Activation Volume Measurements *

MICHEL BEYELER and DAVID LAZARUS **

Section de Recherches de Métallurgie Physique, Centre d'Etudes Nucléaires de Saclay, France

(Z. Naturforsch. **26 a**, 291—299 [1971]; received 6 October 1970)

The determination of the activation volume of diffusion is one of the best methods for the investigation of the relaxation of atoms or ions around defects. This paper discusses two experimental techniques for the determination of the activation volume for diffusion, by studying the effect of hydrostatic pressure on tracer diffusion and on ionic conductivity. Such experiments require a very clean hydrostatic pressure environment, accurate temperature control and measurement, and well defined specimen geometry. The difficulties encountered during such experiments are discussed. Results are given for the activation volumes of diffusion in beryllium and in sodium chloride.

I. Introduction

Determination of the Activation Volume from Measurements of the Self Diffusion Coefficient

In a crystal the self diffusion coefficient D can be written as:

$$D = f a^2 \Gamma_s \tag{1}$$

where f is the correlation factor, a the lattice parameter, and Γ_s the jump frequency:

$$\Gamma_s = n \nu \exp\left\{-\frac{\Delta G}{R T}\right\}. \tag{2}$$

Here n is a constant which depends on the lattice type, ν a vibration frequency generally taken equal to the Debye frequency, and ΔG is the increment in Gibbs free energy necessary to move an atom from a lattice site to a neighboring site. The correlation factor, f, is a constant for self diffusion in cubic metals. In the case of a hexagonal metal (beryllium) there are 3 correlation factors which are not simply geometrical: they also depend on the ratios of the jump frequencies. There are 2 principle diffusion coefficients, one along direction of the C axis and the other perpendicular to it

$$D_\perp = \frac{3 a^2}{2} f_1 \Gamma_\perp + \frac{a^2}{2} f_2 \Gamma_\parallel , \tag{3}$$

$$D_\parallel = \frac{3 c^2}{4} f_3 \Gamma_\parallel . \tag{4}$$

The variation of the free energy as a function of pressure can be expressed in terms of a volume, at a given temperature, from the thermodynamic identity

$$\left(\frac{\partial G}{\partial P}\right)_T = V. \tag{5}$$

If we consider the variation of free energy needed for the diffusion of an atom,

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V. \tag{6}$$

ΔV is evidently the change in volume of the crystal during a diffusional jump.

In the case of a diffusion mechanism involving point defects, this activation volume ΔV can be separated into 2 terms, ΔV_f and ΔV_m corresponding, respectively, to the formation and the migration of the defect.

There are good reasons to presume that ΔV_m is small compared to the atomic volume Ω. The only experimental determinations, due to EMRICK [1, 2] give $\Delta V_m = 0.15\ \Omega$ for gold and about $0.17\ \Omega$ for aluminum. The theoretical calculation of SEEGER, SCHOTTKY and SCHMID [3] give a value for $\Delta V_m = 0.06\ \Omega$ for gold.

An expression for the activation volume per mole is easily derived from (6), (2) and (1):

$$\Delta V = -R T \left(\frac{\partial \log D}{\partial P}\right)_T + R T \left(\frac{\partial \log n f a^2}{\partial P}\right)_T + R T \left(\frac{\partial \log \nu}{\partial P}\right)_T. \tag{7}$$

The first term in (7) is determined experimentally by measuring the diffusion coefficients at the

---

* This paper is published both in Z. Naturforsch. and in the Proceedings of the Marstrand Conference on Atomic Transport in Solids and Liquids, Verlag der Zeitschrift für Naturforschung, Tübingen 1971.

** Permanent address: Department of Physics, University of Illinois, Urbana, Illinois, USA.

[1] R. M. EMRICK, Phys. Rev. **122**, 1720 [1961].

[2] B. J. BUESCHER and R. M. EMRICK, Phys. Rev. Abstracts **1**, 18 [1970].

[3] G. SCHOTTKY, A. SEEGER, and G. SCHMID, Phys. Stat. Sol. **4**, 419 [1964].

same temperature for different pressures. The second term is equal to zero in our experimental conditions, since n and f are geometrical constants, and the variation in the lattice parameter a with pressure is not important for tracer diffusion measurements if the specimen is sectioned at zero pressure. Thus, for tracer diffusion measurements, we may write

$$\Delta V = -R\,T\left(\frac{\partial \log D}{\partial P}\right)_T + R\,T\left(\frac{\partial \log \nu}{\partial P}\right)_T . \tag{8}$$

The term $\partial \log \nu / \partial P$ can be evaluated approximately from the Grüneisen relation

$$\beta = -\frac{\partial \log \Theta_D}{\partial \log V} = \frac{\alpha\, V_0}{C_V\, \chi_0} \tag{9}$$

here β is the Grüneisen constant, Θ_D the Debye temperature, α the volume thermal expansion coefficient, V_0 the molar volume at 0 °K, χ_0 the compressibility, and C_V the molar specific heat.

Since ν is generally taken equal to the Debye frequency, one can write

$$\frac{\partial \log \nu}{\partial P} = \frac{\partial \log \Theta_D}{\partial P} = \left(\frac{\partial \log \Theta_D}{\partial \log V}\right)\left(\frac{\partial \log V}{\partial P}\right), \tag{10}$$

$$\partial \log \nu / \partial P = \chi_0\, \beta\, . \tag{11}$$

This term is generally found to be very small in comparison with the first term in (8).

Determination of the Activation Volume in Ionic Crystals from Ionic Conductivity Measurements

The electrical conductivity can be written as

$$\sigma = \frac{n\, e^2\, a^2\, \nu}{k\, T} \exp\left\{-\frac{\Delta G_m}{k\, T}\right\} \tag{12}$$

where n is the concentration of free carriers, e the electronic charge, a the lattice parameter, ν the atomic vibration frequency, and ΔG_m the free energy for motion of the charge carriers.

In the case of a single class of charge carriers, say mobile cations, ΔG_m is the free energy of migration of cation vacancies. The plot of $\log \sigma\, T$ *v s* $1/T$ displays several domains, as shown for the case of NaCl in Fig. 1. At high temperature there is an almost linear region corresponding to the conductivity in the intrinsic domain, presumably by thermally activated cation vacancies. At intermediate temperature there is a region where the plot shows a curvature due to the contribution also of thermally produced vacancies arising from the presence of polyvalent impurities in the lattice. At still lower temperatures there is an approximately linear region corresponding to the movement of extrinsic cation vacancies. The activation energy is constant in this range if there are no stable vacancy-impurity complexes, and is equal to the migration energy for Na^+ cations. For still lower temperatures, a definite change in curvature can be noticed for samples doped with Ca^{++} ions. At these temperatures, some of the vacancies begin to associate with divalent cations to give electrically neutral complexes.

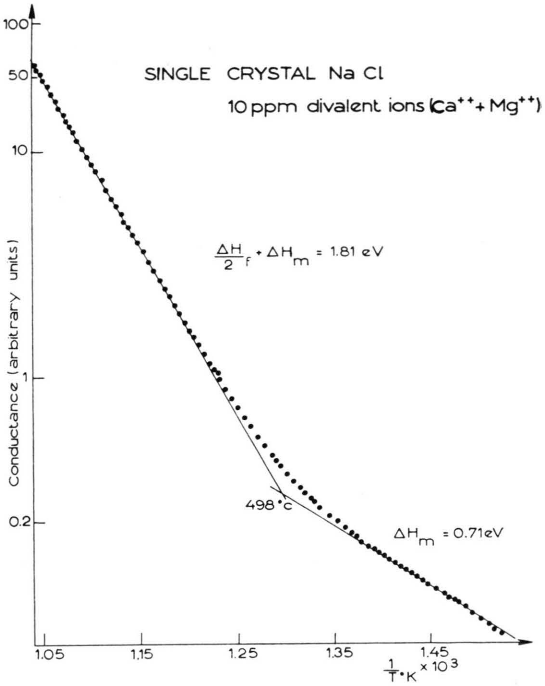

Fig. 1. Temperature dependence of the ionic conductivity of single crystal NaCl 10 ppm divalent ions $(Ca^{++}+Mg^{++})$.

In the intrinsic domain the defect or carrier concentration is given by

$$n = \exp\left\{-\frac{\Delta G_f}{2\, k\, T}\right\} \tag{13}$$

where ΔG_f is the free energy of formation for a Schottky defect.

From Eq. (5), we can define an activation volume for the intrinsic domain

$$\Delta V = \left(\frac{\partial\left(\frac{1}{2}\,\Delta G_f + \Delta G_m\right)}{\partial P}\right)_T , \tag{14}$$

$$\Delta V = -R\,T\left(\frac{\partial \log \sigma\, T}{\partial P}\right)_T + R\,T\left(\frac{\partial \log a^2}{\partial P}\right)_T + R\,T\left(\frac{\partial \log \nu}{\partial P}\right)_T , \tag{15}$$

$$\Delta V = \frac{\Delta V_f^s}{2} + \Delta V_m\, . \tag{16}$$

Here $\Delta V_{\mathrm{f}}^{\mathrm{s}}$ is the formation volume of a Schottky defect and ΔV_{m} is the migration volume of cationic vacancies.

The first term in (15) is derived from measurements of ionic conductivity as a function of hydrostatic pressure. The second and third terms can be evaluated from measurements of the compressibility and from the measured pressure variation of the elastic constants, or from the Grüneisen relation. As in the case of self diffusion, the second and third terms are small compared to the first term in (15).

In the extrinsic domain, n is constant with temperature, and a migration activation volume can be determined directly from the pressure dependence of the conductivity:

$$\Delta V_{\mathrm{m}} = \left(\frac{\partial \Delta G_{\mathrm{m}}}{\partial P}\right)_T . \tag{17}$$

$$\Delta V_{\mathrm{m}} = -R\,T\left(\frac{\partial \log \sigma\,T}{\partial P}\right)_T + R\,T\left(\frac{\partial \log a^2}{\partial P}\right)_T + R\,T\left(\frac{\partial \log \nu}{\partial P}\right)_T + R\,T\left(\frac{\partial \log n}{\partial P}\right)_T , \tag{18}$$

The first term of this expression is determined by measurements of $\sigma\,T$ as a function of pressure. The second and third terms can be evaluated as before. The fourth term measures the effect of pressure on the association of extrinsic vacancies and impurities[4], which can be very important at low temperatures. At high temperatures in the extrinsic region, this term is small.

II. Experimental Techniques

High Pressure — High Temperature Apparatus

To determine activation volumes by measurement of the variation with pressure of the self diffusion coefficients or of the ionic conductivity, the following requirements must be fulfilled:

1) The pressure must be purely hydrostatic to avoid introduction of excess point defects by plastic deformation.

2) The pressure transmitting medium must not contaminate the diffusion samples. Impurities in very small amounts can cause wide variations in the diffusion coefficients. Pure gas must be used for the pressure transmitting medium, since there are no liquids which are chemically stable at the temperatures of the present experiments (up to 700 °C).

3) External heating of the pressure vessel is preferable to avoid temperature gradients, but in the present experiment this technique could only be used to temperatures of 700 °C and pressures of 1 kbar, because of limited strength of the steel available for the pressure vessel. For anneals at higher pressures, up to 10 kbar, the heating must be done inside the pressure vessel, since no known steel vessel of the required dimensions can withstand such high temperatures and pressures for several hours.

These requirements were realized with a Bridgman type apparatus using argon gas as the pressure medium. Two vessels were used, one with external heating for pressures up to 1 kbar, and the second with internal heating for higher pressures.

Pressurization

1 kbar Apparatus

This apparatus has a single compression stage which increases the initial pressure of 150 bar provided by a gas cylinder to a maximum of 1 kbar. An oil compressor drives a piston which compresses the gas in the intensifier and the vessel.

10 kbar Apparatus

There are two compression stages. The first is identical to the 1 kbar apparatus. In the second stage the gas is compressed again by means of a 10 kbar intensifier connected to the vessel.

The pressure is measured by a manganin gauge in one arm of a Wheatstone bridge. It is thus possible to have a continuous measurement of the pressure with good sensitivity and a short response time. The manganin gauge is calibrated by means of a deadweigh free piston gauge. It is important to monitor the pressure as one must compensate for slight drops in pressure due to small leaks and compaction that can occur in the course of long experiments.

Choice of the Pressure Transmitting Medium

The gas used was argon provided by "Air Liquide". Although this gas as received nominally contains only 5 ppm oxygen and 5 ppm water vapor, it must nevertheless be purified. The purification is done after the first stage, for pressures up to 1000 bars. The gas flows in a Nimonic creep resistant tube filled with copper chips. The tube is heated externally with a resistance furnace. During this stage, the oxygen is gettered and the oil aerosol, which may enter during the first compression stage, is cracked. A second purification stage at low temperature traps the water vapor and traces of oil that could be left from the first stage: the gas flows through a steel coil and bubble plates immersed in a bath of dry ice and acetone. It then passes over zeolite which serves to trap any remaining traces of impurities.

It was found that the elimination of water vapor is particularly important in the investigation of NaCl. On the other hand, it was observed that slight traces of oxygen are sometimes helpful in removing the carbon contamination deposit originating from the part of the closure which supports the furnace. For this reason, a slight oxygen partial pressure was

---

[4] C. PIERCE, Phys. Rev. **123**, 744 [1961].

maintained for measurements on NaCl with internal heating.

For the externally heated pressure vessel, the same gas purification method was used. In this case there is no need for oxygen during the ionic conductivity measurements, but the specimen holder must be screened from the steel wall of the vessel. Otherwise, the steel, at high temperature and pressures, undergoes slight changes and some of its constitutive elements may be deposited on the insulating parts of the electrical system, causing short-circuits which badly perturb the conductivity measurements. The experimental set up was therefore placed inside a long quartz tube opening only in a cold zone of the vessel and loosely plugged with fiberglass to stop motion of any particles to the specimen or electrodes when the vessel was pressurized.

Heating

External Heating

External heating of the pressure vessel avoids many problems. Temperature uniformity in the region where the specimen is placed can be maintained with considerable accuracy due to the thermal inertia of the thick walls of the vessel. However, as noted, limitations in the strength of the steels available prohibited operating this vessel at pressures above 1 kbar. The vessel is made of Nimonic steel, with an internal diameter of 10 mm and an external diameter of 40 mm. The vessel is heated by an external furnace of 360 mm length, and the temperature is uniform over a length of 150 mm. The maximum variation of the temperature in this region is less than 1 °C between 300 °C and 900 °C. The temperature of this furnace is controlled by 3 thyristors, the central one controlling the two others.

Internal Heating

The use of internal heating permits anneals at temperatures up to 1200 °C at pressures to 10 kbar. The pressure vessel is equipped with a 170 mm long furnace attached to the end closure plug. The useful length available for samples is only 80 mm for a 10 mm diameter. The resistance is made of 0.5 mm dia Pt 22% Rh wire wound on an alumina tube and coated with an alumina cement. The furnace is heated by 220 V.a.c. curent, stabilized to ± 0.5%.

A variable power source must be available, since there is a rapid drop in temperature when pressure is increased at constant power. To avoid the effects arising from convection currents within the vessel, the free space is reduced to a minimum.

Temperature Measurements

The readings of a thermocouple at a given temperature depend on the pressure. To calibrate the thermocouples we compare the readings of two identical thermocouples placed in an isothermal block [5–7], one pair being at room pressure and the other under high pressure (Fig. 2). From such measurements we find for Pt/Pt 10% Rh thermocouples a temperature correction of 0.5 to 1.0 degrees per kbar at 900 °C and pressures to 10 kbar. The pressure correction is negligible for chromel-alumel thermocouples. However, these couples deteriorate rapidly under pressure at high temperatures. They can, however, be used for short time calibration or for anneals at lower temperatures (below 700 °C).

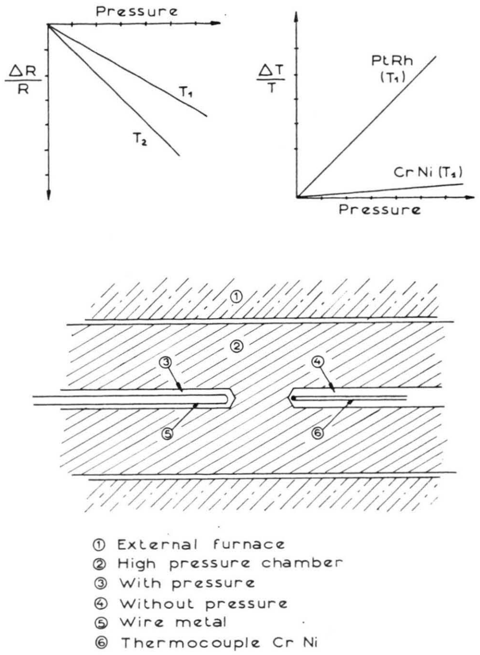

Fig. 2. Pressure dependence of the thermoelectric powers of metals.

This is also a technological difficulty related to the passage of the thermocouple leads through the closure plug. This can be done without discontinuities for chromel-alumel couples, but for Pt/Pt Rh-couples a steel section must be inserted for mechanical reasons, and this can give rise to a temperature error [7, 8].

III. Self-Diffusion of Beryllium

Preparation of samples

The samples were cut out of a single crystal grown by the Czochralski technique, in two directions: parallel and perpendicular to the *C* axis.

---

[5] P. W. Bridgman, The Physics of High Pressure, G. Belland, London 1962.

[6] R. R. Bourassa, Thesis, University of Illinois 1967.

[7] M. Beyeler, Thesis, University of Paris 1968.

[8] G. Martin, D. A. Blackburn, and Y. Adda, Rapport DM 1637 [1967].

A drop of solution containing Be^7 tracer was deposited on the surface of the sample. After the diffusion anneal under pressure, the samples were sectioned with a high precision grinder into 10 to 20 μm thickness sections. The sample was weighed before and after each section, and the activity counted both for the abraded and the remaining parts of the sample.

Experimental results

Self diffusion of beryllium was investigated at 693 °C with single-crystal specimens oriented parallel and perpendicular to the C axis (Fig. 3). The self diffusion coefficients decrease exponentially with increasing pressure. The slopes of the straight lines in the Log D vs. P plot give the activation volume. As a first approximation we find $\Delta V = 5.6\ \mathrm{cm^3/mole}$; if we take into account the third term of Eq. (7), we obtain $\Delta V = 5.8\ \mathrm{cm^3/mole}$, i. e. 1.2 ± 0.1 molar volumes for both directions.

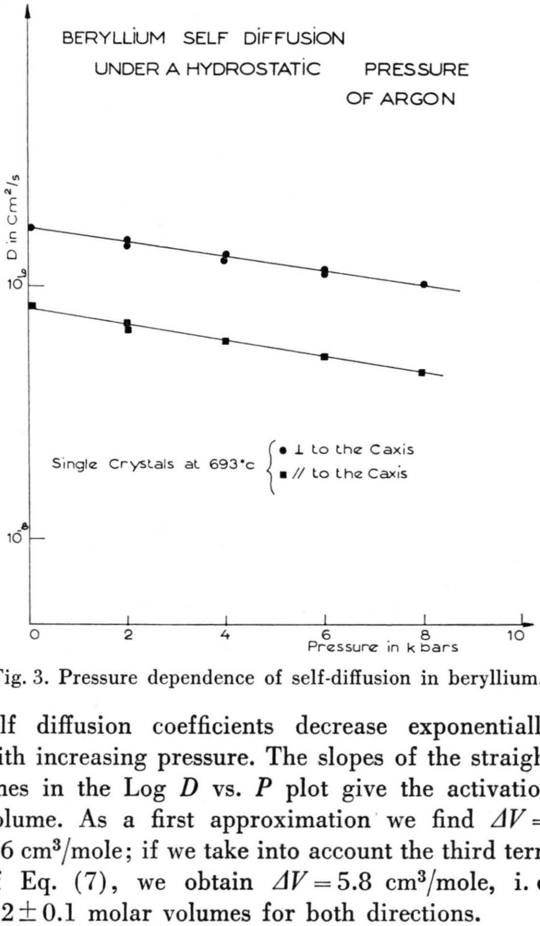

Fig. 3. Pressure dependence of self-diffusion in beryllium.

Discussion

The experimental result can be compared to the theoretical predictions of Friedel. In this model an oscillating potential arises from the variations of the screening by conduction electrons around the defect. The electron density is finite at the origin, and the electronic potential exhibits an oscillation with a wavelength $\lambda_F/2$ (λ_F = Fermi wave length) and an amplitude which decreases as $1/r^3$. An oscillating field $E(r)$ derives from the oscillating potential $V(r)$ and acts on the matrix ions. If this field is equilibrated with an elastic reaction of the matrix, we obtain a size effect.

The Friedel potential corresponding to screening of a unit excess charge is shown in Fig. 4. The nearest neighbor positions are indicated for various metals whose activation volumes are known: Na, K, Li, Ag, Au, Cu, Zn, Al, In, Pb (ignoring relaxation effects around the vacancy).

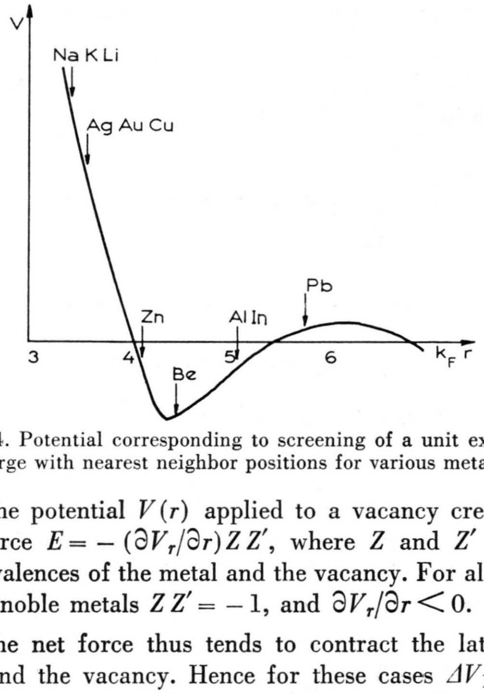

Fig. 4. Potential corresponding to screening of a unit excess charge with nearest neighbor positions for various metals.

The potential $V(r)$ applied to a vacancy creates a force $E = -(\partial V_r/\partial r) Z Z'$, where Z and Z' are the valences of the metal and the vacancy. For alkali and noble metals $Z Z' = -1$, and $\partial V_r/\partial r < 0$.

The net force thus tends to contract the lattice around the vacancy. Hence for these cases ΔV_F is expected to be smaller than the atomic volume Ω of the metal. This is in agreement with the experimental results and the theoretical model of JOHNSON, BROWN, BENNEMAN, GERL and TORRENS[9–13]. For a divalent metal like Zn, $E = -4(\partial V_r/\partial r) > 0$, there is also an inward force on the lattice around the vacancy, and ΔV_F is expected to be smaller than the atomic volume. This agrees with the results of

---

[9] K. H. BENNEMAN and L. TEWORDT, Z. Naturforsch. **15 a**, 772 [1960].

[10] K. H. BENNEMAN, Z. Physik **165**, 445 [1961].

[11] R. H. JOHNSON and E. BROWN, Phys. Rev. **127**, 446 [1962].

[12] R. A. JOHNSON, Phys. Rev. **143**, 423 [1966].

[13] I. M. TORRENS and M. GERL, Phys. Rev. **187**, 912 [1969].

Tomizuka and Norton[14] and those of Gilder reported at this conference.

For beryllium, also a divalent metal, $ZZ' = -4$ but $\partial V_r/\partial r > 0$. This leads to a dilatation of the lattice around the vacancy and ΔV_F is expected to be larger than the atomic volume. Our experimental results agree with this prediction.

For aluminium, which is trivalent, $ZZ' = -9$ and $\partial V_r/\partial r > 0$, hence a dilatation of the lattice should be observed. The experimental results for creep and diffusion[15,16] lead to a value of ΔV_F larger than the atomic volume, consistent with this model.

Indium and lead do not fit this model well. For these metals, $\Delta V_F < \Omega$, where a value larger than the atomic volume is predicted. However, it should be noted that the model of the interaction potential uses only a point charge. This may be justified for metals like beryllium and aluminium whose ion cores are small. But this assumption may be an oversimplification for In and Pb and the ion core leads to the introduction of an additional repulsive term which displaces the asymptotic potential toward increasing values of $k_F r$. With such additional terms, one might then obtain $\partial V_r/\partial r < 0$ for indium and lead.

IV. Ionic Conductivity of NaCl

Preparation of the samples

Measurements were made using pure NaCl single crystals purchased from Harshaw or Quartz et Silice, and NaCl crystals doped with Ca^{++}ions (kindly provided by Brebec and Slifkin). Accurate chemical analyses were performed, permitting separation of the crystals into different categories.

- The purest Harshaw crystals have a divalent cation content smaller than 10 ppm but contain at least 5 to 6 ppm of the divalent ions Ca^{++}, Mg^{++}
- The least pure Harshaw crystals have a divalent cation content of about 20 ppm.
- The Quartz et Silice crystals have a divalent cation content of about 30 ppm.
- The doped crystals have a divalent cation content of 460 ppm.

The electrical contact was provided by silver or gold lacquer or by thin layers of gold or platinum evaporated under vacuum onto the surface. Gold electrodes were used to make good electrical contacts with the painted or evaporated surface deposits.

Silver lacquer was found to be effective up to about 550 °C but evaporated at higher temperatures. Gold lacquer provided good reproducibility up to about 600 °C. Evaporated deposits were found to be the best for high temperatures, especially platinum, which is good to temperatures above 700 °C. The measurements were made in the apparatus shown in Fig. 5. Two bridges, General Radio 1608 A and 1620 A, with a 1 to 10 kHz frequency range, were used.

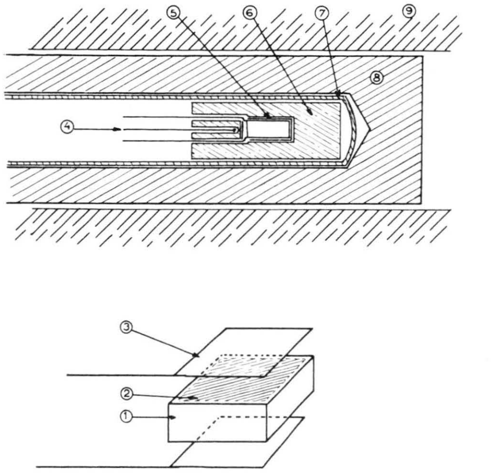

Fig. 5. Apparatus for ionic conductivity measurements.

The measurements were made at 1 kHz. No effect was found for variations in frequency between 100 Hz and 50 kHz.

V. Experimental Results

Intrinsic domain

The activation energy for ionic conductivity was measured in the intrinsic domain and found to be

---

[14] M. A. Norton and C. T. Tomizuka, Bull. Amer. Phys. Soc. **15**, 390 [1970].

[15] B. M. Butcher, H. Hutto, and A. L. Ruoff, Appl. Phys. Letters **7**, 34 [1960].

[16] M. Beyeler and Y. Adda, J. Physique **29**, 345 [1968].

1.81 ± 0.03 eV; this energy corresponds to $\Delta H = \frac{1}{2} \Delta H_f{}^s + \Delta H_m$, where $\Delta H_f{}^s$ is the formation enthalpy of a Schottky defect and ΔH_m the migration enthalpy of the cationic vacancy.

At high temperatures (600 – 700 °C) σT varies exponentially with pressure (for all samples) and ΔV can be determined in first approximation (Fig. 6). We found $\Delta V = (27 \pm 2)$ cm^3/mole; the uncertainly stated includes uncertainties arising from problems in temperature measurement. The second and third terms of Eq. (15) can be estimated and their sum is found equal to 3% of the first term, negligible in view the other experimental uncertainties.

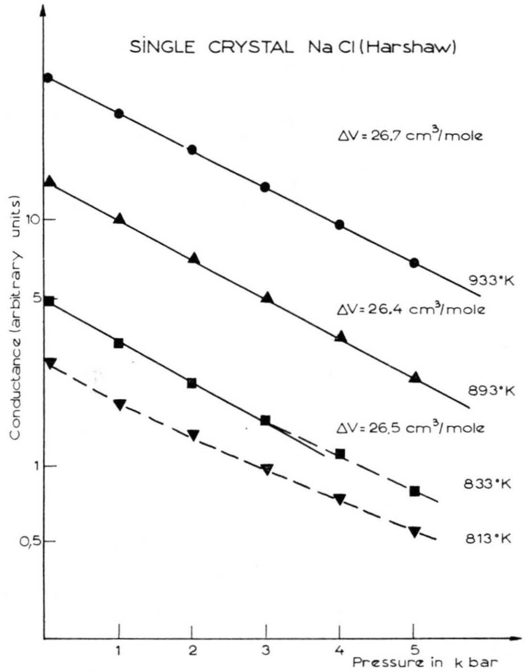

Fig. 6. Pressure dependence of the ionic conductivity of NaCl.

For lower temperatures (500 – 600 °C) the variation of σT with pressure is not purely exponential, and the values of ΔV determined in this way vary with temperature and do not appear to correspond to the self diffusion volume in the intrinsic range.

Investigation of the extrinsic domain

Several Harshaw crystals were investigated and found to have a variable concentration of divalent ions, both by chemical analysis and conductivity measurements. Hence the temperature of the knee and the temperature range in which there is a linear variation of $\log \sigma T$ as a function of $1/T$ are not identical for all specimens. For samples in which the ion concentration ($Ca^{++} + Mg^{++}$) is less than 10 ppm, the knee occurs at about 500 °C, and the curve $\log \sigma T$ vs. $1/T$ is linear between 440 and 385 °C. For samples with divalent concentrations ($Ca^{++} + Mg^{++}$) between 10 and 20 ppm, the temperature of the knee varies between 500 and 520 °C, and the temperature ranges for the linear variation of the curve vary from 451 – 402 to 478 – 420 °C. Values of the migration energy obtained for the Harshaw specimens are between 0.71 and 0.72 eV.

NaCl crystals purchased from Quartz et Silice have concentrations of divalent ions between 20 and 30 ppm. The temperature of the knee can reach 537 °C and the linear part of $\log \sigma T$ vs. $1/T$ is found in the temperature range 490 – 430 °C. The migration energy is 0.73 eV for these samples.

Heavily doped NaCl specimens (460 ppm) exibit a linear part of the extrinsic range at high temperatures. This range (680 to 553 °C) was easily investigated; the migration energy was found to be 0.75 eV. This result is in excellent agreement with Jain and Dahake [17] who found a migration energy of 0.75 eV, for any divalent impurity at a concentration greater than 100 ppm.

Examination of the curves of $\log \sigma T$ vs. $1/T$ of specimens heavily doped with Ca^{++} (Fig. 7) indicates a change in curvature after the first linear part (680 – 553 °C). One observes a curved zone followed by another linear section for the temperature range 348 – 254 °C. As is well known, the corresponding activation energy in the lowest temperature range is $\frac{1}{2} \Delta H_a + \Delta H_m$, where ΔH_m is the activation energy for the migration of a cationic vacancy and ΔH_a the binding energy of a vacancy to an impurity. A total energy of 0.95 eV was found for this region corresponding to a binding energy of 0.40 eV for a migration energy of 0.75 eV. This value agrees with Brebec and Slifkin's results [18] 0.45 eV for Ca^{45} tracer diffusion in samples of NaCl, pure and doped with Ca^{++}.

The activation volume for migration of Na^+ ions was determined from the variation of the migration enthalpy with pressure (Fig. 8). For Harshaw undoped crystals $\Delta V_m = (6.9 \pm 1.4)$ cm^3/mole, while

---

[17] S. C. Jain and S. L. Dahake, Indian J. of Pure and Appl. Phys. **2**, 71 [1964].

[18] L. Slifkin and G. Brebec, Rapport CEA R. 3769 [1969].

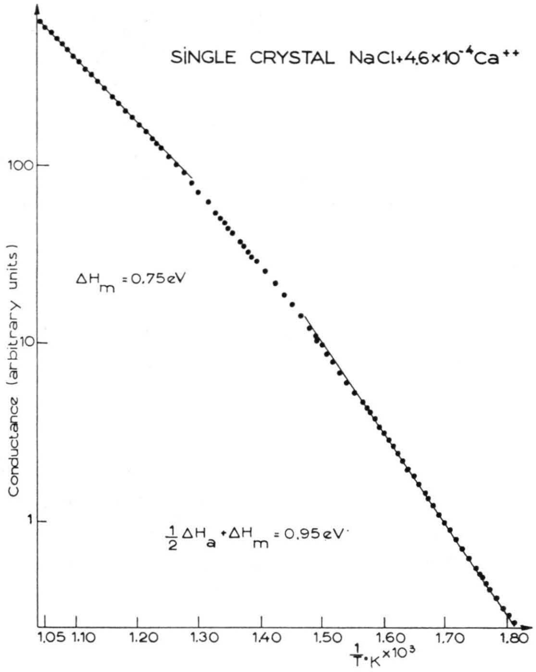

Fig. 7. Temperature dependence of the ionic conductivity of single crystal NaCl 460 ppm divalent ions.

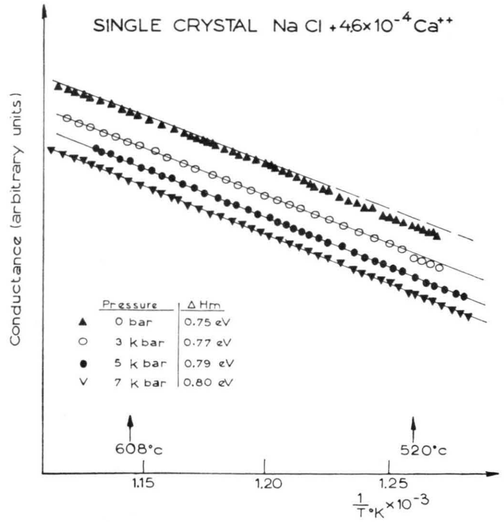

Fig. 8. Pressure dependence of the migration enthalpy of single crystal NaCl 460 ppm divalent ions.

for heavily doped crystals,

$$\Delta V_{\mathrm{m}} = (7.6 \pm 1.6)\,\mathrm{cm}^3/\mathrm{mole}.$$

The migration volume has also been determined using the relationship:

$$\Delta V_{\mathrm{m}} = -RT\left(\frac{\partial \log \sigma T}{\partial P}\right)_T + RT\left(\frac{\partial \log a^2}{\partial P}\right)_T + RT\left(\frac{\partial \log n}{\partial P}\right)_T.$$

For Harshaw crystals,

$$\Delta V_{\mathrm{m}} = (6.5 \pm 0.5)\,\mathrm{cm}^3/\mathrm{mole}.$$

For heavily doped crystals

$$\Delta V_{\mathrm{m}} = (6.7 \pm 0.5)\,\mathrm{cm}^3/\mathrm{mole}\quad (\text{Fig. 9}).$$

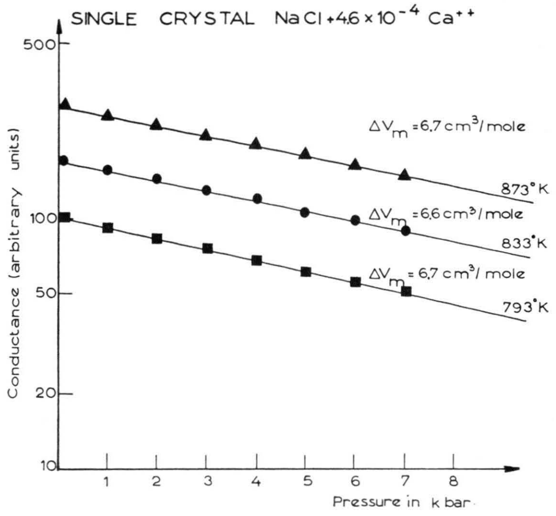

Fig. 9. Pressure dependene of the ionic conductivity of single crystal NaCl 460 ppm divalent ions.

One can thus consider as the activation volume of migration of Na^+ ions the value

$$\Delta V_{\mathrm{m}} = (6.6 \pm 0.6)\,\mathrm{cm}^3/\mathrm{mole}.$$

VI. Discussion

Since the molar volume of sodium metal is 5.4 cm³, ΔV_{m} represents 1.22 ± 0.12 sodium atomic volumes. This value may be interpreted by assuming that the coulomb forces play a greater role on the dilatation of the lattice than the forces of repulsion at short distances, during the jump process.

The activation volume for self diffusion has been determined in the intrinsic range:

$$\Delta V_{\mathrm{D}} = \frac{\Delta V_{\mathrm{f}}^{\mathrm{s}}}{2} + \Delta V_{\mathrm{m}}.$$

Since ΔV_{m} has been measured, the volume of formation of the Schottky defect is found to be

$$\Delta V_{\mathrm{f}}^{\mathrm{s}} = (40.8 \pm 5)\ \mathrm{cm}^3/\mathrm{mole}.$$

The molar volume of NaCl is 27 cm³/mole, therefore

$$V_{\mathrm{f}}^{\mathrm{s}} = (1.51 \pm 0.18)\ \Omega.$$

This result implies that the first neighbors of a vacancy relax outward from it. This result is consistent with the coulomb repulsion expected between the uncompensated nearest neighbors of a vacancy.

In the mixed zone, a range of values of the activation volumes was obtained. The values of σT do not vary exponentially with pressure even for temperatures corresponding nominally to the intrinsic range. Indeed, a shift of the intrinsic range towards higher temperatures was observed with increasing pressure. This result indicates a rapid suppression of the concentration of thermally produced vacancies with increasing pressure, consistent with the large value found for ΔV_f^s. Because of this rapid suppression, it is difficult to find any extensive intrinsic conductivity range under pressure for crystals containing more than $10-20$ ppm of divalent impurities.