0.95	0.93	0.94		
3000	1.03	1.05	1.02		
6000	1.08	1.14	1.08		
9000	1.11	1.21	1.18		

560°C. The high-temperature slope of data from these crystals gives an activation energy of 0.75 ev, in good agreement with previous investigations.³⁵ Results from the crystal with 9 × 10⁻⁴ mole fraction impurity are questionable because of a low slope (0.61 ev) at high temperatures. This low slope is determined from two high-temperature points only, and it is possible that an error was made in measurement. Only with the crystal of lowest impurity content do the high pressure measurements approach the temperature region of complete dissociation.

Below the temperature at which association occurs, the conductivity drops more rapidly than exponentially with decreasing temperature because of the decreasing concentration of free vacancies. The application of pressure accentuates this effect. A pressure increase is roughly equivalent to a temperature decrease. For example, at 300°C a pressure of 10⁴ kg/cm² reduces the conductivity by about the same amount as a temperature decrease of 60°C. At 500°C the same pressure is equivalent to a temperature decrease of about 80°C.

As a measure of the effect of pressure, it is of interest to calculate the change in slope of the $\ln \sigma T$ vs T^{-1} curves with pressure, even though the energies derived from the slopes include terms both from the mobility and from the free vacancy concentration. The curves are not straight lines over any of the temperature region measured, but the curvature is relatively small, and a straight line gives a good fit over a limited temperature range. The results are shown in Table I for the temperature ranges 400°-500°C and 250°-300°C. Also included in the same table are the activation energies for motion, as determined from the high temperature atmospheric pressure measurements. The temperature range of the data used for this calculation for each crystal is indicated. The errors in energy due to scatter of the data points for each of these calculations are about ±0.02 ev.

³⁵ A. S. Nowick and R. W. Dreyfus, Bull. Am. Phys. Soc. 5, 200 (1960).

B. Potassium Chloride Doped with Strontium Chloride

Pressure measurements have been made on several samples from a crystal of KCl grown from a melt containing 2 × 10⁻⁴ mole fraction SrCl₂. It was found to contain 10⁻⁴ mole fraction SrCl₂, within about 20%, by comparison with the conductivity data of Kelting and Witt.⁷ Isotherms of a typical run are shown in Fig. 4. The high- and low-temperature regions appear to be completely equivalent to those in NaCl. In the intermediate region between about 300° and 380°C, however, the peculiar slope changes shown in the figure always appear. When isotherms in this region are measured immediately after the sample has been at a higher temperature, the behavior is more nearly similar to that of doped NaCl. In Fig. 4 the solid curves were measured at increasing temperature, and the dotted curves were measured in order of decreasing temperature after the sample had been at 500°C. To determine if this difference was due to relaxation of strain in the crystal, part of the boule was annealed in vacuum at 550°C for half a day, slowly cooled, and then prepared for a conductivity run. The behavior was exactly as before. It thus appears that the anomalous results are due primarily to a changing concentration of free vacancies, either from association with the impurities or aggregation of the impurities into larger complexes.

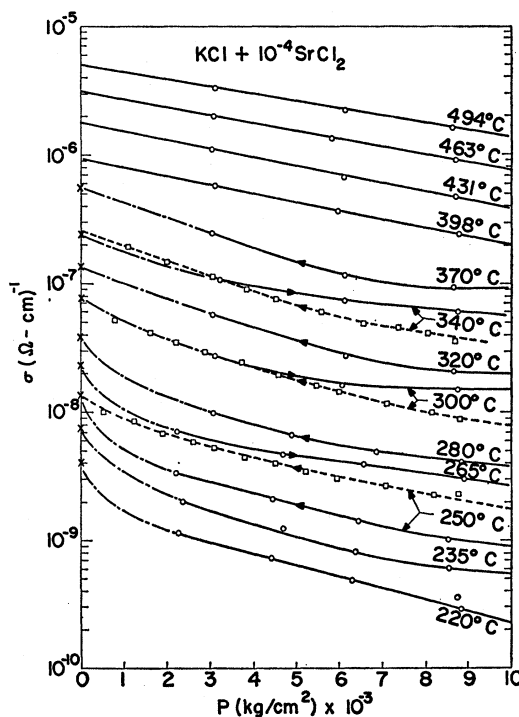


FIG. 4. Isotherms of conductivity vs pressure from sample of KCl + 10⁻⁴ mole fraction SrCl₂. The isotherms indicated by a solid curve were measured in order of increasing temperature; those indicated by a dashed line were measured in order of decreasing temperature after the sample had been to 500°C.

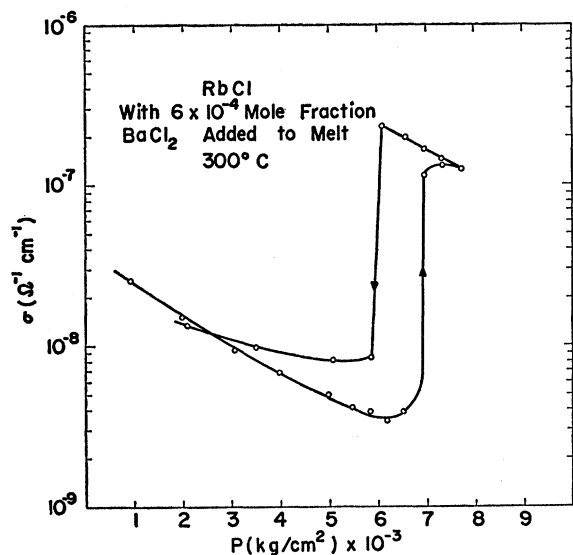


FIG. 5. Conductivity vs pressure through the transition pressure for sample of RbCl.

These are the same processes which occur in NaCl, but apparently they take much longer to reach equilibrium in KCl. Typically there are 10 to 20 minutes between successive measurements. However, occasional measurements over a considerably longer interval have not given noticeably different results. The effect of pressure as evidenced by a change in effective activation energy is shown in Table I with the similar results for NaCl. Only the high-temperature slopes are given because of the anomalous low-temperature behavior.

C. Rubidium Chloride Doped with Barium Chloride

RbCl doped with BaCl₂ was the third system studied. Measurements were made on two crystals, grown from melts containing 6×10^{-3} and 6×10^{-4} mole fraction of BaCl₂. The impurity content of the crystals is not known. Even the purer crystal was noticeably cloudy, while the more impure crystal was very milky in appearance indicating that some fraction of the impurity was precipitated out in a separate phase at room temperature.

RbCl undergoes a pressure transition from the NaCl to the CsCl crystal structure in the general vicinity of 6000 kg/cm². The transition is quite easy to follow from observations of the ionic conductivity and results in an order of magnitude increase in conductivity. The results of one run through the transition point with a sample from the purer crystal are shown in Fig. 5. Starting from a single crystal specimen in the low-pressure phase, the transition proceeded rather slowly, requiring about 45 minutes to go to completion. When pressure was reduced, the reverse transition went much more rapidly, with most of the conductivity change oc-

curing in less than two minutes. This rapid change could occur because the sample was no longer a single crystal, and there were many more centers of nucleation from which the transition could proceed. The sample was drastically modified in appearance after having undergone the transition. Originally, it was a fairly clear rectangular parallelepiped with smooth surfaces. Afterward, it was much more cloudy, the surface was pebbled, the edges were cracked and distorted, and as nearly as could be determined from the irregular dimensions, the volume had increased by several percent. The hysteresis in the pressure transition has been observed before³⁶; apparently it results from the presence of impurities and tends to decrease in width with purer samples. Bridgman lists the transition pressure as about 5700 kg/cm² from 0°–100°C. The transition pressure found in the present experiment at 300°C is about 6100 kg/cm².

Measurements below the transition pressure showed several anomalous effects. The high temperature part of one run on a sample from the heavily doped crystal indicated a definite decrease in activation energy with increasing pressure up to the maximum of 5000 kg/cm². A plot of $\ln \sigma T$ vs T^{-1} for the data from this run is shown in Fig. 6. Between 300° and 450°C, the effective activation energy decreased from 1.6 eV at atmospheric pressure to 1.3 eV at 5000 kg/cm². At lower temperatures the slope decreased considerably more, the effective energy at 5000 kg/cm² from 220°C to 265°C being

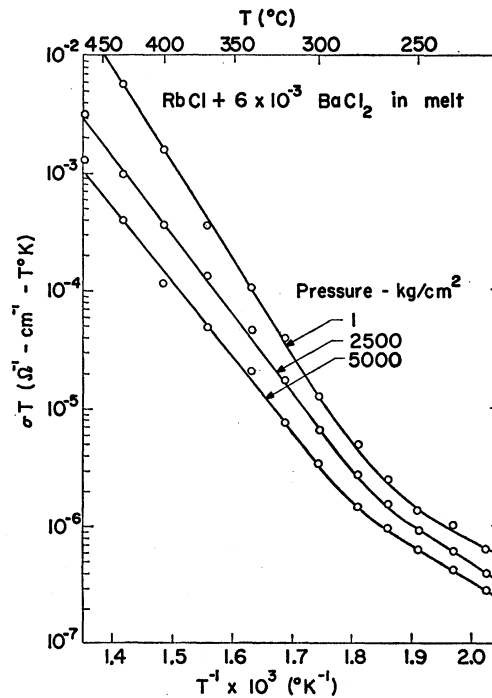


FIG. 6. Isobars of conductivity times temperature vs reciprocal temperature for RbCl sample showing apparent decrease in activation energy with increasing pressure.

³⁶ P. W. Bridgman, see reference 33, p. 233.

0.6 ev. Since no separate atmospheric pressure measurements were made on these crystals, the atmospheric pressure points in Fig. 6 are extrapolated from pressure data ending at 1000 kg/cm². Another run was made on an adjacent sample in an attempt to verify this behavior. The second run showed considerably more scatter. On the basis of the limited data no quantitative conclusions should be drawn about the anomalous behavior. Perhaps the most probable explanation is that more of the barium is going into solution at the higher temperatures introducing many more free vacancies and accentuating the pressure effect. A possible alternative explanation will be discussed in the following section.

IV. DISCUSSION

A. Calculation of Activation Volumes

In calculating the activation volume from diffusion experiments in metals under pressure it is usually possible to neglect the pressure dependence of the pre-exponential factor in the diffusion coefficient. In the present experiment, uncertainties in the pressure dependence of the pre-exponential factors in the expression for ionic conductivity are one of the major sources of error in the determination of the activation volume. Values for the experimentally measured term in Eq. (4), $(\partial \ln \sigma T / \partial P)_T$, in units of $10^{-4} \text{ kg}^{-1} \text{ cm}^{-2}$ vary from -1.2 to almost -3.0 . The pressure variation of the lattice parameter is deducible from the isothermal compressibility. Using Bridgman's values for the compressibility, $2(\partial \ln a / \partial P)_T = -0.026$ for NaCl and -0.034 for KCl, in the same units as above. The frequency factor ν_0 is normally assumed to be of the order of the Debye frequency, and the pressure dependence of the Debye frequency should give a reasonable estimate of the change in ν_0 . From Lazarus's²³ measurements of pressure dependence of the adiabatic elastic constants of NaCl and KCl it is possible to calculate this quantity. ν_D increases about 5% in NaCl under a hydrostatic pressure of 10^4 kg/cm^2 , so that $(\partial \ln \nu_0 / \partial P)_T = 0.05 \times 10^{-4} \text{ kg}^{-1} \text{ cm}^2$. In KCl, ν_D decreases by about 1.5%, so $(\partial \ln \nu_0 / \partial P)_T = -0.015 \times 10^{-4} \text{ kg}^{-1} \text{ cm}^2$.

Due to the binding energy between a vacancy and a divalent impurity, there is a strong dependence of n_f on both temperature and pressure. This is by far the largest and most uncertain correction to be made in this calculation. Lidiard^{2,37} has developed a theory for the degree of association as a function of temperature and impurity concentration. Bassani and Fumi³⁸ have done a fairly complete calculation of the binding energy of the complex. However, there appear to be no specific calculations of the pressure dependence of the association or the binding energy. In the absence of such calculations a correction for the effect has been made in a purely empirical and self-consistent manner. Knowing the true activation energy for the dissociated region at

³⁷ A. B. Lidiard, Phys. Rev. **94**, 29 (1954).

³⁸ F. Bassani and F. G. Fumi, Nuovo cimento **11**, 275 (1954).

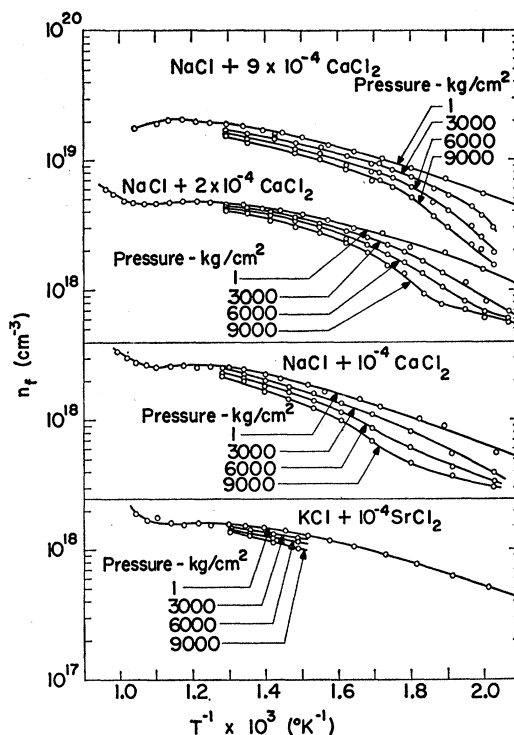


FIG. 7. Calculated concentration of free vacancies.

atmospheric pressure, the concentration of impurity, the electronic charge, and the lattice parameter, the product of the effective frequency factor and the entropy term can be calculated. Presumably, at lower temperatures and at atmospheric pressure all of these terms remain essentially constant except for n_f . With this assumption, n_f can be calculated at atmospheric pressure as a function of temperature from the conductivity data by rearranging Eq. (1) in the form

$$n_f = \frac{\sigma T k}{e^2 a^2 \nu_0 \exp(\Delta S_m / k)} \exp(\Delta H_m / kT), \quad (5)$$

where the Gibbs free energy has been separated into enthalpy and entropy terms.

In the crystals of NaCl and KCl containing 10^{-4} mole fraction of impurity, the vacancies are almost completely dissociated at 500°C at atmospheric pressure. It seems reasonable to assume that, for these crystals, there will be no large changes in n_f with pressure at the highest temperatures. The only gross effect of pressure will then be through the $P\Delta V_m$ term in the enthalpy. Changes in a and ν_0 are small compared to the uncertainty in the exponential term. Assuming an atmospheric pressure activation energy of motion in NaCl of 0.75 ev, the pressure dependence of n_f is determined by varying the $P\Delta V_m$ term in the enthalpy until, at reasonably low pressures (3000 kg/cm²), the calculated concentration of free vacancies is slightly below that at atmospheric pressure at 500°C. This value

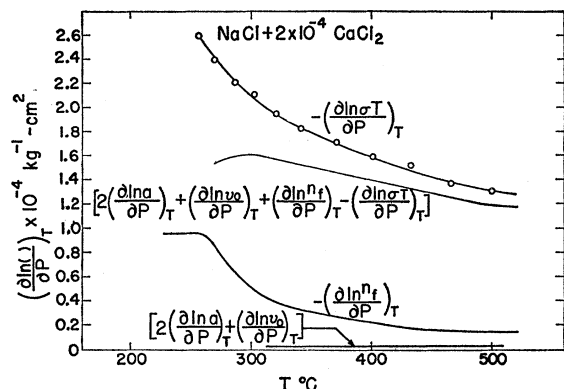


FIG. 8. Sample plot of terms involved in calculation of activation volume.

for $\Delta V_m (7.7 \times 10^{-6} \text{ ev} \cdot \text{kg}^{-1} \cdot \text{cm}^2)$ is then used to calculate n_f over the entire range of temperature and pressure for all the CaCl_2 -doped NaCl crystals. Semilogarithmic plots of n_f vs T^{-1} for all the doped NaCl crystals, calculated in this manner, are shown in Fig. 7. From these sets of curves it is possible to determine $(\partial \ln n_f / \partial P)_T$.

The same procedure is followed with KCl. The atmospheric pressure activation energy is taken as 0.76 ev. The $P\Delta V$ correction term to the enthalpy gives a best fit with $\Delta V_m = 7.3 \times 10^{-6} \text{ ev} \cdot \text{kg}^{-1} \cdot \text{cm}^2$. A plot of $\ln n_f$ vs T^{-1} is shown in Fig. 7 together with the similar results for NaCl.

As a typical example, plots of all the terms in Eq. (4) as a function of temperature are shown in Fig. 8 for a sample from the NaCl crystal containing 2×10^{-4} mole fraction CaCl_2 . The circled points are the calculated slopes determined from the data. The curve showing the sum of all the terms is determined from the smoothed data and correction curves. The activation volume can be determined from this curve.

A plot of the calculated activation volume vs $T^\circ\text{C}$ for all the NaCl and KCl samples is shown in Fig. 9. For NaCl, the calculated values range between 7 and 8 cc/mole. The two samples with lower impurity content should give more reliable results since association effects

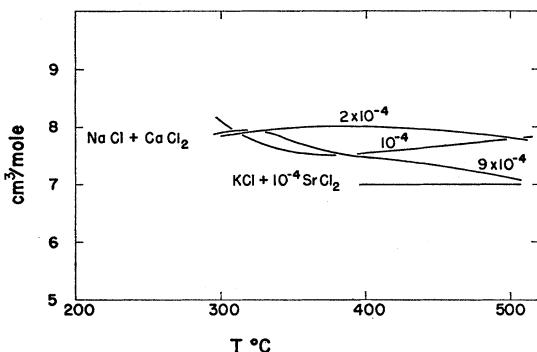


FIG. 9. Calculated activation volume of motion for NaCl and KCl vs temperature.

are smaller. These samples give values ranging from 7.5–8.0 cc/mole. The true activation volume for motion in NaCl then appears to be about 7.7 cc/mole, within limits of about ± 0.5 cc/mole. The calculated value for KCl is 7.0 cc/mole, independent of temperature. The lack of temperature dependence is almost certainly fortuitous in view of the results for NaCl, and the same limits of error should probably be assigned to the activation volume of KCl.

As a check on the internal consistency of this method for determining the effect of pressure on the concentration of free vacancies, the ΔV_m determined from the $P\Delta V_m$ correction term to the enthalpy should agree with the final calculated value. Converting to cc/mole, these values are 7.5 cc/mole for NaCl and 7.1 cc/mole for KCl, and are quite close to the final values mentioned above.

Keyes³⁹ has developed an expression relating the activation volume to the activation energy and the isothermal compressibility based on a strain energy model in which the work involved in creating or moving a defect is assumed to go entirely into elastic strain of the crystal. According to this model,⁴⁰ the activation volume and activation energy can be related by

$$\frac{\Delta V}{\Delta G} = -\beta + \left(\frac{\partial \ln C}{\partial P} \right)_T, \quad (6)$$

where $\beta = -[(1/V)(\partial V/\partial P)_T]$ is the isothermal compressibility, and C is an appropriate elastic shear modulus. Using the Grüneisen model of a solid, in which

$$\left(\frac{\partial \ln C}{\partial \ln V} \right)_P = \left(\frac{\partial \ln C}{\partial \ln V} \right)_T = \frac{d \ln C}{d \ln V} = -(2\gamma + \frac{1}{3}), \quad (7)$$

Eq. (6) can be written in the form

$$\Delta V = k\beta\Delta G, \quad (8)$$

where $k = 2(\gamma - \frac{1}{3})$, and γ is the Grüneisen constant. Using quoted values for the Grüneisen constants⁴¹ and compressibilities,⁴² values of 8.4 cc/mole and 9.9 cc/mole are obtained for ΔV_m in NaCl and 10.5 cc/mole for ΔV_m in KCl.

It is possible to eliminate the approximations involved in applying the Grüneisen model for materials in which data are available on the pressure dependence of the elastic constants. Brooks⁴³ has shown that the proper average shear modulus to be used in elastic energy

³⁹ R. W. Keyes, in *Report of Lake George Conference on Very High Pressure* (John Wiley & Sons, Inc., New York, 1960); *J. Chem. Phys.* **29**, 467 (1958); *ibid.* **32**, 1066 (1960).

⁴⁰ R. W. Keyes, *Acta Met.* **6**, 611 (1958).

⁴¹ L. S. Darken and R. W. Gurry, *Physical Chemistry of Solids* (McGraw-Hill Book Company, Inc., New York, 1953), p. 159.

⁴² P. W. Bridgman, see reference 33, p. 163

⁴³ H. Brooks, in *Impurities and Imperfections* (American Society for Metals, Cleveland, Ohio, 1955).

calculations for vacancy motion in a cubic crystal is

$$C = \frac{3}{5}C_{44} + \frac{1}{5}(C_{11} - C_{12}). \quad (9)$$

Using Bridgman's compressibility data and Lazarus's measurements of the elastic constants in NaCl and KCl, values for ΔV_m of 6.6 cc/mole and 9.0 cc/mole are obtained from Eq. (6).

The present experimental value for ΔV_m in NaCl falls between the values predicted by Eqs. (6) and (8). The measured value in KCl is considerably lower than that predicted by either Eq. (6) or (8). It may be noted that the predicted values indicate that ΔV_m should be larger in KCl than in NaCl, while the experimental results indicate just the reverse. A possible explanation of the result will be discussed below.

It is also of interest to compare the results of the present experiment with previous measurements of ΔV . The only major previous experiment involving the effect of pressure on ionic conductivity is that of Kurnick,²⁰ who studied pure and doped AgBr. His value for ΔV_m of silver vacancies, 7.4 cc/mole, is quite close to the values found in the present experiment.

As has been discussed, an apparently more surprising comparison can be made between the relative sizes of the activation volumes in ionic crystals and those in metals. The present experiment and that of Kurnick show that ΔV_m for cation vacancies in ionic crystals is comparable to or larger than the volume actually available to the cation in the crystal lattice. Also, the values for ΔV_f ²⁰ and ΔV_i ¹⁹ for Schottky defects in AgBr are found to be larger than the molecular volume. On the other hand, all the pressure experiments on metals indicate that the total activation volume, $\Delta V_f + \Delta V_m$, is considerably smaller than the atomic volume, usually by about a factor of two. The only experiment²¹ which measures ΔV_m for vacancies in a metal separately indicates that for gold ΔV_m is only 15% of the atomic volume.

These differences can probably be completely explained in terms of relaxation of the lattice neighbors around a defect. The large size of ΔV_f in ionic crystals arises because the nearest neighbors of a given ion are repelled when it is removed to the surface to form a vacancy. It is difficult to calculate ΔV_m in the ionic crystals, but the same general idea of Coulomb repulsion of ions around the defect complex may be invoked to explain the relatively large observed values. On the other hand, Tewordt⁴⁴ has shown that considerable inward relaxation may occur about a vacancy in copper, so that $\Delta V_f \approx 0.5$ atomic volume. This is close to the value found for ΔV_i in most metals. Presumably most of the observed volume must be attributed to ΔV_f for the vacancies. This is consistent with the very small ΔV_m for vacancies in gold found by Emrick, and indicates that there must be considerable relaxation in the vicinity of a diffusing vacancy in metals.

B. Correlation between Activation Energy and Small Shear Modulus

Considerable success has been achieved in empirically relating the small shear modulus in various materials to the activation energy for defect motion,²² since most of the energy involved arises from shear strain in the vicinity of the moving atom. Lazarus²³ found that, in KCl, the small shear modulus C_{44} decreases by about 7% with the application of 10^4 kg/cm² pressure; while in NaCl, C_{44} increases by about 2% over the same pressure range. It then appears that an interesting test of this correlation could be made by comparing the effect of pressure on ionic conductivity in NaCl and KCl. On first observation, the results of this experiment appear to indicate that the correlation does not hold. The effects of pressure are almost identical on NaCl and KCl, at least in the high-temperature region. On the other hand, as mentioned above, it would be more reasonable if the activation volume for KCl were larger than for NaCl, since the potassium ion occupies over twice the volume of the sodium ion. Also, Keyes's empirical expression indicates that ΔV_m should be larger in KCl than in NaCl. It may be that a larger ΔV_m in KCl, and hence a larger $P\Delta V_m$ term in the enthalpy of motion, serves to mask a decrease in the potential-energy term arising from the decrease in C_{44} . The result would then be seen as the small apparent ΔV_m observed.

The decrease in C_{44} with pressure in KCl is due to an approaching pressure transition from the NaCl to the CsCl crystal structure at a pressure somewhat beyond the range of the available equipment. RbCl undergoes the same phase transition at about 6000 kg/cm² and exhibits the same behavior of C_{44} as KCl.²⁴ In the earlier discussion, it was pointed out that one run on RbCl in the present experiment indicated a decreasing activation energy with increasing pressure. This may be evidence for the correlation between activation energy and the small shear modulus, but experimental uncertainties make it impossible to draw quantitative conclusions.

C. Low-Temperature Behavior

Perhaps the most puzzling part of the NaCl and KCl data is the low slope and the curvature of the low-temperature isotherms. Above 300°C, the calculated values of ΔV_m are independent of temperature within experimental error. Also, there is no indication of a pressure dependence of ΔV_m in this temperature range. This implies that isotherms of $\ln \sigma$ vs P should be straight lines with steadily increasing slope with decreasing temperature. Association of the vacancies with the divalent impurities should cause a further increase in slope of the isotherms. This corresponds to the observed behavior at higher temperatures. The low-temperature behavior is just the reverse.

The curvature of the low-temperature isotherms over the pressure range actually covered by the data is

⁴⁴ L. Tewordt, Phys. Rev. **99**, 61 (1958).

fairly small. In most cases a straight line can be drawn through the pressure data with none of the data points deviating by more than 10%. This is near the limit of error of the low-temperature points but is considerably greater than the error in measurement of points along the curved isotherms at higher temperatures. The curvature occurs uniformly in all runs in the same direction and it is felt to be real. The slopes of the best straight lines drawn through the low-temperature pressure data for a given run average 15–20% less than the slope of the lowest temperature isotherm of the same run which is plotted as a straight line. These same straight lines generally extrapolate to the atmospheric pressure data at a temperature about 10°C lower than that measured by the internal thermocouple. There appears to be no reason for believing that the internal thermocouple could be in error by this amount.

Since these are ac measurements, the observed conductivity could contain a contribution resulting from relaxation of electric dipoles formed by divalent impurities and cation vacancies in a bound complex. Measurements of this effect have been made by Haven¹⁴ and others¹³ by dielectric loss techniques. The contribution to ac conductivity from these dipoles is of the form

$$\sigma_{\text{assoc}} = \frac{2 n_{\text{assoc}} e^2 a^2}{3 kT} \times \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}, \quad (10)$$

where n_{assoc} is the concentration of associated vacancies, ω is the angular frequency of the applied field, and τ is the relaxation time of the complex. The other terms are the same as in the dc conductivity expression. Qualitatively, this explanation fits the observed behavior quite well. At around 200°C, most of the vacancies are associated with the divalent impurities. At this temperature, we find, from Haven's data, in NaCl doped with CaCl₂ that $1/\tau \approx 4 \times 10^6 \text{ sec}^{-1}$. In the present experiment, ω is much less than this value, so there should not be a maximum contribution from the associated pairs (which will occur when $\omega = 1/\tau$). However, one effect of pressure is to reduce $1/\tau$, so there could be an increasing contribution from the pairs at increasing pres-

sure. For the NaCl crystal containing 10^{-4} mole fraction CaCl₂, the maximum possible contribution to the conductivity calculated from Eq. (10) is only about 5% of the observed value at 10^4 kg/cm^2 , even at the lowest temperature measured, 220°C. In order for the low-temperature isotherms to be extrapolated in a straight line from 10^4 kg/cm^2 to atmospheric pressure reasonably close to the atmospheric pressure data, and with a slope equal to, or larger than, that of the higher temperature isotherms, the high-pressure conductivity must be lower by 20–50%. Thus, this mechanism is probably not the primary cause of the observed anomaly.

Another possible mechanism for enhancing the low-temperature conductivity is a contribution from diffusion along dislocations or grain boundaries. It is possible that this mechanism is masked at atmospheric pressure by the bulk conductivity, but that the effect of pressure is considerably greater in depressing the bulk conductivity than the short-circuiting contribution. Kurnick,²⁰ using polycrystalline samples of AgBr, found that the results from his 202°C isotherm failed to agree with those at 251° and 289°C. Accordingly, he made some measurements with a single-crystal specimen. He found that the conductivity of the single crystal was identical with that of the polycrystalline samples at the higher temperatures, but deviated significantly at 202°C, particularly at pressures above 5000 kg/cm². He considered that the discrepancies could probably be ascribed to grain boundary conduction. It seems probable that the same mechanism can explain the anomalies observed in the present experiment.

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