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Electrical Conductivity of AgI to 100 kbar*

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The electrical conductivity of AgI has been determined to 100 kbar at room temperature, using a 1-kc/sec 20-V pulse as source. Conductivity increases with pressure in the low-pressure phase, stable to 2.5 kbar, and then decreases in the two high-pressure phases. The increase in the low-pressure phase is in agreement with its negative thermal expansion. A reversal of slope above 45 kbar in the cubic (NaCl-type) phase is explained in terms of the formation of I3-, recently reported from spectroscopic studies, in amounts decreasing with pressure to 70 ± 5 kbar, where I_3 is no longer present.

INTRODUCTION

Wagener¹ determined that the electrical conductivity (σ) of AgI increases with pressure to 100 bars at 100°C. Mrgudich² measured σ of compressed AgI pellets at atmospheric pressure. The measurements of Riggleman and Drickamer³ were in the 20-280-kbar range, using direct current. In the present experiments, σ is studied to 100 kbar to provide an overlap with the above data, as well as to determine the pressure dependence of σ in a recently reported phase,^{4,5} stable in the 2.5 to 4.0-kbar region at room temperature. Duecker and Lippincott⁶ report a 500-fold increase in σ associated with the transition to this phase.

EXPERIMENTAL METHODS

The experimental arrangement has been described by Stromberg and Stephens,⁷ the sample being confined between Bridgman anvils by pyrophyllite. Pressure calibration⁸ was achieved using materials with known phase transformations between 5 and 90 kbar.9 Cylindrical specimens, 6.4 mm in diameter and 3.5 mm thick, were prepared in a piston-cylinder die to within 1% of crystal density. This method results in a mixture of stable wurtzite- and metastable sphalerite-type structures, both of which undergo a transformation at approximately 2.5 kbar.¹⁰

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- ³ B. M. Riggleman and H. G. Drickamer, J. Chem. Phys. 38, 2721 (1963)
- ¹ A. Van Valkenburg, J. Res. Natl. Bur. Std. **68A**, 97 (1964).
 ⁵ B. L. Davis and L. Adams, Science **146**, 519 (1964).
 ⁶ H. C. Duecker and E. R. Lippincott, Science **146**, 1295 (1964).
- ⁷ H. D. Stromberg and D. R. Stephens, Am. Soc. Mech. Engrs.
- Paper 64-Wa/Pt.-13 (1964). R. S. Gilmore and S. Katz (personal communication).

⁹ In this work we report pressures according to the scale of Bridgman, corrected by Kennedy and LaMori, and Drickamer.

The reader may choose to adopt the NaCl scale of R. N. Jeffery, J. D. Barnett, H. B. Vanfleet, and H. T. Hall, J. [Appl. Phys. 37, 3172 (1966), lowering the values reported here. ¹⁰ W. A. Bassett and T. Takahashi, Am. Mineralogist **50**, 1576

The electrical circuitry consisted of a audio generator, a simple resistance network, and an oscilloscope to measure voltage. A 1-kc/sec rectangular wave, 20 V peak to peak, was used as a source (a) to minimize electrode polarization and (b) to separate self-induction effects. The fixed resistance values limited the current through the specimen to 1 mA. Platinum foil was inserted between the specimen and anvil to ensure good contact and to render the electrodes inert. Values of σ measured in this manner have been corrected for compressibility, assuming a linear change using Bridgman's data.¹¹ Powdered AgI was obtained from Fisher Scientific Company.

RESULTS

For a pellet of AgI formed by precompression to 3 kbar and then cycled to 50 kbar, the initial σ value of $(2.38)10^{-4} \Omega^{-1} \cdot \text{cm}^{-1}$ (Fig. 1) falls close to Mrgudich's value of (2.24) $10^{-4}\Omega^{-1} \cdot \text{cm}^{-1}$ for mixed-phase (wurtzite and sphalerite) material. Tubandt¹² has shown that at atmospheric pressure the charge is carried solely by Ag⁺. The initial increase is in agreement with the measurements of Wagener at 100°C and is consistent with AgI containing both the wurtzite and the sphalerite forms. Such an increase in σ with pressure is thermodynamically in agreement with a negative thermal expansion of the low-pressure forms.¹³⁻¹⁵ Payne and Lawson¹⁶ have pointed this out and have used Wagener's data to calculate the pressure dependence of the activation parameters describing the diffusion of the ionic charge carrier. Since the initial values obtained here result from both the stable and metastable lowpressure forms, in unknown proportions, no attempt

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[†] Contribution No. 68-2.

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 ¹⁶ B. R. Lawn, Acta. Cryst. **17**, 1341 (1964).
 ¹⁶ R. T. Payne and A. W. Lawson, J. Chem. Phys. **34**, 2201 (1961).

has been made to calculate the activation quantities from the initial slope of the conductivity (Fig. 1).

With the initial slope attributed to the low-pressure form, the remainder of the data may be interpreted in terms of the phase diagram of AgI and the mechanical properties of the high-pressure cell. The geometry of the pressure cell is such that, during a transformation involving a volume discontinuity in the sample material, the applied load is increasingly supported by the confining solid, pyrophyllite. As a result, the transition, measured by electrical or other properties, appears spread out over an interval of applied force. Over this interval, the containing medium is compressed until the transformation in the sample is completed. However, the actual pressure on the sample cannot increase until the volume change associated with the transformation is complete.

From the calibration for the apparatus, the first inflection point (A, Fig. 1) occurs at 2.5 ± 1.0 kbar. The data between A and B (Fig. 1) are attributed to the phase change first reported by Van Valkenburg,⁴ the transformation being completed at the maximum (B, Fig. 1). Between B and C (Fig. 1), σ of this new phase decreases with pressure, as for most ionic conductors. Between C and D the transformation to the highpressure cubic (NaCl) form takes place. This interpretation of the low-pressure portion of the data is supported by (a) sound-velocity experiments on AgI in the same apparatus, in which two transformations are observed as marked changes in compressional-wave velocity and within experimental error, occur over the same applied load ranges as those between A and B, and C and D (Fig. 1); (b) ΔV for the two phase transformations are 3% and 13%, as calculated from the ratio of applied axial force in Fig. 1 and from the total ΔV for both transitions of 16.3%, as given by Bridgman.¹¹ The assumption underlying this calculation is that the rate of change of specimen volume with applied force is the same during the two transitions. These transitions are spread out over $(2.6) 10^3$ and (11.0) 10³ kg, respectively, resulting in the above volume changes. These agree well with the results of Neuhaus and Hinze,17 who measured the volume changes directly as 3.5% and 13.0%.

Neuhaus and Hinze also measured σ in the 1-bar–8kbar range, using a low-voltage dc source, with results qualitatively in agreement with Fig. 1. Their interpretation, however, differs somewhat from that given above.

Between D and E (Fig. 1), σ of the cubic phase decreases with pressure. From the calibration of the apparatus and a consideration of the above volume changes, point E is estimated to be approximately 45 ± 5 kbar. Above this pressure, σ increases to about 70 ± 5 kbar (F, Fig. 1). No phase transformations have



FIG. 1. Log σ versus applied load. Sereval pressure points, taken from the calibration for the apparatus, are shown on the abscissa for comparison.

been reported in this region^{4,11} and none have been observed by us in a diamond high-pressure cell.

DISCUSSION

Recently, Moore and Skelly¹⁸ have reported the presence of I_3^- in AgI above the transition to the cubic form (D, Fig. 1) and have indicated that the concentration of I₃⁻ is pressure dependent, going through a maximum and falling to zero before the transformation to the form stable above 97 kbar.³ A complete interpretation of σ in this region requires the transport numbers of the ionic charge carriers, information that is not presently available. However, if I⁻ is assumed not to contribute significantly to conduction at these pressures, due to its large ionic radius, the formation of I_3^- may decrease σ by inhibiting the movement of Ag⁺. This may come about either through chemical bonding or by altering the concentration of defects associated with the movement of Ag⁺. Thus, as the concentration of I_3^- decreases with pressure, σ would increase as Ag⁺ becomes more mobile (E to F, Fig. 1), until I_3^- no longer exists. Above this point, the pressure dependence of σ is normal, being controlled only by the activation volume for diffusion of Ag⁺ and not by the formation of I_3^- .

The break in slope at G (Fig. 1) may be the onset of the transformation to the form stable above 97 kbar. Transformation to this phase could not be completed within the physical limits of the pressure cell. Van Valkenburg⁴ has estimated the volume change at this transition to be 10%-20%, based on the observed change in index of refraction.

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¹⁸ M. J. Moore and D. W. Skelly, J. Chem. Phys. 46, 3676 (1967).

The 500-fold increase in σ , reported by Duecker and Lippincott at approximately 2.5 kbar during the initial phase change, is not observed in these studies. This may be due to a combination of (a) photodissociation and (b) a high mobility of charge carriers resulting from the large pressure gradient in their apparatus.¹⁹

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R. S. Gilmore calibrated the high-pressure equipment as part of another study. The authors are indebted to him for his technical assistance and numerous discussions. The experimental work was performed at Rensselaer. R. N. S. gratefully acknowledges funds made available at Chicago through the Petroleum Research Fund of the American Chemical Society.

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Effect of Adsorption of Gases on the Semiconductive Properties of All-trans β -Carotene

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The presence of various adsrobed gases increases the semiconduction currents in crystalline powder of β -carotene by several orders of magnitude and decreases the activation energy for semiconduction. The current increase depends on the amount and nature of the adsorbed gas. The process is reversible simply by desorbing the gases. The kinetics of the conductivity rise follow the Roginsky-Zeldovich equation for the adsorption-time correlation. It has been noted that the adsorbed gases have no effect on the σ_0 term, i.e., the mobilities of the charge carriers and the number of conducting states do not change. A value of $\sigma_0 \approx 1.0 \times 10^{-3} (\Omega \cdot \text{cm})^{-1}$ has been measured. Assuming a value for the radius of polarization field, R=5.3 Å and using the measured values of the dielectric constant, values for the activation energies of β -carotene with adsorbed O₂ and methanol, and also the increment in current expected, have been predicted. The measured values are in good agreement with these. We conclude that the changes in the effective dielectric constant (possibly due to formation of donor-acceptor complexes) and the consequent changes in the activation energy can satisfactorily account for the electrical behavior of all-*trans* β -carotene crystals when various gases are adsorbed on it.

I. INTRODUCTION

Adsorption of gases changes the semiconductive properties of both organic and inorganic solids in a reversible manner-reversible because one can return to the initial value of current simply by desorbing the gases. It has been known since the work of Fritsch,¹ Hartmann,² and Meyer³ that for inorganic semiconductors the activation energy for the production of free-current carriers decreases with an increase in the concentration of defects or impurities. In organic semiconductors also, it has been observed to be a general phenomenon that the activation energy for semiconduction changes with gas adsorption-a lowering of the activation energy increases the conductivity. Adsorption of oxygen increases the semiconduction current in all-trans β carotene powder by three orders of magnitude⁴ and the activation energy is decreased by 0.23 eV. The conductivity of dry lipids⁵ and proteins⁶ increases on hydration and the increase in current can be completely accounted for by the decrease in activation energy.

The increase in current and the lowering of activation energy depends on the amount of water adsorbed. It has been proposed by Rosenberg⁶ that in proteins, the adsorbed water increases the effective dielectric constant of the protein and lowers the work necessary to separate the charges due to the increase in the polarizability of the medium. The increase in dielectric constant may be due to (a) physical mixture with a gas of higher dielectric constant, (b) an interaction between the adsorbed molecule and the substrate leading to some change in the molecular state of the semiconducting material which produces an increase in the molecular polarizability, and (c) the formation of a chargetransfer complex, in which the partially dative groundstate (D^+A^-) may contribute a larger dipole moment.

From a study of the semiconduction of anthracene and chloranil when exposed to iodine and amine vapors, respectively, Labes et al.,7 concluded that formation of charge-transfer complexes at the surface leads to carrierinjection processes in the bulk. The conductivity of a zinc oxide thin film increases in the same order as the electron-donating properties of the functional group of

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