

Pressure Dependence of the Electrical Conductivity of Ag_2HgI_4

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The electrical conductivity of Ag_2HgI_4 is primarily ionic above the order-disorder transition temperature of 50°C . Below this critical temperature, there is an appreciable electronic component. The effect of pressure, at all temperatures, is initially to increase the conductivity. However, the conductivity passes through a maximum and decreases between 4000 and 6000 kg/cm^2 . This unusual pressure behavior is not explicable in terms of any simple model. A new phase, which is presumably an analog of that occurring in AgI , appears above about 6000 kg/cm^2 . The conductivity in this phase is primarily electronic even at high temperatures. The data also suggest the possible existence of still another new phase between 4000 and 6000 kg/cm^2 . Despite the complicated pressure dependence, the temperature dependence has a simple activation energy at all pressures except in the immediate vicinity of the transition point.

I. INTRODUCTION

THE original purpose of the investigation reported here was to carry out a more extensive experimental comparison of the electrical behavior of Ag_2HgI_4 and Cu_2HgI_4 in an effort to ascertain the role of the monovalent cation.

These systems, originally studied by Ketelaar¹ are ordered at low temperatures and disordered somewhat above room temperature. Each divalent cation in the structure is associated with a vacancy in order to preserve its electrical neutrality. Above the disordering temperature T_c , both cations and the vacancy are randomly distributed on the cation sites; below T_c , they have specific ordered sites within the unit cell.

A great many interesting phenomena are associated with the order-disorder process. The following properties have been studied: specific heat,² phase diagram,³ structure,⁴⁻⁹ electrical conductivity as a function of temperature,¹⁰⁻¹² and cation diffusion.¹³ Most of the later measurements refer only to Ag_2HgI_4 , and suggest that Ketelaar's original model is oversimplified.

The experiments undertaken by us revealed such complex behavior that the original purpose was abandoned and concentration was focused on the silver salt alone. Although many of our measurements agree

in broad outline with previous results, where overlap occurs, they disagree in one major respect. Our results indicate that the conductivity in the low-temperature phase of Ag_2HgI_4 has a major electronic component, and hence cast doubt on previous theoretical discussions. Secondly, our data indicate that the pressure dependence of the electrical conductivity is rather complex, suggesting the existence of at least one and possibly two new phases.

The bulk of the work reported in the succeeding sections relate to these discrepancies. In Sec. II, we describe the experimental procedures. In Sec. III, we present the data on the temperature and pressure dependence of the electrical conductivity. In Sec. IV, we report some transport experiments. In Sec. V, some measurements on the thermal expansion of Ag_2HgI_4 are described. Finally, in Sec. VI, we give a brief summary of our results.

II. EXPERIMENTAL PROCEDURE

The Ag_2HgI_4 was made in the manner previously described by Ketelaar¹ by coprecipitating it from a solution of HgI_2 in KI and AgNO_3 . The powder was dried by leaving it 24 h under high vacuum at room temperature. X rays were used to establish that the resulting material had the known structure of the desired compound.

Pellets, $\frac{1}{2}$ in. o.d. and about $\frac{1}{4}$ in. thick, were pressed in a steel die to about 10 000 kg/cm^2 . Spring loaded electrodes of either Ag or Pt foil were used.

The conductivity of the samples was measured on ESI model 250C1 ac bridge driven at 1000 cps by a Hewlett-Packard Model 202C audio oscillator. Bridge balance was detected by a Tektronix oscilloscope Model 310A coupled to a Tektronix Type 1121 pre-amplifier to improve sensitivity.

The sample was mounted inside a pressure vessel in Dow-Corning 200 silicone (3 centistoke) which could be pumped to a pressure of 8000 kg/cm^2 by an intensifier and a Hydraulic Engineering Company air pump, Model SC 10-600-30. The temperature of the pressure

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⁹ S. Hoshino, *J. Phys. Soc. Japan* **10**, 197 (1955).

¹⁰ J. A. A. Ketelaar, *Z. Physik Chem.* **26B**, 327 (1934).

¹¹ J. A. A. Ketelaar, *Trans. Faraday Soc.* **34**, 874 (1938).

¹² L. Suchow and G. R. Pond, *J. Am. Chem. Soc.* **75**, 5242 (1953).

¹³ K. E. Zimen, G. Johansson, and M. Hillert, *J. Chem. Soc.* **1949**, Suppl. 2, S-392.

vessel was raised by an external resistance furnace. The temperature was measured by a Chromel-Alumel thermocouple placed inside the pressure vessel. The pressure was determined by the resistance change of a spool of manganin wire, calibrated by the freezing point of mercury.

The thermal expansion measurements were made on powdered samples mounted on a glass slide with stop-cock grease. A General Electric XRD-5 diffractometer was used. The sample was heated by a carbon resistance painted on the back of the slide. The temperature was measured by a point contact thermocouple immersed in the matrix containing the sample.

Two types of transport measurements were carried out. The first type was a standard Tubandt technique in which three pellets were clamped in series between a silver anode and a platinum cathode. After the passage of a given amount of charge, the electrodes and the individual pellets were weighed. This procedure is fraught with difficulty. As the current passes through the sample, heating occurs and the sample disorders. It was impractical to limit the current because of the time required to obtain a sensible change in weight in the various components of the cell. As an alternate method of estimating the electronic component in the current, a sample was clamped between a platinum and a silver electrode and the change in current was observed when the voltage across the sample was reversed. In addition, the same technique was employed with graphite replacing the platinum.

III. TEMPERATURE AND PRESSURE DEPENDENCE OF THE ELECTRICAL CONDUCTIVITY

The determination of the conductance of Ag_2HgI_4 is beset by a number of difficulties associated with hy-

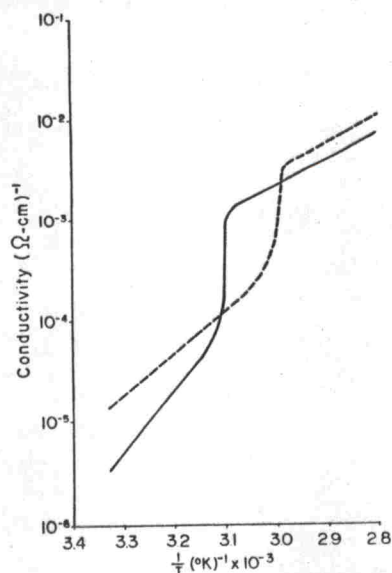


FIG. 1. The ac conductivity of Ag_2HgI_4 as a function of reciprocal temperature at atmospheric pressure (solid line) and 5000 kg/cm^2 (dotted line).

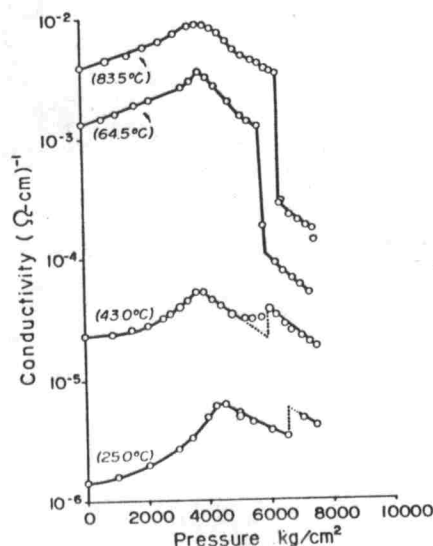


FIG. 2. The ac conductivity of Ag_2HgI_4 as a function of pressure at four different temperatures spanning the order-disorder transition temperature at 50°C.

steresis and polarization effects. If the sample is heated above the disordering temperature of 50°C and subsequently recooled, many hours must be waited before reproducible data can be obtained in the ordered phase. Firstly, an equilibrium amount of order must be established through diffusion. Secondly, a small amount of AgI appears to be formed upon cooling through the transformation owing to small deviations from perfect stoichiometry. This possibility is suggested by the known phase diagram and is confirmed by x-ray studies as described in Sec. II. Part of the hysteresis observed on freshly prepared samples undoubtedly is connected with the fact, reported by Olsen and Harris,⁸ that the room-temperature crystal structure of virgin precipitate differs from that of material cycled through the disordering temperature. As a result of these effects, the base resistance at room temperature decreases as a function of the number of thermal and pressure cycles through the transition temperature and the time subsequent to the last cycle. For this reason, care must be exercised in comparing various isobars. It has been our practice to normalize the base resistance at room temperature by interpolation to corresponding points in the history of the sample. Consequently, the absolute values are considerably more uncertain than the relative values on a given curve.

Figure 1 shows the absolute electrical conductivity of Ag_2HgI_4 as a function of temperature at atmospheric pressure and 5000 kg/cm^2 . This data is in substantial agreement with that of Suchow and Pond,¹² which differ appreciably from that of Ketelaar. The activation energy above the 50°C transition is 12.1 kcal/mole as compared to the value of 10.2 kcal/mole obtained by Suchow and Pond.

Figure 2 exhibits the pressure dependence of the normalized resistance of Ag_2HgI_4 as a function of

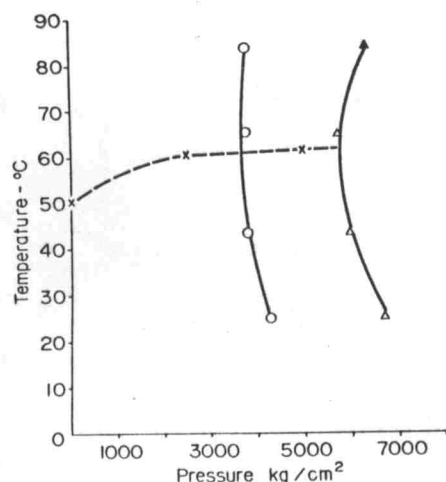


FIG. 3. A tentative phase diagram for Ag_2HgI_4 in the P - T plane. The triangles represent the boundary of the clearly defined high-pressure phase. The circles represent the maxima in conductivity as a function of pressure, which may delineate another phase boundary. The crosses represent the locus of the order-disorder transformation.

pressure at four different temperatures. Three different regimes are evident. In the first of these, extending up to about 4000 kg/cm^2 , the electrical conductivity increases. This observation is consistent with previous data obtained by Wagener¹⁴ up to about 150 kg/cm^2 on doped AgI . In the second regime, extending up to about 6000 kg/cm^2 , the conductivity decreases, returning to about its initial value at room pressure. In the third regime, above 6000 kg/cm^2 , the conductivity jumps to either higher or lower values, depending on whether the temperature is either below or above 50°C. Above this abrupt transition the conductivity decreases with increasing pressure in a normal manner. To avoid fatigue effects observed after pressure cycling, all samples were annealed at 85°C between each pressure run.

The anomalous behavior of the conductivity is strong evidence for a phase transition at approximately 6000 kg/cm^2 . Presumably, this transition is analogous to that occurring at 3000 kg/cm^2 in pure¹⁵ AgI which is known to transform from a ZnS structure to a NaCl structure. Local attempts to verify this surmise with respect to the mixed salt by x-ray diffraction have proved inconclusive.

The maximum in conductivity at approximately 4000 kg/cm^2 , observed at all temperatures, is also suggestive of a phase transition. In Fig. 3, we have plotted the discontinuities in conductivity at 6000 kg/cm^2 and the maximum in conductivity at 4000 kg/cm^2 as a tentative phase diagram. We have superimposed the order-disorder transition observed as a function of temperature as a dotted line which we have

extrapolated linearly to its intersection with the higher-pressure phase boundary.

The large decrease in conductivity observed at the higher-pressure phase boundary for higher temperatures as compared to the increase at lower temperatures (below 50°C) suggest that the high-pressure phase above 6000 kg/cm^2 is ordered.

Owing to the peculiar dependence of the resistance on pressure, it is impossible to assign an unambiguous value to an activation volume. As we show in the next section, the conductivity of the salt has an appreciable electronic component at low pressures and becomes almost completely electronic in the high-pressure phase. For this reason it does not seem profitable to attach any particular significance to the activation volume.

IV. TRANSPORT MEASUREMENTS

As explained in Sec. II, below 50°C it was impossible to carry out a Tubandt experiment in a reasonable period of time without overheating the sample so that, at least part of the time, the sample was in the high-temperature disordered phase. Partial success was obtained in a few experiments, which indicated that at least some of the transport of charge was via electrons.

To confirm this result, an asymmetrical cell was constructed with one silver and one platinum electrode. The dc resistance was alternately measured with the

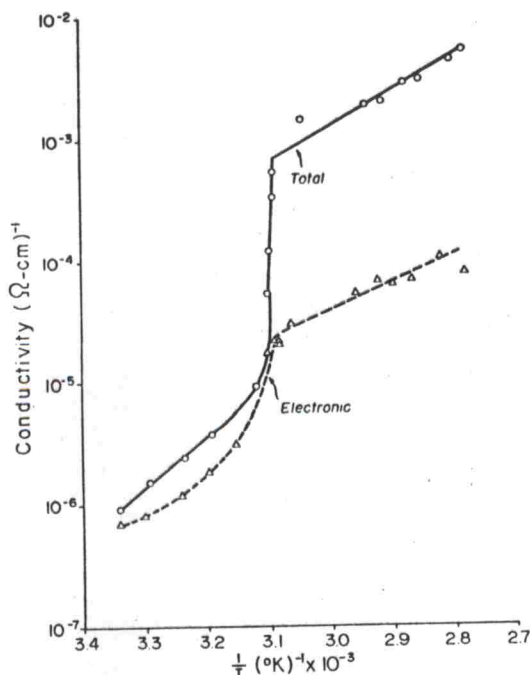


FIG. 4. The dc conductivity as a function of the reciprocal temperature. The solid line represents the total instantaneous conductivity measured with the platinum electrode as cathode. The dashed line represents the electronic contribution measured with the platinum electrode as anode.

¹⁴ K. Wagener, *Z. Physik. Chem.* **23**, 305 (1960).

¹⁵ R. B. Jacobs, *Phys. Rev.* **54**, 325 (1938).

platinum electrode as cathode and as anode. If the assumption is made that the platinum electrode blocks all of the Ag^+ ion transport, the resistance with the platinum as anode determines the electronic component of the conductivity, while the resistance with the platinum as cathode determines the total conductivity. The two conductivities are plotted as a function of temperature at atmospheric pressure in Fig. 4 and, as a function of pressure, at two different temperatures in Fig. 5. Note the large electronic component in the low-temperature phase at atmospheric pressure. This component becomes negligible above the disordering temperature compared to the ionic conductivity, in agreement with the transport data of Ketelaar. It is somewhat surprising that the general dependence of the conductivity on pressure below 6000 kg/cm^2 is the same despite difference in relative proportions of the electronic and ionic components.

The general features of the dc conductivity measurements reflect those of the ac measurements very well. However, they are only semiquantitative owing to progressive changes in the samples as a function of time. Some of these changes arising from polarization effects are reversible; some are permanent due to silver dendrite formation and other more obscure sources of hysteresis such as temporary segregation in the salt. It was found that the electronic component of the conductivity was dependent on the voltage difference applied across the electrodes, becoming smaller, the smaller the applied voltage. In all the

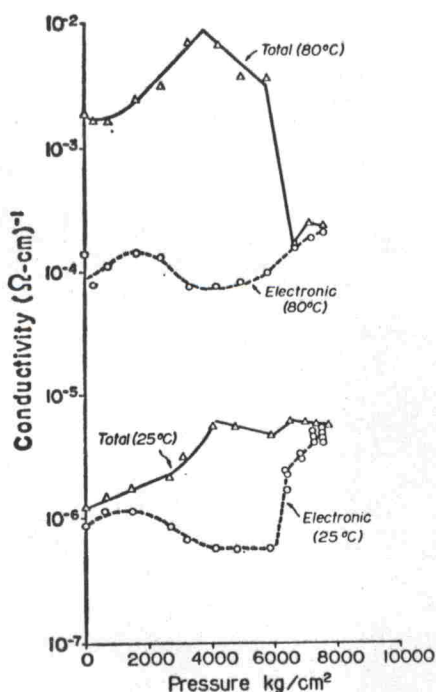


FIG. 5. The total and electronic dc conductivity as a function of pressure at 25° and 80°C.

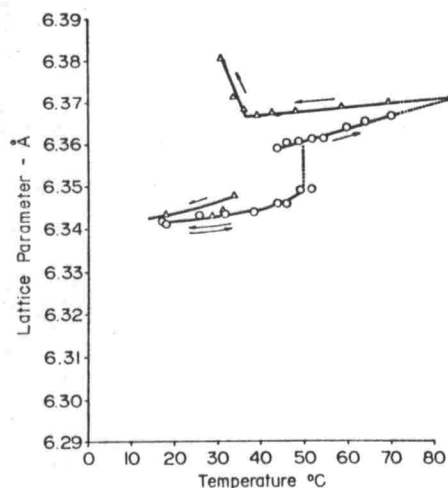


FIG. 6. The lattice parameter of Ag_2HgI_4 as determined from the (220) reflections with increasing and decreasing temperature in the neighborhood of the transition temperature at atmospheric pressure.

data reported here, the conductivity is that observed initially upon application of the voltage because secondary polarization effects change the observed current as a function of time. In the high-temperature phase, if the dc voltage is maintained for a period of the order of an hour or more, silver is deposited at the cathode and HgI_2 and I_2 are formed at the anode. This reaction results in a large drop in both the ionic and electronic components. Simultaneously, the cell is converted to a battery with an emf of 0.6 V. This emf gradually disappears over the period of a day if the cell is short circuited. The resistance of the cell is permanently changed owing to the loss of I_2 .

Because of the possibility that the platinum may actually go into solution as its potential is increased, the experiments were repeated with a graphite electrode replacing the platinum. The resulting data were in substantial agreement with those reported here, except that the electronic component was no longer dependent on applied voltage, lending credence to our general interpretation of the transport experiments. Our assumption of blocking of the Ag^+ ion by the platinum electrode is further supported by ac conductance measurements on a sample with two platinum electrodes. In this case, the conductance is strongly frequency dependent and there is a large capacity between the electrodes suggesting a large accumulation of charge at the boundaries. These effects were not present when silver electrodes were used.

V. THERMAL EXPANSION

The crystal structure of Ag_2HgI_4 is open to discussion. Hahn, Frank, and Klinger⁶ report that it belongs to the space group S_4^2 in contradistinction to the copper salt which belongs to the space group D_{2d}^{11} . Olsen and Harris report that the silver salt also belongs to the

same space group as the copper salt, although apparently its structure is a function of prior chemical and thermal history. Both sets of authors are agreed that it is pseudocubic, the former reporting the tetragonal dimensions as $a = 6.340kx$; $c = 12.608kx$; $c/a = 2.000$. This cell is twice that originally reported by Ketelaar. For our purposes, it suffices to treat the cell as cubic as we are only interested in ascertaining a linear expansion coefficient.

Figure 6 shows the lattice dimension as recorded by observing the diffraction maximum from the (220) planes. Below the transformation, the sample expands linearly with increasing temperature, corresponding to a constant linear thermal expansion coefficient of $19.2 \times 10^{-6}/^{\circ}\text{C}$. At the 50°C transformation, there is a discontinuity in volume corresponding to 1.27 cc/mole . Above the transition, the value of the linear thermal coefficient of expansion is larger, namely $41.4 \times 10^{-6}/^{\circ}\text{C}$. As the temperature is now decreased through the transformation, a certain amount of hysteresis occurs, similar to that reported by other authors.¹⁶ Below the transformation a new phase appears which we have tentatively identified as AgI. This phase gradually disappears as a function of time when the temperature is lowered below the transformation. Such a result is not surprising in view of the known phase diagram⁸ and the possible deviation of our samples from ideal chemical stoichiometry.

The purpose of this experiment was to establish the sign of the thermal expansion coefficient of Ag_2HgI_4 in view of the increase in conductance observed with increasing pressure. It has been suggested^{17,18} that such a pressure dependence of the conductivity, if ionic, would be associated with a negative thermal expansion coefficient. The experiments reported here do not support this model. The thermal expansion

coefficient is positive in a region where the ionic conductivity predominates and is increasing with pressure, e.g., at 80°C between 0 and 4000 kg/cm^2 .

Finally, it is of interest to compare the directly observed shift in disordering temperature with pressure with that calculated from the Clapeyron equation. Ketelaar reports a latent heat at the transition of 1.135 kcal/mole . The observed change in volume from the x-ray data is 0.875 cc/mole . These values correspond to a value of $dP/dT = 3.95 \text{ cal/cc } ^{\circ}\text{C}$. The experimental value is $3.9 \text{ cal/cc } ^{\circ}\text{C}$. The agreement is probably fortuitous considering the experimental errors involved in accurately estimating the latent heat and change in volume at the transition and the slope of the rather nonlinear transition line.

VI. SUMMARY

The principal conclusions drawn from the experiments described above are as follows:

- (1) The initial effect of pressure is to increase the conductivity of Ag_2HgI_4 .
- (2) The low-temperature, low-pressure phase has a large electronic component to the electrical conductivity.
- (3) A new phase appears at pressures above 6000 kg/cm^2 in which the conductivity is primarily electronic.
- (4) The data suggest the possibility of still another new phase at pressures between 4000 and 6000 kg/cm^2 .
- (5) The observed shift of the order-disorder transition pressure is in agreement with that calculated from the Clapeyron equation.
- (6) The anomalous dependence of the conductivity on pressure is at variance with the models which suggest that such a dependence is only possible if the thermal expansion coefficient is negative.

ACKNOWLEDGMENT

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¹⁷ A. W. Lawson, S. A. Rice, R. D. Corneliussen, and N. H. Nachtrieb, *J. Chem. Phys.* **32**, 447 (1960).

¹⁸ A. W. Lawson and R. T. Payne, *J. Chem. Phys.* **34**, 2201 (1961).