EFFECT OF HYDROSTATIC PRESSURE ON IONIC CONDUCTIVITY OF SILVER CHLORIDE

By Kiyoshi Shimizu

The variation of the ionic conductivity of the single crystal of silver chloride has been measured as a function of hydrostatic pressure up to 700 kg/cm² in the intrinsic and extrinsic ranges. The pressure coefficients of the conductivity were in good agreement with the calculated values, and it was revealed that the mobility is much affected by the applied pressure.

Introduction

The ionic conductivity of silver chloride crystal was markedly increased by plastic deformation and the conductivity increase was mainly ascribed to the increase of the concentration of silver ion vacancies produced by plastic deformation[1]. On the other hand, the ionic conductivity of the silver chloride crystal decreases with applied hydrostatic pressure and the conductivity decrease would be due to the decreases of the mobility and/or the concentration of charge carriers by hydrostatic compression. The variation of the ionic conductivity of silver chloride with hydrostatic pressure has been previously reported by Jost, Nehlep and Mennenöh[2]. Their measurements were made on the fused polycrystals up to 300 kg/cm² at about 300°C. The early result gives -2.5×10^{-4} cm²/kg as the pressure coefficient and the later -3.0×10^{-4} cm²/kg.

It is clearly necessary to measure the ionic conductivity of the single crystal as a function of pressure in both the intrinsic and the extrinsic ranges and to reveal the pressure effects on the mobility and on the formation of charge carriers respectively. The purpose of this report is to describe such experiments at pressures up to 700 kg/cm² and at temperatures from 30 to 110°C.

Experimentals

The procedure of the preparation of single crystal and specimens was the same as that in the previous experiments[1]. Electrodes were applied with silver paint. The pressure vessel contained a sample holder, lead wires and a thermocouple of chromel-alumel which were insulated with teflon sheets and porcelain tubes from the vessel as shown in Fig. 1. The relative positions of the sample holder and the thermocouple were strictly adjusted by the inner tubes of porcelain

1) K. Shimizu, *This Journal.* **30**, 1 (1960)
2) W. Jost and G. Nehlep, *Z. phys. Chem.*, B34, 348 (1936)
    W. Jost and S. Mennenöh, *ibid.*, **196**, 188 (1950)
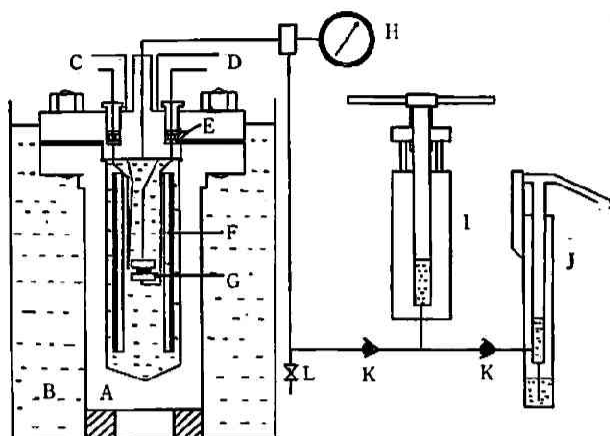   S. Mennenöh, *Z. Electrochem.*, **54**, 433 (1950)

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Fig. 1 Schematic layout of apparatus

A: high pressure vessel
B: temperature bath
C: thermocouple
D: lead wires with porcelain tube
E: teflon sheet
F: inner tube of porcelain covered with steel
G: sample holder, electrodes and specimen
H: pressure gauge
I : oil injector
J : hand pump
K: check valve
L: exit valve

and steel. The specimen was compressed in a silicone oil by an oil injector and the pressure was measured with a calibrated Bourdon type pressure gauge. The pressure vessel was immersed in a temperature bath of liquid paraffin. 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. There was, however, a temporary change of temperature in the vessel, when the pressure was altered, so that it was necessary to take care of the reestablishment of temperature equilibrium after each alteration of pressure.

Results

The conductivity of the intrinsic range is given by

$$\sigma = \sigma_0 \exp\left[-\left(\tfrac{1}{2}W_0 + U_0\right)/kT\right] \qquad (1)$$

with
$$\sigma_0 = \gamma BC\sqrt{NN'}e^2a^2\nu/kT,$$

where W_0 is the formation energy of charge carrier and U_0 is the mobility energy at absolute zero temperature, ν vibrational frequency, e charge of an electron, a ionic distance, N number of ion-pairs per cm^3, N' number of interstitial positions per cm^3, γ numerical factor due to the change of vibrational frequency by lattice defects, B and C numerical factors due to the changes of activation energies with temperature, $W=W_0+bT$ and $U=U_0+cT$, by the dilation of the lattice.

From Equation (1), it follows that

$$\left(\frac{\partial \ln \sigma}{\partial P}\right)_T = \frac{\partial \ln \sigma_0}{\partial P} - \frac{1}{kT}\frac{\partial}{\partial P}\left(\tfrac{1}{2}W_0 + U_0\right).$$

Now, in the temperature range of this experiment, the first term in the right-hand side may be negligible; we may thus write

$$\left(\frac{\partial \ln \sigma}{\partial P}\right)_T = -\frac{1}{kT}\frac{\partial}{\partial P}\left(\tfrac{1}{2}W_0 + U_0\right) = \frac{V_0\chi}{kT}\frac{\partial}{\partial V}\left(\tfrac{1}{2}W_0 + U_0\right) = -\frac{\ln(BC)\chi}{\alpha T}, \qquad (2)$$

where χ is the compressibility of the crystal, α the coefficient of volume expansion, and $BC=$

$\sigma_0/\gamma\sqrt{NN'}e^2a^2\nu/kT$. Therefore, we can beforehand calculate the value of the pressure coefficient at each temperature by using the values of χ, α and σ_0 obtained from the experimental results at atmospheric pressure and $\gamma\sqrt{NN'}e^2a^2\nu/kT$ calculated with each numerical value as follows:

$$\sqrt{NN'} \fallingdotseq N = 2.3 \times 10^{22}/cm^3, \quad e = 1.6 \times 10^{-19}\ coulomb, \quad a = 3.91 \times 10^{-8}cm,$$

$$\chi = 2.18 \times 10^{-6}cm^2/kg^{[3]}, \quad \alpha = 3 \times 3.29 \times 10^{-5}/^\circ C^{[4]}, \quad \nu = 10^{12}/sec\ and\ \gamma = \frac{1}{2}.$$

On the other hand, in the extrinsic range, the concentration of charge carriers is frozen in, so that the pressure coefficient depends on only the term of $\partial U_0/\partial P$. However, the concentration of charge carriers, n, must be beforehand determined. In this experiment, the value of n was calculated with the experimental results of conductivity at 30°C and mobility and it was evaluated thus: $n = 5 \times 10^{14}/cm^3$. The calculated values of the pressure coefficient are listed in the Table shown later.

The experimental results are summarized in Fig. 2. The conductivity was derived from the measured conductance at high pressure and high temperature and the dimensions at atmospheric pressure and room temperature. The error arose from the disregarding of any changes in dimensions with pressure and temperature is very small. In the figure, the upper curve shows the conductivity at atmospheric pressure, which is represented in the conventional forms as follows:
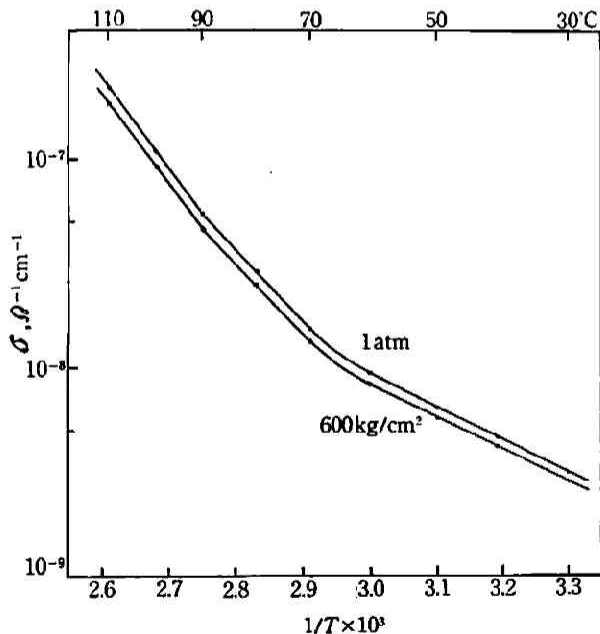

Fig. 2 Conductivity of AgCl at two pressures

$$\sigma = 1.6 \times 10^4 \exp(-19,000/RT) \cdots\cdots\cdots\cdots\cdots\cdots\cdots (90\sim110°C),$$
$$\sigma = 1.0 \times 10^{-1} \exp(-6,225/RT) \cdots\cdots\cdots\cdots\cdots\cdots (30\sim50°C),$$

and the lower curve the conductivity at 600 kg/cm². The conductivity decreased with increasing

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3) T. W. Richards and G. Jones, *J. Am. Chem. Soc.*, **31**, 158 (1909)

4) *International Critical Table* (1933), Vol. III, p. 43

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pressure.   The detailed pressure variation of the conductivity is shown in Fig. 3.   In the
intrinsic range, the variation of log σ was linear and reversible.   On the other hand, in the
extrinsic range, the variation of the conductivity was linear for increasing pressure, but not
reversible and the conductivity was lower for decreasing pressure than for increasing pressure.
After reducing pressure to the atmospheric pressure, the conductivity was lower than it was before
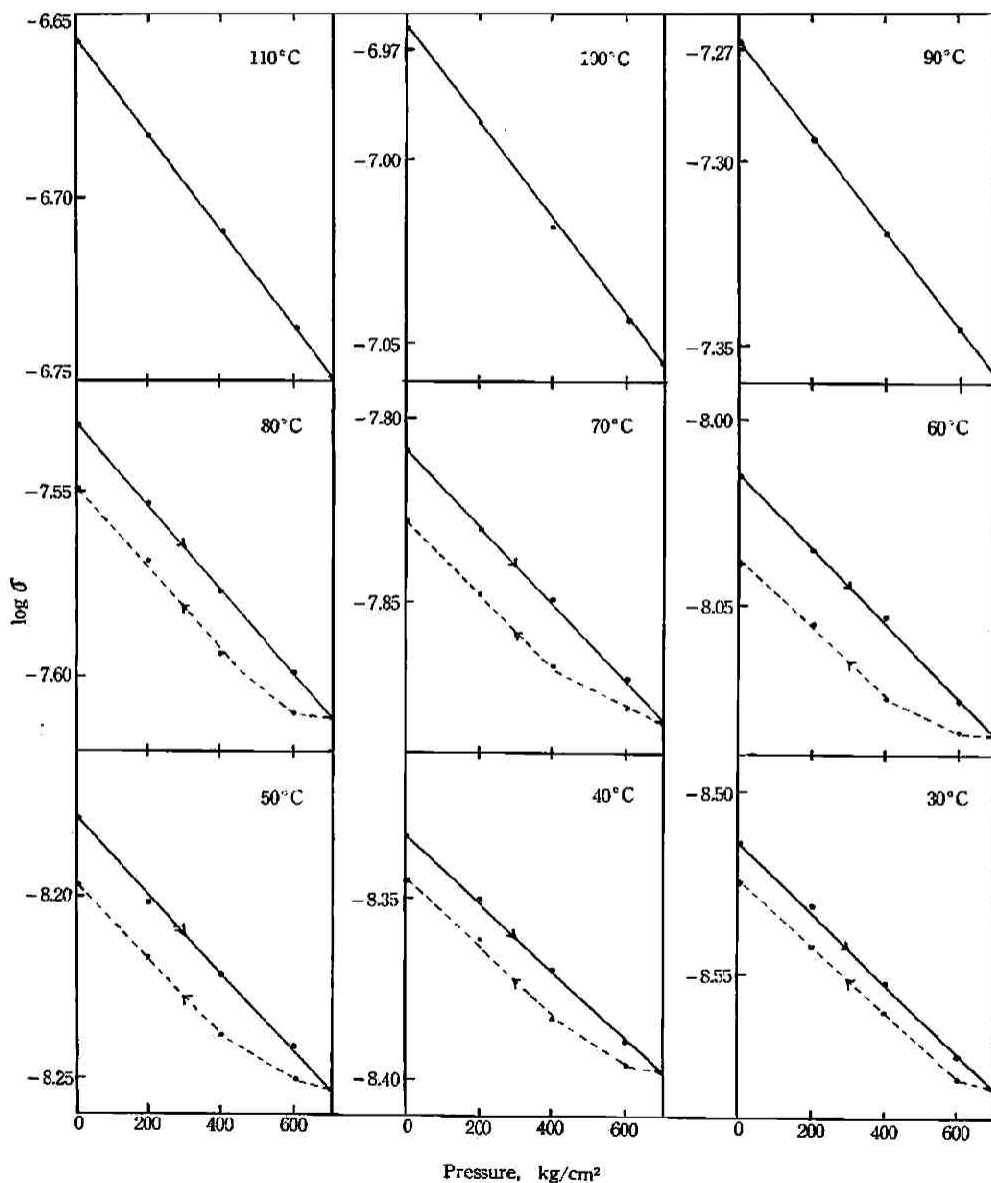

Fig. 3   Pressure dependence of conductivity of AgCl at various temperatures

The arrow indicates the direction of the variation of pressure.

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the run, but, the conductivity increased very slowly to a value near its pre-run value in the case of high temperature in this range. The pressure coefficient of the conductivity, $\partial \ln \sigma / \partial P$, is given by the slope of $\log \sigma \sim P$ curve. As shown in the Table, the pressure coefficients were $-3.0 \times 10^{-4} \text{cm}^2/\text{kg}$ in the intrinsic range and $-2.2 \sim -2.5 \times 10^{-4} \text{cm}^2/\text{kg}$ in the extrinsic range respectively, and these values were in good agreement with the calculated ones.

Table   Pressure coefficient of conductivity of silver chloride

Temp. °K	$-\left(\frac{\partial \ln \sigma}{\partial P}\right)_{\text{obs.}}$ cm²/kg	$-\left(\frac{\partial \ln \sigma}{\partial P}\right)_{\text{cal.}}$ cm²/kg
303	2.2×10^{-4}	2.3×10^{-4}
313	2.2	2.2
323	2.3	2.1
333	2.3	2.1
343	2.4	2.0
353	2.5	2.0
363	3.0	3.2
373	3.0	3.1
383	3.0	3.0
$BC = 1.86 \times 10^2$	$C = 2.27 \times 10$	

In Fig. 4 is shown the variation of the conductivity of the polycrystal and the deformed crystal with hydrostatic pressure. In the intrinsic range, both the polycrystal and the deformed crystal showed the same variation of conductivity, $\partial \ln \sigma / \partial P = -3.0 \times 10^{-4} \text{cm}^2/\text{kg}$, as the single crystal. In the extrinsic range, they showed hysteresis and the absolute values of the pressure coefficient were larger ($> 2.7 \times 10^{-4}$) at 30°C as compared with that of the single crystal and decreased by repeated compressing.

Considerations

The absolute value of the pressure coefficient in the extrinsic range is smaller than that in the intrinsic range and that difference is about $-1 \times 10^{-4} \text{cm}^2/\text{kg}$. In the extrinsic range, the concentration of the charge carriers (silver ion vacancies) does not depend on the temperature and we may suppose that the change of the concentration of vacancies with applied pressure is small; the pressure may thus affect only the mobility energy. On the other hand, in the intrinsic range, the pressure effect on the formation energy of vacancies would emerge with the effect on that of the mobility, as the vacancies are formed on the basis of the thermodynamical conditions. Therefore, the difference mentioned above would be ascribed to the effect of pressure on the formation energy of vacancies. Then, the pressure effect on the mobility energy is about 70% of the total pressure effect, so that, this may suggest that the mobility energy depends more
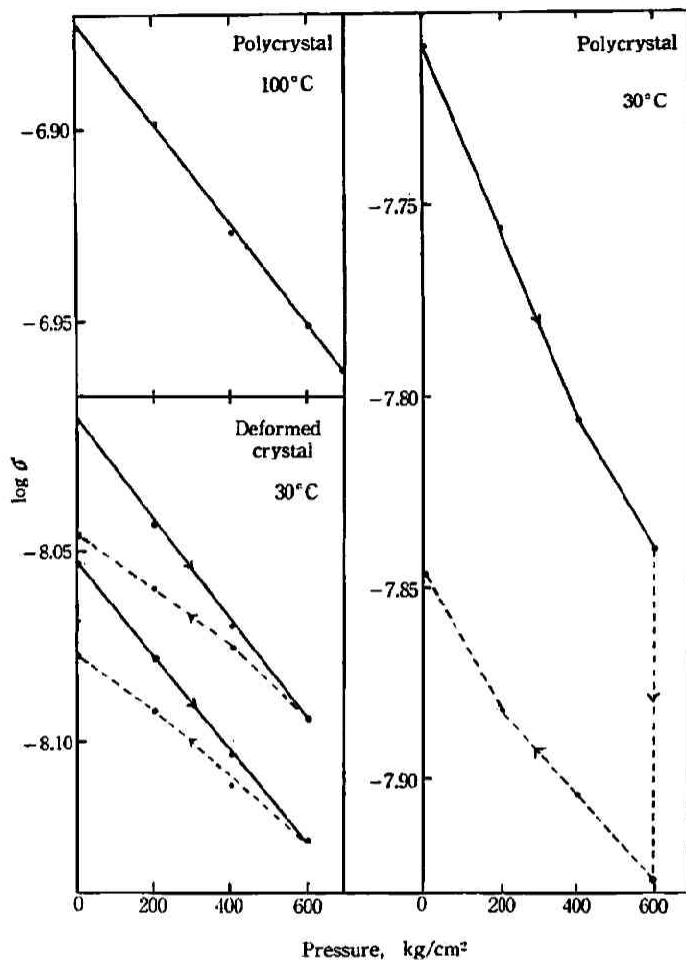
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Fig. 4 Pressure dependence of conductivity of polycrystal and deformed crystal of AgCl

The arrow indicates the direction of the variation of pressure. The specimen of polycrystal, at 30°C, was maintained at 600 kg/cm² for 15 hours.

highly on the lattice distance than the formation energy of vacancies, as the value of the mobility energy is smaller than that of the formation energy of vacancies.

In the extrinsic range, however, the conductivity was lower for decreasing pressure than for increasing pressure and the conductivity, after reducing pressure to the atmospheric pressure, increased very slowly to a value near its pre-run value. The discrepancies of the pressure coefficient between the experimental results and the calculated values are comparatively large at 70 and 80°C. This temperature range corresponds to that turning from the extrinsic range to the intrinsic range. The formation of free vacancies may commence, for instance, because of the dissociation of vacancies from the associated complexes with impurity ions and the formation of vacancies may thus be affected by pressure. Namely, the concentration of free vacancies would decrease somewhat with applied pressure and in the case of decreasing pressure the recovery of the concentration of free vacancies would retard, as the temperatures are not high enough to form the vacancies. The specimens of the polycrystal and deformed crystal have large pressure

coefficients and show the remarkable hysteresis. It is probable that these phenomena are related to the disorder of the lattice, such as mosaic structure, as the specimens of the polycrystal and the deformed crystal are in the state of higher disorder. The disordered regions may be rearranged in a more proper orientation under high pressures and at that time, some of the vacancies may be annihilated in the disordered regions.

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The Laboratory of Physical Chemistry
Kyoto University
Kyoto, Japan

Appendix

Correction : Effect of Plastic Deformation on Ionic Conductivity of Silver Chloride. K. Shimizu
[*Rev. Phys. Chem. Japan*, **30**, 1 (1960)]

In the last paragraph of "Considerations" of the previous paper[5], the association energy of positive ion vacancy and impurity has been confused with the activation energy for the rate of association. In alkali halide crystals, the association energy of positive ion vacancy with divalent impurity is about 0.4 eV and the estimated one in the silver chloride is about 0.2~0.3 eV.

If we assume that the activation energy for the rate of dissociation of the silver ion vacancy and impurity ion is the sum of the activation energy for the migration of silver ion vacancy, 0.27 eV, and the association energy, the activation energy for the rate of the association process should correspond to the activation energy for the migration of silver ion vacancy. The experimental value, 0.20 eV, is somewhat small. This discrepancy may be caused by two reasons. The activation energy for migration of silver ion vacancy would be lowered, in the direction of the impurity ion, in the proximity of a multivalent positive ion because of the change of the potential energy between the two charges. For the another reason, we must take account of the variation of the concentration of the free vacancies at $t=\infty$, n_∞, with temperature, though we supposed that the n_∞ did not depend on the temperature. The higher the temperature, the smaller the value of the n_∞, and $k=k'/n_\infty$, so that the slope of $\log k \sim 1/T$ curve would be steeper than that of $\log k' \sim 1/T$ curve which was obtained in the experiment.

5) K. Shimizu, *This Journal*, **30**, 8 (1960)