

## An Investigation of the Space Charge Distribution in Silver Chloride by ac Techniques

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Alternating current conductance and capacitance experiments have been performed to investigate the space charge distribution in the solid phase near a silver chloride-aqueous solution interface. The results of these experiments are consistent with those obtained by dc techniques and demonstrate the existence and the nature of the space charge region.

### Introduction

The existence of a space charge distribution of point defects near the surface of an ionic solid in contact with various environments has been proposed by Frankel (1) and by Grimley and Mott (2). In this work the space charge distribution in the solid near a silver chloride-aqueous solution interface is studied. When a silver chloride crystal is in contact with an aqueous solution containing an equilibrium concentration of silver ions, Grimley and Mott suggest that the thermodynamic requirement of the equality of the electrochemical potentials of silver ions in both phases leads to the existence of the space charge potential across the interface. The magnitude of this potential depends on the silver ion concentration in the solution. Corresponding to the space charge potential there is a distribution of point defects in the solid near the interface. In silver chloride it consists of silver ion vacancies and silver ion interstitials. For crystals of sufficiently small thickness, the stoichiometry of the crystal at equilibrium therefore depends on the environments with which it is in contact.

The measurement of charge transport across a thin single crystal of a specific crystallographic orientation in contact with various environments is a useful approach to investigate the properties of the space charge distribution. The mobile species or equivalently the potential determining ions in silver chloride are the silver ions. The transport phenomenon of ionic charges, however, is analogous to the

space charge limited electronic transport across semiconductor junctions. In our previous paper (3) we have reported the results of dc measurements across silver chloride-aqueous solution interfaces. These results demonstrate the existence and nature of the space charge distribution in the solid near the interface. In this paper, our purpose is to report an investigation by ac techniques.

Direct current conductance measurements (3, 4) as a function of the applied voltage across thin silver halide crystals in contact with aqueous solutions of various silver ion concentrations have shown that the conductance of the crystal depends on the silver ion concentration in the solution. The current-voltage relationship is found to be non-ohmic. Both these observations suggest that the ionic transport in the solid is space charge limited.

Steidel *et al.* (3) and Hoyen (5) have reported dc potential relaxation experiments. From the results of these experiments, from the dc conductance data and from a diffusion controlled transport model similar to that used in the theory for semi-conductor junctions, (6) they have been able to calculate the magnitudes of the space charge potential in the solid at the silver chloride-aqueous solution interface. Since the crystals in their work contain approximately 20 ppm of divalent cation impurities, the silver ion vacancy is the predominant defect. For these crystals the magnitude of the space charge potential in the solid is negative relative to the bulk potential being zero. The space charge potential corresponds to a deficiency of silver ion vacancies near the interface.

The purpose of this investigation is to perform

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ac conductance and capacitance measurements at various frequencies on silver chloride–aqueous solution systems as a function of temperature and crystal orientation. Since the frequency dependence of the ac conductance and capacitance depends on the magnitude of the space charge potential, a comparison between the results from ac measurements and those from dc experiments is made to confirm the previous conclusions (3) on the nature of the space charge distribution.

## Experiments

The silver chloride crystals used in this work are obtained from Harshaw Chemical Company, Cleveland, Ohio. The silver ion vacancy concentration in these crystals is calculated from ac conductance data using an average of the literature values of the mobility (7, 8). From these data, the silver chloride crystals contain approximately 20 ppm of divalent cation impurities.

The crystals are oriented by back Laue X-ray techniques. In order to reveal the effects of a space charge distribution on the ionic transport across the crystals, single crystals of sufficiently small thickness are required. Single crystals of specific orientation are first cut into slices of approximately 0.15 cm thick using a chemical string saw and a 20 wt % KCN solution. The slices are reduced to approximately 0.05 cm thick by polishing on a cloth wheel wetted with a 5 wt % KCN solution. The final thickness of approximately 0.010 cm is obtained by dipping the crystal in a 5 wt % KCN solution. The thickness of the crystal is measured with a Reichert microscope. Standard X-ray and optical techniques are used to examine the crystals to ensure they are strain free.

The ac conductance and capacitance measurements are made in a lucite cell schematically shown in Fig. 1. The silver chloride crystal is mounted in the center of the cell with Dow Corning Silicone cement, 732 RTV. The area of the exposed crystal surface is approximately 0.3 cm<sup>2</sup>. The cell is filled with 1M KNO<sub>3</sub> solution containing a specific concentration of silver ions. The silver ion concentration is denoted by  $P_{Ag}$  which is defined similarly to pH. Solutions of various  $P_{Ag}$  are prepared by adding appropriate amounts of AgNO<sub>3</sub> or KCl. The solutions are equilibrated with silver chloride particles to obtain an equilibrium solubility product. A 1M KNO<sub>3</sub> solution is required to maintain an approximately constant ionic strength. Silver electrodes are placed in each solution for electrical measurements. The cell is placed in a temperature bath controlling to  $\pm 0.02^\circ\text{C}$ .

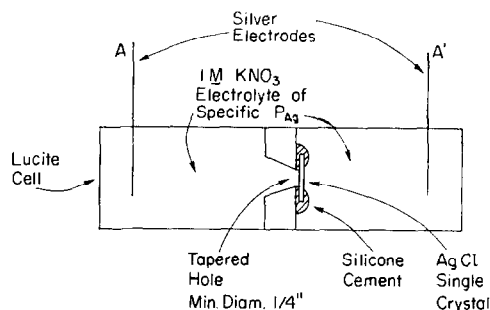


FIG. 1. Schematic diagram of conductance cell used for ac measurements.

The ac bridges used in the experiments measure the equivalent circuit of a parallel resistor  $R_m$  and capacitor  $C_m$ . The contribution from the solution phase can be ignored (5) and the measured  $R_m$  and  $C_m$  correspond essentially to the contribution from the crystal phase. In order to make ac measurements, either a Wayne–Kerr universal bridge or a General Radio capacitance bridge 1615-A is coupled with a General Radio oscillator 1203-B and a tuned amplifier null detector 1232-A. The latter system gives a wider frequency range from 20 to 10<sup>5</sup> Hz and better precision. Therefore most of the data are obtained using the General Radio system. Measurements are made as a function of frequency and applied voltage. It is noted that no appreciable applied voltage dependence is observed for voltages up to 0.8 V. All the data reported in this paper are measured at 0.3 V. The accuracy of the measurements is approximately 5%. In the next section the experimental results are reported as a function of temperature and crystal orientation.

## Results and Discussion

The ac conductance and capacitance measurements are made on crystals of the same orientation and exposed to the same environment but of varying thickness to show that the measured conductance  $G_m$  and capacitance  $C_m$  correspond to the contribution from the solid phase. Figure 2 shows the data obtained using the General Radio system at 28°C for two (100) crystals of thickness 0.00726 cm and 0.00955 cm in contact with a solution of  $P_{Ag}$  of 4.8. Qualitatively the frequency dependence of  $G_m$  and  $C_m$  represents the following physical situation. At low frequencies the measured  $G_m$  and  $C_m$  approach the steady state dc values. With increasing frequency, the frequency dependence results because the defect distribution of silver ion vacancies is not in phase with the applied potential distribution.

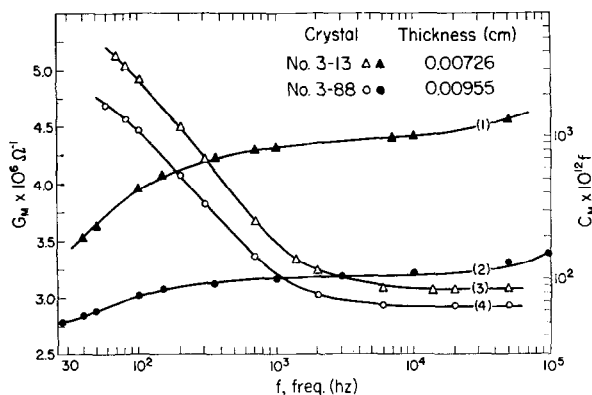


FIG. 2. Curves (1) and (2): Experimental conductance vs. frequency curves (3) and (4): Experimental capacitance vs. frequency. Two (100) AgCl crystals,  $T = 28^\circ\text{C}$ , area of exposed crystal  $0.3\text{ cm}^2$ ,  $P\text{Ag} = 4.8$ .

At the high frequency limit, the frequency is so large that the defect distribution does not deviate from its equilibrium distribution. Consequently the space charge distribution does not affect the charge motion at high frequencies and both  $G_m$  and  $C_m$  correspond to the values for the bulk crystal. In Fig. 2, the ratio of the thickness of the crystals is 1.32. At high frequencies, the ratios of  $G_m$  and  $C_m$  have this same value. The agreement leads to the conclusion that the measured  $G_m$  and  $C_m$  correspond to the contribution from the crystal phase. It should be noted also that in Fig. 2 a larger frequency dependence is observed for the thinner crystal. This is consistent with the qualitative picture that the contribution from the space charge region becomes more important for decreasing crystal thickness.

In Fig. 3 the data using a Wayne-Kerr bridge are shown for a (210) crystal of 0.0128 cm thickness in contact with a solution of  $P\text{Ag}$  of 4.8. Comparing these data with those in Fig. 2, the only significant difference is due to the variation in crystal thickness. This indicates that the space charge distribution in these crystals is not strongly effected by the crystal orientation. Since the interfacial potential also enters into the equilibrium consideration (2), the value of this potential affects the magnitude of the space charge voltage. The interfacial potential or equivalently the  $\chi$ -potential (9) at the silver chloride-aqueous solution interface results from the crystal lattice distortion and from the oriented dipoles in the solution phase. The comparison discussed above suggests that the  $\chi$ -potentials for the (210) and the (100) crystals do not vary significantly.

The effects of temperature upon the frequency

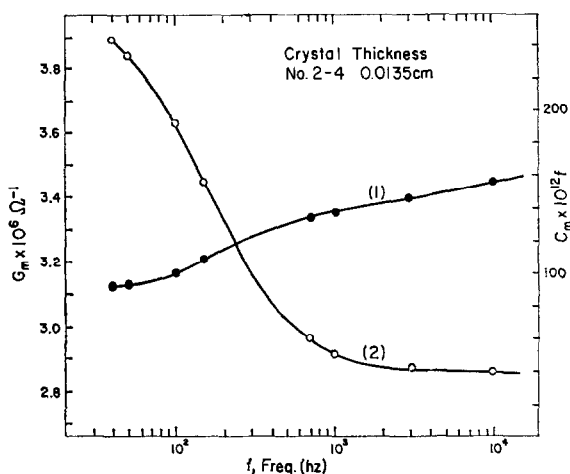


FIG. 3. Curve (1): Experimental conductance vs. frequency curve (2): Experimental capacitance vs. frequency (210) AgCl crystal,  $T = 28^\circ\text{C}$ , area of exposed crystal  $0.3\text{ cm}^2$ ,  $P\text{Ag} = 4.8$ .

dispersions are shown in Fig. 4 where the data are obtained with the General Radio bridge for a  $P\text{Ag}$  of 4.8 and a (100) orientation. At high frequencies the increase in the magnitude of  $G_m$  with temperature reflects an increase in the silver ion vacancy mobility. In the temperature range of the experiments, the space charge potential remains approximately constant (5). The variation of  $G_m$  and  $C_m$  in the low frequency region shows qualitatively that for a higher mobility, the defect distribution remains in phase with the applied potential at a higher frequency. This fact is observed in Fig. 4 where the  $G_m$  and  $C_m$  curves at higher temperatures level off at

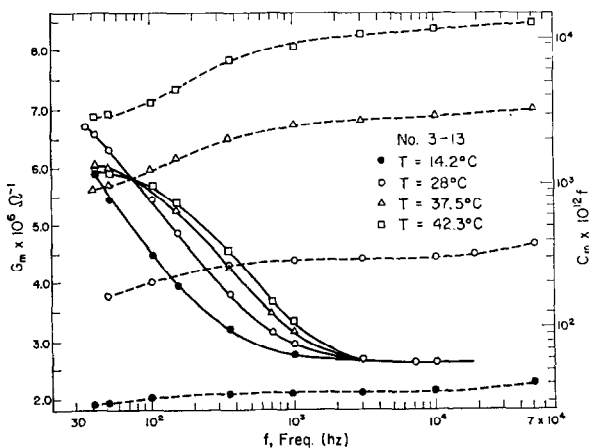


FIG. 4. Dashed lines: Experimental conductance vs. frequency. Solid lines: Experimental capacitance vs. frequency (100) AgCl crystal, area of exposed crystal  $0.3\text{ cm}^2$ ,  $P\text{Ag} = 4.8$ , thickness of crystal 0.00726 cm.

higher frequencies as they asymptotically approach the low frequency dc limit.

In order to interpret the ac experimental results and to compare them with the dc experimental results, a quantitative analysis has been made based on a diffusion controlled transport model (5). This proposed ionic transport model depends only on the following variables: The magnitude of the space charge potential, the temperature, the concentration and mobility of the silver ion vacancy, the permittivity and the thickness of the crystal. Physically this model relies on the fact that the space charge distribution of point defects near the surface of the silver chloride crystal represents a barrier to charge transport across the solid-liquid interface. Except for the space charge potential, the other variables can be determined by independent experiments. In the following discussion it is shown that using the values of the space charge potential obtained from the dc experimental results and the proposed transport model, the calculated frequency dispersion curves are consistent with the measured ones. The detailed description of the quantitative analysis is given elsewhere (5). The following discussion outlines the space charge limited transport model.

Since the silver ion vacancy concentration in the space charge region varies with the position, the frequency dispersion cannot be represented by a single relaxation process. The continuity equation for vacancy motion has to be solved. Following MacDonald (10) and Jaffe (11), the continuity equation is written as

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} + u \frac{\partial(nE)}{\partial x} \quad (1)$$

where  $n$  is the concentration of vacancies,  $D$  is the diffusion coefficient for vacancies,  $E$  is the electric field, and  $u$  is the mobility of vacancies.

Ignoring the higher harmonics, the voltage  $V$ , the field and the concentration of vacancies may be expanded as

$$V(x, t) = V_0(x) + V_1(x) e^{i\omega t} \quad (2)$$

$$E(x, t) = E_0(x) + E_1(x) e^{i\omega t} \quad (3)$$

$$n(x, t) = n_0(x) + n_1(x) e^{i\omega t} \quad (4)$$

where  $V_0$ ,  $E_0$  and  $n_0$  are the equilibrium values, where  $V_1$ ,  $E_1$  and  $n_1$  are the amplitudes of the fundamental deviations and where  $\omega$  is the angular frequency equal to  $2\pi f$ . Substituting equations (2), (3), and (4) into equation (1), the continuity equation becomes

$$i\omega n_1 = D \frac{d^2 n_1}{dx^2} + u \frac{d(n_1 E_0 + n_0 E_1)}{dx} \quad (5)$$

The total ionic current  $J$  can be written as (10, 11)

$$J = \frac{1}{l} \int_0^l \left[ eu(n_1 E_0 + n_0 E_1) + eD \frac{dn_1}{dx} + i\epsilon\omega E_1 \right] dx \quad (6)$$

where  $e$  is the magnitude of the electronic charge,  $\epsilon$  is the permittivity and  $l$  is the crystal thickness. The real and imaginary parts of the current correspond to the conductance and capacitance.

In order to calculate the capacitance and conductance at a given frequency  $\omega$  and an applied voltage  $V_a$ , Eq. (5) is solved first numerically with appropriate boundary conditions obtaining  $V_1(x)$ ,  $n_1(x)$  and  $E_1(x)$ . From these values, the capacitance and conductance can be calculated from Eq. (6). The boundary conditions and the assumptions used are:

1.  $n_1 = 0$  at  $x = 0$  and  $x = l$ , corresponding to no interfacial blocking.
2.  $\int_0^l E_1(x) dx = V_a$ .
3.  $E_1$  and  $n_1$  are related through the Poisson's equation.
4. In the bulk crystal  $V_0(x) = 0$  and  $n_0(x)$  equals the bulk value  $n_0(b)$ .
5. Following Dilworth (12),  $V_0(x)$  in the space charge region at the interface is assumed to be a parabolic function of distance. In this region  $n_0(x) = n_0(b) \exp[eV_0(x)/kT]$ .
6. The impurity ions are immobile and no other relaxation process contributes to the measured capacitance and conductance.

From dc work (3), at a PAg of 4.8 the space charge potential  $V_0$  at  $x = 0$  and  $x = l$  is approximately  $-0.26$  V measured relative to bulk  $V_0 = 0$ . Using this value and literature values of mobility and permittivity, the capacitance and conductance of the crystal is calculated as a function of frequency and crystal thickness for a temperature of 28C. The results of the calculation are shown in Fig. 5. A comparison of the curves in Fig. 2 and Fig. 5 indicates reasonable agreement. The exact agreement between the curves is not expected as the calculation is sensitive to the values of the mobility and permittivity. Better values for these parameters can be obtained of course by independent experiments.

In order to calculate the temperature dependence of the frequency dispersion, the space charge potential is assumed not to vary significantly in the

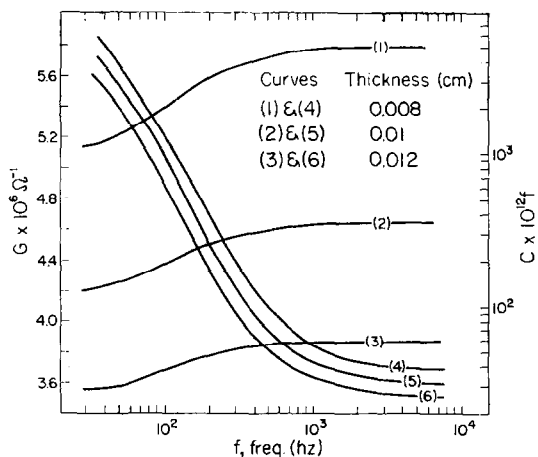


FIG. 5. Curves (1), (2), (3): Theoretical conductance vs. frequency curves (4), (5), (6): Theoretical capacitance vs. frequency  $D = 5 \times 10^{-8}$  cm<sup>2</sup>/sec.,  $V_0(0) = -0.26$  V, area of exposed crystal 0.3 cm<sup>2</sup>,  $T = 28^\circ\text{C}$ .

experimental temperature range. The literature value of the activation energy (7, 8) is used to calculate the temperature variation of the mobility. With these assumptions and the values of the parameters used above, the dispersion curves are calculated and shown in Fig. 6. Comparing the curves in Fig. 4 and Fig. 6, the essential features of the experimental curves are reproduced by the calculation. At the higher temperature, the calculated curve does level

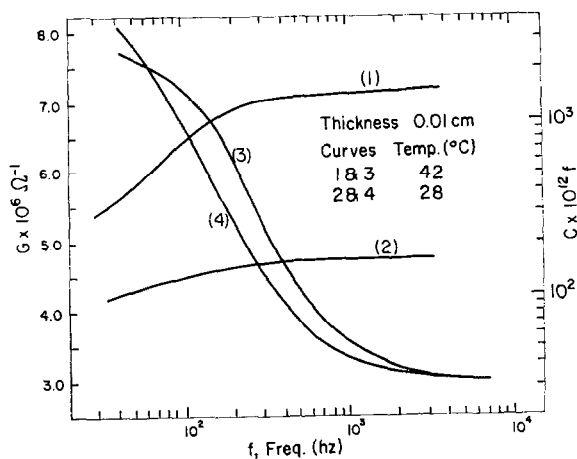


FIG. 6. Curves (1) and (2): Theoretical conductance vs. frequency curves (3) and (4): theoretical capacitance vs. frequency  $D = 5 \times 10^{-8}$  cm<sup>2</sup>/sec.,  $V_0(0) = -0.26$  V, area of exposed crystal 0.3 cm<sup>2</sup>.

off at higher frequencies as the low frequency limit is approached.

In conclusion, the following statements may be made:

1. The results of the model calculation confirm the qualitative interpretation made on the experimental results and justify the assumptions used in the model analysis.
2. The ac experimental results are consistent with the conclusions from the dc studies on the space charge distribution in silver chloride.
3. The model proposed by Grimley and Mott on the space charge distribution is supported experimentally. For ionic crystals of small dimensions, the stoichiometry of the crystal depends on the environments with which it is in contact.

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