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EFFECT OF HYDROSTATIC PRESSURE ON IONIC CONDUCTIVITY
OF SODIUM CHLORIDE

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The variation of the ionic conductivity of the single crystal of sodium chloride has been measured as a function of hydrostatic pressure up to 600 kg/cm² over the temperature range from 200 to 300°C. In this temperature range, the conductivity is due to the motion of the positive ion vacancies freed from the impurity-complexes. The activation volume for migration of the positive ion vacancies is 9.3 cc/mole, which is almost in agreement with Pierce's value.

Introduction

It is one of the important problems to know about the amount of the volume change due to the lattice distortion necessary for the formation of defects and their migration in the solid. It is possible to estimate the amount of this volume change by measuring the isothermal variation of ionic conductivity with pressure. The pressure dependence of the ionic conductivity of silver chloride, which has the defects of Frenkel type, was measured by Jost¹⁾, Kurnick²⁾ and the author³⁾. On the other hand, in the crystal having the defects of Schottky type, Pierce⁴⁾ has recently studied the pressure dependence of the ionic conductivity of the doped NaCl and KCl crystals and obtained the activation volume for motion of positive ion vacancies $\Delta V_m = 7.7$ and 7.0 cc/mole respectively. The author has independently examined the variation of ionic conductivity of NaCl under pressures up to 600 kg/cm² in the temperature range from 200 to 300°C. It is significant that the pressure dependence of the conductivity is measured in the range of comparatively low pressures with no extrapolation from very high pressures to atmospheric pressure because of the behavior described later.

In the extrinsic range, the ionic conductivity is entirely due to migration of the positive ion vacancies and given by

$$\sigma = ne\mu, \quad (1)$$

where n is the number of the free positive ion vacancies per cm³, e electronic charge and μ mobility of the free positive ion vacancies. The mobility and the concentration of the free vacancies can be expressed as follows:

1) W. Jost and S. Mennenöh, *Z. physik. Chem.*, **196**, 188 (1950)

2) S. W. Kurnick, *J. Chem. Phys.*, **20**, 218 (1952)

3) K. Shimizu, *This Journal*, **30**, 73 (1960)

4) C. B. Pierce, *Phys. Rev.*, **123**, 744 (1961)

$$\mu = \frac{a^2 e \nu_0}{kT} \exp\left(-\frac{\Delta G_m}{kT}\right) \quad (2)$$

and

$$n = \sqrt{N n_c} \exp\left(-\frac{\Delta G_f}{2kT}\right), \quad (3)$$

where a is the lattice parameter, ν_0 an atomic vibration frequency, k Boltzmann's constant, T the absolute temperature, N the number of positive ion sites per cm^3 , n_c the number of impurity-complexes per cm^3 , ΔG_m the change in Gibbs free energy associated with the migration of vacancies and ΔG_f that for the formation of vacancies. According to the thermodynamic relation, the differentiation of Gibbs free energy with respect to pressure at constant temperature yields the expression

$$\left(\frac{\partial G}{\partial P}\right)_T = V, \quad (4)$$

so that, as the result of the differentiation of Eq. (1) with respect to pressure, the activation volume ΔV_m can be expressed by

$$\Delta V_m = kT \left[\left(\frac{\partial \ln n}{\partial P}\right)_T + 2 \left(\frac{\partial \ln a}{\partial P}\right)_T + \left(\frac{\partial \ln \nu_0}{\partial P}\right)_T - \left(\frac{\partial \ln \sigma kT}{\partial P}\right)_T \right]. \quad (5)$$

In the right-hand side of Eq. (5), the last term is measured experimentally, but the others are estimated with some approximations.

Experimentals

The single crystal was prepared by Kyropoulos' method. Specimens were cleaved in $1 \times 5 \times 8 \text{ mm}$ from the single crystal and annealed in the NaCl powder at 600°C for 6 hours and slowly cooled to room temperature. Electrodes were applied with silver paint. The pressure vessel contained a sample holder, lead wire and a thermocouple of chromel-alumel which were insulated with teflon sheets and porcelain tubes from the vessel as in the previous experiments³⁾. The specimen was compressed in a silicone oil by an oil injector and the pressure was measured with a calibrated Bourdon type gauge. The pressure vessel was heated in an electric furnace. Conductivity measurements were made for both increasing and decreasing pressures by means of a capacitance bridge at 1,000 c. p. s. at constant temperature.

Results

A plot of $\log \sigma T \sim 1/T$ exhibits two linear ranges and the break in the curve occurs at about 270°C as shown in Fig. 1. The activation energy in the range of high temperatures is 0.87 eV , in the range of low temperatures being 1.10 eV . The conductivity in the extrinsic range has been shown to depend upon the presence of divalent impurities in the crystal and the changes

in activation energy in this range have been referred to the dissociation of positive ion vacancies from the impurity-complexes. The break of the curve at about 270°C may be due to the completion of the dissociation process between the positive ion vacancies and the divalent impurities. The activation energy in the range of low temperatures, 1.10 eV, would represent the activation

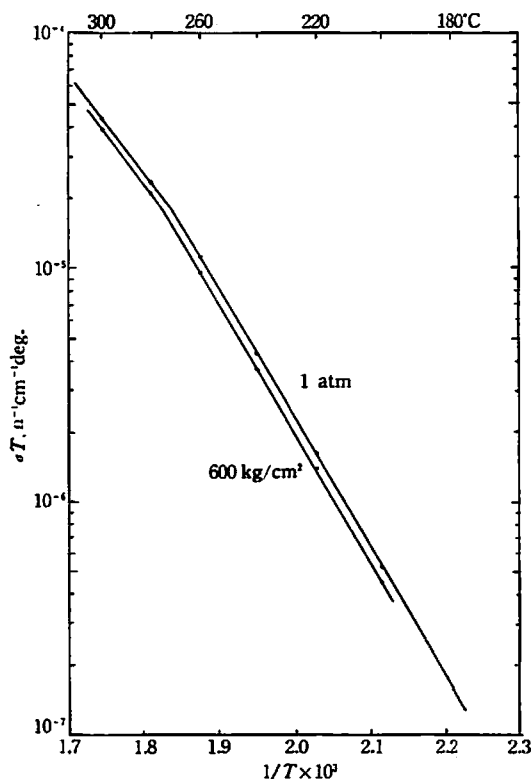


Fig. 1 Ionic conductivity of NaCl at two pressures

energy of mobility plus the energy for association between the positive ion vacancies and the divalent impurities. On the other hand, the energy in the range of high temperatures, 0.87 eV, would represent only the activation energy of mobility. Then the value of the association energy obtained from this change is 0.46 eV. These values are in fair agreement with those obtained hitherto⁵⁾ and the concentration of the positive ion vacancies would be $2.2 \times 10^{17}/\text{cm}^3$ at 300°C.

The plots of $\log \sigma \sim P$ are shown in Fig. 2. The conductivity decreases exponentially with increasing pressure at the high temperatures, though the plots somewhat deviate systematically from the straight lines at high pressures in the range of low temperatures. The slopes of these curves give the pressure coefficient of conductivity, $(\partial \ln \sigma / \partial P)_T$, which are $-1.9 \sim -3.2 \times 10^{-4} \text{ kg}^{-1} \text{ cm}^2$ in the temperature range of 300~200°C, provided that at low temperatures are used the initial slopes from 1 atm to 200 kg/cm².

5) H. W. Etzel and R. J. Maurer, *J. Chem. Phys.*, **18**, 1003 (1950)

F. Seitz, *Rev. Modern Phys.*, **26**, 14 (1954)

D. B. Fischbach and A. S. Nowick, *J. Phys. Chem. Solids*, **2**, 226 (1957)

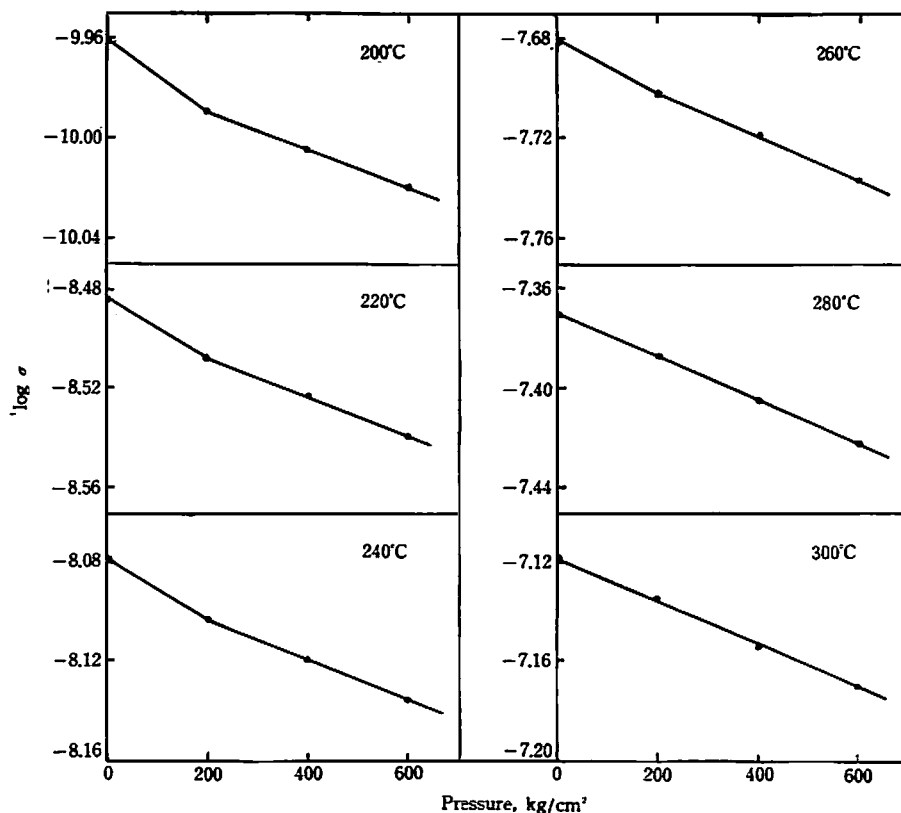


Fig. 2 Pressure dependence of conductivity of NaCl at various temperatures

Considerations

In order to obtain the activation volume for the migration of positive ion vacancies, ΔV_m , the terms in the right-hand side except the last term in Eq. (5) must be evaluated with some approximations as in Pierce's result. The pressure variation of lattice parameter $2(\partial \ln a / \partial P)_T = -0.029 \times 10^{-4} \text{ kg}^{-1} \text{ cm}^2$ is calculated from the Bridgman's value for the compressibility at 75°C ⁶⁾ and that of the vibration frequency, $(\partial \ln \nu_0 / \partial P)_T$, would be $0.041 \times 10^{-3} \text{ kg}^{-1} \text{ cm}^2$, supposing that the $(\partial \ln \nu_0 / \partial P)_T$ would be the same order as the pressure variation of the Debye frequency, ν_D , which is calculated from Blackman's equation⁷⁾ with the adiabatic elastic constants under high pressures⁸⁾.

The pressure dependence of the concentration of free positive ion vacancies is calculated with some suppositions. As mentioned above, the impurity-complexes would almost completely dissociate at 300°C . It is not unlikely that the pressure effect on the concentration of free positive

6) P. W. Bridgman, *The Physics of High Pressure*, p. 163 (1949)

7) M. Blackman, *Proc. Roy. Soc. (London)*, A149, 126 (1935)

8) D. Lazarus, *Phys. Rev.*, 76, 545 (1949)

ion vacancies would be negligible at that temperature as well as on the lattice parameter, the vibration frequency and the entropy term in Gibbs free energy, and that the pressure variation of the conductivity would be mainly caused by the pressure effect on the activation energy for migration of free positive ion vacancies through the $P\Delta V_m$ term, which is shown in Fig. 3. Then,

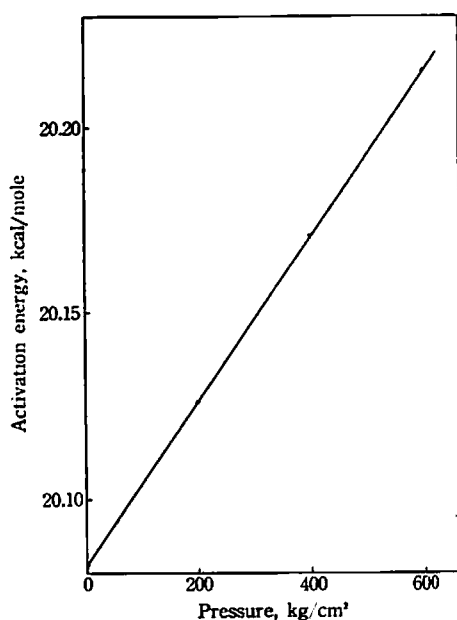


Fig. 3 Variation of activation energy for migration of positive ion vacancies of NaCl with pressure

the variation of the concentration of free positive ion vacancies with pressure at low temperatures can be calculated with the experimental values of the conductivity and the pressure variation of the activation energy as shown in Fig. 3, which would be supposed to be independent of the temperature.

The plots of these results and $\Delta V_m/kT$ are summarized in Fig. 4. It is reasonable that the extension line of the smooth curve of $\Delta V_m/kT$ passes on the points of $(\partial \ln \sigma / \partial P)_T$ at high temperatures. The activation volume ΔV_m is calculated from the smooth curve of $\Delta V_m/kT$ and is $9.3 \text{ cm}^3/\text{mole}$. This value is, in contrast with that in metals, rather larger than the volume actually available to positive ion in the crystal lattice and is by about $1 \text{ cm}^3/\text{mole}$ larger than that of Pierce's result. This discrepancy may be caused by that of the pressure coefficients of conductivity in the completely dissociated range of the impurity-complexes.

As shown in Fig. 2, the pressure coefficient of conductivity changes with increasing pressure at low temperatures. This may be due to the variation of the pressure effect on the activation energy and/or on the concentration of free positive ion vacancies. The later may be caused by the retardation for equilibrium concentration between the free positive ion vacancies and impurity-complexes, or by the generation of vacancies by moving dislocations. In this case, it is expected that the irreversible phenomena of conductivity would be observed in decreasing pressure.

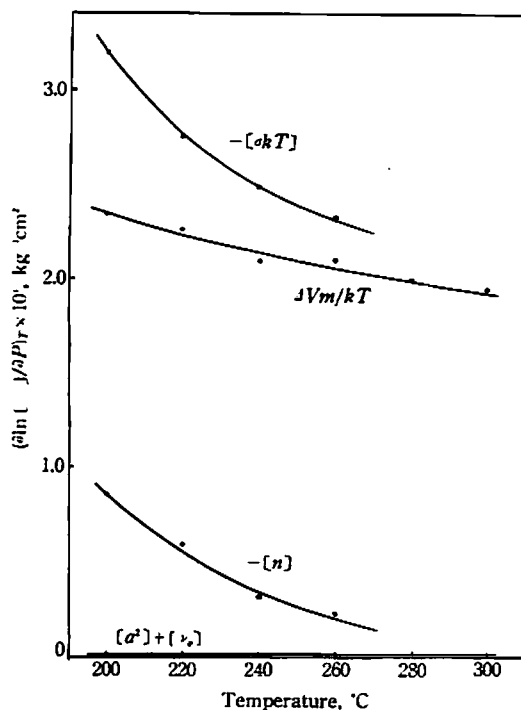


Fig. 4 Plot of terms in Eq. (5) for calculation of activation volume ΔV_m

An alternative explanation for these phenomena is concerned with the change of the conductivity mechanisms, as suggested by Pierce⁴⁾, bulk and dislocation bundles, of which the pressure effect on the activation energy may be different, though the conductivity along the dislocation bundles has not been experimentally ascertained in alkali halide crystals. The bulk conductivity is predominant at low pressures so that the pressure would affect the bulk conductivity, but at high pressures the conductivity along the dislocation bundles, which may be generated by compression, would take the place of the bulk conductivity and the pressure would explicitly affect this type of mechanism.

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