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Effect of pressure on ionic conductivity in rubidium silver iodide and silver iodide

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The effect of pressure on the ionic conductivity of $RbAg_4I_5$ and AgI has been measured, using single crystals and polycrystalline samples, up to pressures of 6 kbar. The activation volumes for motion in α-$RbAg_4I_5$ and β-$RbAg_4I_5$, respectively, are -0.4 ± 0.2 and -0.2 ± 0.1 cm^3/mole. In α-AgI, the motion volume increases from 0.56 ± 0.1 cm^3/mole at 435 K to 0.8 ± 0.1 cm^3/mole at 623 K. These values are unusually small in relation to the activation energies and are not consistent with the strain-energy model or a domain-diffusion mechanism. The logarithms of the ionic conductivities of α- and β-$RbAg_4I_5$ increase linearly at first and then decrease quadratically with pressure. This is related to the large quadratic pressure dependence of the second-order transition temperature $\Delta T_c(\mathrm{K}) = 0.141 P(\mathrm{kbar}) + 0.111 P^2(\mathrm{kbar}^2)$. The variation of the 122-K transition temperature with pressure is $\Delta T_c(\mathrm{K}) = 5.65 P(\mathrm{kbar}) - 0.53 P^2(\mathrm{kbar}^2)$, implying a molar volume change of $V_\beta - V_\gamma = 0.37 \pm 0.01$ cm^3/mole and a change in compressibility $K_\beta - K_\gamma = (0.033 \pm 0.001) \times 10^{-11}$ cm^2/dyn across the transition. The ionic conductivity of γ-$RbAg_4I_5$ initially decreases with an activation volume of 9 ± 1 cm^3/mole, and then levels off with increasing pressure. The negative activation volume for conduction along the c axis in β-AgI has been confirmed. Both low-temperature phases have large formation volumes consistent with the theory of Rice *et al.* of transitions to the superionic phase.

I. INTRODUCTION

A. Ionic conductivity in superionic conductors

A group of materials known as superionic conductors or solid electrolytes has recently aroused widespread interest not only as a result of their potential use in high-energy-density batteries, but also because of their remarkable physical properties. Of these materials, $RbAg_4I_5$ and AgI have two of the highest ionic conductivities. From estimates of the maximum ionic conductivity possible in a superionic conductor such as AgI, it is evident that nearly all the silver ions must contribute to the conductivity. This is an essential characteristic of all superionic conductors. The almost complete disorder of one species of ion raises several important questions. First of all, as the number of defects becomes equal to the number of ions, it becomes impossible to identify vacancies and interstitials—there are no regular lattice sites. This difficulty can be resolved by treating all the ions as interstitials with more than one available site. Secondly, do the ions spend more time on their interstitial sites or between them? Eckold *et al.*,[1] in a neutron-diffraction study of AgI, conclude that the flight time is actually longer than the residence time. However, a recent extended x-ray absorption fine structure (EXAFS) experiment[2] indicates the opposite. At any rate, the two times are manifestly comparable. Finally, cooperative effects between the moving ions must be significant in these systems; the Coulomb repulsion between diffusing ions may govern which sites are occupied and when a diffusion jump can occur.

Numerous models[3-10] have been proposed to account for the short residence times, the interactions between the ions, the characteristically low activation energies, and certain first- and second-order phase transitions which sometimes accompany superionic conductivity. All of these models must, in the end, yield the classical Arrhenious expression for the conductivity observed experimentally. This does not mean that cooperative effects are unimportant, simply that they have been absorbed into the classical parameters. Indeed, there is strong evidence that the mobile ions interact, namely, the occurrence order-disorder phase transitions in some systems. There is also evidence that the ions of the host lattice may cooperate in the diffusion jump: a recent molecular-dynamics study[11] of α-AgI shows that the movement of the I ions is crucial in describing the diffusion of the Ag ion.

$RbAg_4I_5$ has both a second- and first-order phase transition as shown in Fig. 1. At the 208-K transition, the Ag ions partially order, slightly changing the slope. The 122-K transition induces a sharp two-orders-of-magnitude decrease in the conductivity. The three different phases, from high temperature to low, are designated α, β, and γ. Geller[12,13] has recently succeeded in solving the crystal structures of the α and β phases.

Pardee and Mahan[14] pointed out the Ising-like behavior of existing heat-capacity data[15] near the 208-K transition; they proposed a model[16] giving an Ising-like Hamiltonian for order-disorder transitions in superionic conductors. Based on

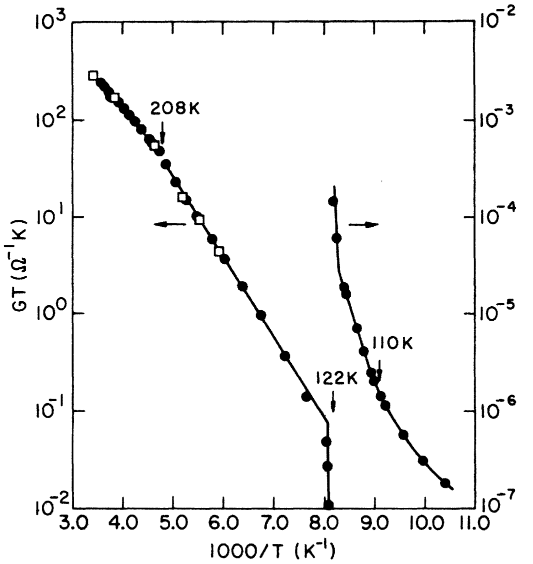

FIG. 1. Temperature dependence of the conductance of a $RbAg_4I_5$ pellet sample (closed circles) and of a single crystal normalized to the pellet's room-temperature value (squares).

ac calorimetry, optical birefringence studies,[17] and the crystal structures determined by Geller, Salamon[18] proposed a Jahn-Teller-like model for the 208-K transition. In this model there are 24 equivalent tetrahedral sites per unit cell arranged in pairs sharing a face. Pseudospin operators represent the occupation of one or the other of these sites, and the spins are then coupled by the induced lattice distortions or phonons. An Ising Hamiltonian for the effective interaction may be written

$$H_{\mathrm{eff}} = -\sum_{ij} J_{ij} S_i^z S_j^z , \tag{1}$$

where the sum is over all pairs of sites, and J_{ij} is a coupling energy. The critical-point exponents found from the heat-capacity and optical studies agree well with those predicted by the Ising model.

In addition, a careful examination[19] of the ionic conductivity near the second-order transition shows that the activation enthalpies do not change discontinuously forming a simple knee. Instead, $d(\ln\sigma)/dT$ scales with the singular part of the specific heat implying a direct relation between the ordering enthalpy of the Ag ions and the difference of activation enthalpies between the two phases.

Hexagonal AgI (β-AgI) transforms to the superionic, body-centered cubic modification (α-AgI) at 420 K via a first-order transition. The crystal volume decreases by about 6% (Ref. 20) going from the β to α phases, and pressure strongly reduces the transition temperature. There is also another low-temperature cubic modification (γ-AgI) that is metastable.

There has been some disagreement in the literature over the existence of an order-disorder transition in AgI, analogous to that at 208 K in $RbAg_4I_5$, at around 703 K. Perrot and Fletcher[21] report a singularity in the heat capacity at 703 K contingent on preserving sample stoichiometry; Jost[22] observes none. Kvist and Josefson[23] originally did not find a knee in their conductivity studies, but more recently[24] have seen a decrease in activation enthalpy for conduction and an increase in activation enthalpy for diffusion at 683 K. These results remain puzzling in view of the connection between diffusion and the conductivity through the Nernst-Einstein equation.

Rice, Strässler; and Toombs[25] theorize that the first-order transitions are the result of increasing Frenkel disorder below the transition. The interstitials interact with the strain field they create and, at a critical concentration, the defect population becomes unstable. The important result of their model is that the activation volume below T_c has an upper and lower bound requiring large formation volumes. They find that the conditions are approximately met by AgI. Hydrostatic pressure should lower (raise) the transition temperature in this model, if the formation volume below T_c is negative (positive), since it is energetically favorable for more interstitials to form. The model does not account in any way for the change in crystal structure at the transition; it is therefore only qualitatively valid.

B. Pressure dependence of ionic conductivity

A useful parameter in sorting out diffusion mechanisms is the activation volume. It can be determined by diffusing radioactive tracers under pressure or, in ionic crystals, by measuring the effect of pressure on the conductivity. In the case of some superionics, such as $RbAg_4I_5$, the high diffusivities at room temperature and the difficulties in growing large single crystals clearly point to the measurement of ionic conductivity as the most convenient method. According to reaction-rate theory[26] the diffusivity of the interstitials may be written

$$D_i = \eta a^2 \nu e^{-\Delta G_m/kT} , \tag{2}$$

where η is a geometrical factor near unity, a is a jump distance, k is Boltzmann's constant, and T is the absolute temperature. ν is an average frequency with which the interstitial attempts to surmount a Gibbs free-energy barrier of height ΔG_m; ν is sometimes equated to the Debye frequency ν_D. The ionic conductivity is simply related to the diffusion coefficient by the Nernst-Einstein relation

$$\sigma = n_i \mu_i e = n_i e^2 D_i / kT \,, \tag{3}$$

where μ_i and n_i are the mobility and concentration of the interstitials. n_i is given by

$$n_i / N_0 = e^{-\Delta G_f / 2kT} \,, \tag{4}$$

where N_0 and ΔG_f are the concentration of ions on the disordered sub-lattice and the Gibbs free energy of formation for a Frenkel defect. The ionic conductivity for interstitial diffusion may be rewritten in terms of the thermodynamic parameters for diffusion

$$\sigma = (N_0 e^2 / kT) \eta a^2 \nu \exp\left[- \frac{(\Delta G_f / 2 + \Delta G_m)}{kT} \right] \tag{5a}$$

$$= \frac{N_0 e^2}{kT} \eta a^2 \nu \exp \frac{\Delta S_f / 2k + \Delta S_m}{k} \left[\exp \frac{-\Delta E_f / (2 + \Delta E_m)}{kT} \right] \times \left[\exp \frac{-P \Delta V_f / (2 + P \Delta V_m)}{kT} \right] . \tag{5b}$$

Here the ΔS's, ΔE's, and ΔV's are changes in entropy, internal energy, and volume for the formation and motion of defects; P is the external pressure. The activation volume can be easily extracted from Eq. (5b):

$$\Delta V = \Delta V_f / 2 + \Delta V_m \tag{6a}$$

$$= -kT \left(\frac{\partial \ln \sigma}{\partial P} \right)_T + kT \left(\frac{\partial \ln \nu}{\partial P} + \frac{2 \partial \ln \alpha}{\partial P} \right) . \tag{6b}$$

The last term is small and can be estimated from the compressibility K, and the Grüneisen constant γ:

$$\Delta V = -kT \left(\frac{\partial \ln \sigma}{\partial P} \right)_T + kT \left(\gamma K - \tfrac{2}{3} K \right) \tag{7}$$

In the superionic phases of AgI and $RbAg_4I_5$, all the silver ions may be treated as interstitials, giving

$$\Delta V = \Delta V_m \, . \tag{8}$$

Theory has had only modest success in calculating activation volumes. In the strain-energy model of Zener and Keyes[27,28] ΔV is related to ΔG by

$$\Delta V = \left[\left(\frac{\partial \ln C}{\partial P} \right)_T - K_T \right] \Delta G \,, \tag{9}$$

where C is an effective shear modulus, and K_T is the isothermal compressibility. This expression is also obtained for, and is thought to be more valid for, the relationship between ΔV_m and ΔG_m. This theory explains the negative activation volume of hexagonal AgI: it has a negative coefficient ot thermal expansion that leads to mode softening under pressure in the Grüneisen approximation. In many cases, however, only order-of-magnitude agreement is found.[26]

The dynamical theory developed by Rice,[29] Slater,[30] and Flynn[26] treats a diffusion jump as a superposition of phonons. ΔV_m is related to ΔG_m by the effect of pressure on the frequency of a typical phonon involved in the jump process

$$\Delta V_m = \frac{1}{\nu^2} \left(\frac{\partial \nu^2}{\partial P} \right)_T \Delta G_m \, . \tag{10}$$

Short-wavelength optical modes should be most efficient in producing a jump in ionic crystals. This casts further doubt upon the reliability of the strain-energy model, which is usually formulated in terms of acoustical-mode moduli. Unfortunately, data on the pressure dependence of the optical-mode phonon frequencies are scarce.

In superionics, such as $RbAg_4I_5$ and AgI, considerable effort is saved by not having to separate the migration from the formation volume. However, this simplification is more than overcome by difficulties in interpretation. All of the problems in characterizing superionic diffusion with an activation energy are present when discussing activation volumes. Just as cation-cation interactions enter into migration energies, they can enter into migration volumes. Despite these difficulties, ΔV_m is a valuable test of a complete theory of superionic conductivity. At least, some qualitative statements can be made about ΔV_m. Domain motion or any collective motion involving large numbers of atoms would almost certainly have an activation volume which is large compared to normal salts. If the diffusion process is basically the same as in normal Frenkel disordered salts, one would expect activation volumes around 2 cm^3/mole. A very small or negative activation volume would be evidence that the usual picture of diffusion is inaccurate for these materials.

C. Present experiment

Studies of the ionic conductivity as a function of temperature have not led to a full understanding of diffusion in superionics. The aim of the present experiment was to elucidate the diffusion mechanism and the nature of the collective interactions between the mobile ions in two superionics, $RbAg_4I_5$ and AgI, by measuring their activation volumes and the effect of pressure on their phase transitions. Measurements were made on their low-temperature phases to help distinguish the properties of the disordered state from those of normal salts.

$RbAg_4I_5$ and AgI were chosen for a number of reasons. A large amount of information that facilitates the interpretation of results already exists:

structure,[12,13,31,32] elastic properties,[33,34] ionic conductivity,[22,35,36] heat capacity,[17,21] neutron scattering,[1,37] and optical studies[38,39] have been done on one or both materials. $RbAg_4I_5$ and AgI are similar in many respects: both compounds are primarily composed of Ag and I, have cubic high-temperature phases with nearly the same conductivities, and have low-temperature phases with low conductivities. These similarities invite comparisons and allow some generalization of results. In terms of sample preparation, the two materials are complementary. Single crystals of the room-temperature modifications α-$RbAg_4I_5$ and β-AgI can be grown, but single crystals of γ-$RbAg_4I_5$ and α-AgI are difficult, if not impossible, to obtain due to the destructive first-order structural transformations. Comparison of pressed-pellet and single-crystal data for superionic $RbAg_4I_5$ provides a check on the reliability of pressed-powder sample data for superionic AgI. $RbAg_4I_5$'s 208-K phase transition has been thoroughly investigated except for the effect of pressure; AgI's questionable 703-K transition requires more attention.

Several studies[40,41] of the effect of pressure on the ionic conductivity of β-AgI have been made, including a determination of the variation of the first-order transition temperature with pressure. No corresponding pressure work has been done on β or γ-$RbAg_4I_5$. Schock and Hinze,[41] in their study of β-AbI, reported a sudden change in the activation volume for conduction in the c-axis direction at 345 K and irreversible changes in the conductivity at pressures in excess of 1 $k$bar, for single crystals. These effects were absent in their pressed-pellet results and those of Hoshino and Shimoji.[40] The single-crystal data merit confirmation.

Since conductivities are of the order of $1(\Omega\,\mathrm{cm})^{-1}$, one of the major difficulties encountered in measuring conductances in the superionics is the fabrication of low-resistance contacts. In this experiment, sample resistances were kept as high as possible to alleviate this problem. The small size of the $RbAg_4I_5$ single crystals made the preparation of long thin samples impossible; in this case, it was necessary to use a four-wire ac technique. Section II describes sample preparation and the experimental apparatus in more detail.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

A. $RbAg_4I_5$

High pressures were generated with an Aminco 30 000-psi air-driven gas compressor and a Harwood 15 : 1 intensifier powered by an air-driven oil compressor. Argon gas was used as the pressure medium whenever possible; at the low temperatures required for some of the runs on $RbAg_4I_5$, helium gas was substituted. The pressure was measured to within 1% absolute with a Harwood manganin gauge.

The pressure vessel was machined from Vasco Max 300 maraging steel and hardened to a yield strength of 300 000 psi. It was surrounded by a vacuum can connected to a vacuum system and into which helium exchange gas could be bled. Details of the design of the apparatus have been reported elsewhere.[42] The vacuum can was immersed in a Dewar of liquid nitrogen. A Pt resistance thermometer and a heater winding were wound directly around the pressure vessel. An Associated Electrical Industries, Ltd. resistance-thermometer bridge and controller controlled the current through the heater windings. The four enameled copper leads and two fiberglass insulated Chromel-Alumel thermocouple wires were brought out through frozen oil seals.

Two different sample holders were used for the $RbAg_4I_5$ measurements, one for single crystals and one for pellets. The single-crystal sample holder consisted of a cradle-shaped Teflon support with a varnished copper block fit snugly into a rectangular slot. A thermocouple, insulated at the tip, was inserted into the middle of the copper block. The crystal was thermally connected to the copper with a small dab of silicone grease. The pellet sample holder was identical except for a cylindrical cavity replacing the copper block. The thermocouple was positioned within a few millimeters of the pellet. A subsequent check demonstrated the absence of any detectable thermal gradients in the vicinity of the sample.

The conductances of all the pellet samples and one or two of the single crystals (contact resistance was negligible in some of the low temperature runs) were measured with a General Radio 1608-A impedance bridge and a Hewlett-Packard 302A wave analyzer serving as a tuned null detector. The frequency could be varied from 1 to 50 kHz to insure that there was no capacitive electrode blocking. With the electrode arrangements, to be described later, it was found that the conductances were frequency independent, and most runs were made at 1 or 10 kHz. Conductances were so small for the γ-$RbAg_4I_5$ samples, that they had to be measured indirectly on the capacitance circuit of the bridge.

In the single-crystal samples, conductances were so large that they were measured with a four-wire ac technique to circumvent the contact resistance problem. A variable-frequency signal generator and Hewlett-Packard power amplifier suppled a constant current through a decade reference resistor and the sample. The voltages across the sample and the reference resistor were measured with an ac digital voltmeter; the conductivity was proportional to the ratio of these two voltages. A blocking capacitor after the amplifier prevented any dc current from flowing through the sample and electrolyzing the contacts. Again, conductances were found to be frequency independent, and runs were usually made at 10 kHz. Voltages across the sample were of the order of 50 mV.

Critical temperatures were detected by changes in resistivity. At the 208-K transition, there is a singularity in $d(\ln\sigma)/dT$. An x-y recorder was used to monitor the resistance of the sample continuously through the transition. The relative positions of the inflection point could be determined to within 0.1 K. The 122-K transition was observed on the x-y recorder by the discontinuous change in sample conductance.

Single crystals of $RbAg_4I_5$ were grown from solution according to the method of Manning, Venuto, and Boden.[43] The success of this method seemed to depend on the ambient humidity: erratic results were obtained until the temperature-controlled water baths were replaced with an incubating oven ventilated with dried air. Powdered $RbAg_4I_5$ was prepared by melting stoichiometric amounts of dried 99.999% AgI(subsequent chemical analysis contradicted this claim: see Sec. III.) and 99.99% RbI in a platinum crucible, rapidly quenching the melt, and pulverizing it with a mortar and pestle. It was important to quench the melt in order to obtain single-phase $RbAg_4I_5$: if it were cooled slowly, a solid mixture of AgI, Rb_2AgI_3, and $RbAg_4I_5$ would result since the compounds are incongruently melting, as is evident from the complicated phase diagram.[44] Estimates of the absolute conductivity from the pressed powder sample measurements indicated the quenching was successful in suppressing the formation of unwanted compounds.

Preparations of useful samples from the single crystals and powdered chemical included several steps. The single crystals, whose largest dimensions were often smaller than 5 mm, were sanded into thin rectangular slabs, using 600-grit sandpaper. A number of electrode arrangements were tried. The lowest resistance and most durable contacts were made by melting small amounts of Ag powder into the surface of each corner. Fine lead wires were attached to the Ag powder using a special toluene-base Ag paint purchased from Micro-Circuits Co. Pressed-pellet samples were formed in a $\frac{3}{8}$-in. maraging steel die. Powdered $RbAg_4I_5$ was pressed cold at pressures of 75 000 to 100 000 psi for about a day, yielding pellets that were 99% of observed bulk density. Most of these pellets were mounted on wood with beeswax and cut to a zig-zag shape with a small carborundum cutoff wheel, to maximize the resistance. The beeswax was then dissolved with trichlorethylene to free the sample. Contacts were formed by melting in V-shaped filaments of 0.005-in. Ag wire. Typical room-temperature resistances for these samples were ~200 Ω. A few of the pellets were made into high-conductance samples useful for exploring the γ phase by melting Ag powder into the entire surface of each face and attaching leads with the special Ag paint.

The conductance as a function of temperature at atmospheric pressure was measured using a high-conductance pellet sample (one with electrodes covering each face), through all three phases. Near room temperature, lead resistance was corrected for; near liquid-nitrogen temperatures, where low sample conductance forced the use of the capacitance circuit of the bridge, lead capacitance was corrected for. The data points were taken by adding exchange gas to rapidly cool to the desired temperature and then removing it to allow partial equilibrium. The conductivity of one single crystal was estimated at several temperatures using a series expansion for a rectangular block with point electrodes.[45,46] These values agreed well with the results of Owen and Argue.[35]

Most runs measuring the effect of pressure on the 208-K phase transition were conducted by pressurizing, and then heating the single crystal at a rate sufficiently slow to preclude any thermal lag between the sample and the thermocouple. No hysteresis was found between heating and cooling on these runs. A few of the initial runs, however, needed corrections for just such thermal lag; a smaller lag was present in the pressurized runs than in the zero-pressure runs because of the additional thermal conductivity of the gas. The effect of pressure on the thermocouple emf was estimated by allowing the pressure vessel to come into complete equilibrium at the set point, at 1 bar and at 4 kbar. A correction of 0.02 K/kbar was added to the temperature. A reference point at 1 bar was taken for each sample; any dependence of T_c on different samples could then be subtracted off. However, this precaution proved to be unnecessary since all T_c's fell within 0.1 K of one another.

The effect of pressure on the 122-K transition was measured in a similar fashion, only on pellet samples instead of single crystals. Care was taken to pass through the transition slowly. Yet, a residual hysteresis of 2 K was unavoidable. Again, a data point at 1 bar was taken for each of the two samples so that any sample dependence of T_c could be subtracted off.

B. AgI

The high-pressure apparatus used for the AgI studies was nearly identical to that used for the $RbAg_4I_5$ studies. A dry-ice–acetone cold trap was added in the pressure line before the pressure vessel to prevent oil contaminants from reaching the sample. The vessel itself was a duplicate, but a tube furnace replaced the vacuum can. The sample holder was of the same design as the $RbAg_4I_5$ pellet cradle, except that it was machined from Lavite. For the single-crystal measurements, a small leaf-spring contact was fastened to the holder by one of the screws. It held the sample against a piece of silver foil on the bottom of the cylindrical cavity.

The AgI single crystals were grown using the following method due to Hills.[47] AgI was added to a saturated solution of KI until no more would dissolve. A small amount of concentrated KI solution was added to dissolve any remaining AgI. The resulting solution was poured into crystalizing dishes which were placed inside jars with distilled water in the bottom. As evaporated water slowly diluted the solution, AgI, in the form of hexagonal pyramids, was precipitated. The solution was kept in the dark for one to two months; typical crystals obtained after this time were 4 mm high and 3 mm across the base. A semiquantitative mass spectrographic analysis indicated the crystals contained 300-ppm (within a factor of 5) K. The major divalent impurities present were Fe (100 ppm) and Ca (80 ppm). These crystals could be easily cleaved perpendicular to the c axis by mounting them on a glass slide with beeswax and slicing them with a razor blade. The faces of the sections were coated with Ag paint or alcohol dag to form contacts. Pellets were made by cold pressing AgI powder for about a day at 75 000 to 100 000 psi, giving sample densities of 96%–98% of the observed bulk density. To make high-resistance samples, the pellets were glued to wood using Duco cement and slits cut into them using a $\frac{3}{32}$-in. end mill. Then, acetone was used to dissolve the glue. Contacts were made by melting in 0.005-in. Ag wires. A few samples had melted-in Pt wires to ascertain whether excess silver from the contacts was affecting the conductivity. Typical sample resistances above the first-order transition were ~100 Ω.

All conductance measurements on AgI samples were done with the impedance bridge operating at 1 kHz or, in some instances, 10 kHz to overcome electrode blocking. Because of the relatively loose coupling between the furnace and the pressure vessel, temperature equilibrium was established much more slowly than for the low-temperature vessel. For this reason, the conductance as a function of temperature was measured as the sample gradually heated or cooled. Temperature stability was quite good, once achieved; the maximum variation during a pressure run was 0.5 K. No correction for the effect of pressure on the thermoelectric power of the Chromel-Alumel thermocouple was made since in the temperature range studied the correction term is less than 0.1 K/kbar.[48] The variation of the 420-K transition with pressure was measured and a search for the 703-K transition undertaken with the x-y recorder arrangement described.

III. RESULTS

A. $RbAg_4I_5$

Several runs measuring the temperature dependence of the conductance were made on pellet samples. Figure 1 shows the results from one such run as well as data from a four-wire, single-crystal measurement normalized to the same room-temperature conductance. Four-wire measurements below 150 K were troublesome because the high resistance between the voltage probes gave rise to a large noise background. The 208- and 122-K phase transitions are evident. A least-squares analysis of the pellet data gives $\Delta E_\alpha = 0.12 \pm 0.01$ eV and $\Delta E_\beta = 0.17 \pm 0.01$ eV for the activation energies, in agreement with other investigations.[19]

Figures 2 and 3 show the results for pressure runs on single crystals in the α and β phases, respectively. Corrections for the compressibility have been made using the room-temperature bulk modulus (1.09×10^{11}) dyn/cm^2.[33] More than thirty samples were used, but in many cases the sample or one of the contacts broke during the run, and the data were discarded. Sometimes, data could only be taken on increasing or decreasing pressure. For example, the 156-K run was made using the impedance bridge to measure the resistance between two of the contacts on decreasing pressure; one of the other contacts opened during pressurization. All of the other runs were four-wire measurements, however. The 211-K data were taken just above the transition to illustrate the effect of pressure on the inflection point. The most striking feature of the data, in general, is the small size of the effect; the conductances vary by at most 10% in 6 kbar. Another interesting feature is the nonlinearity of the plots; the conductivity increases slightly at first and then decreases. The lines through the data are least-squares fits to a quadratic. A more complete discussion of the curvature will be deferred until

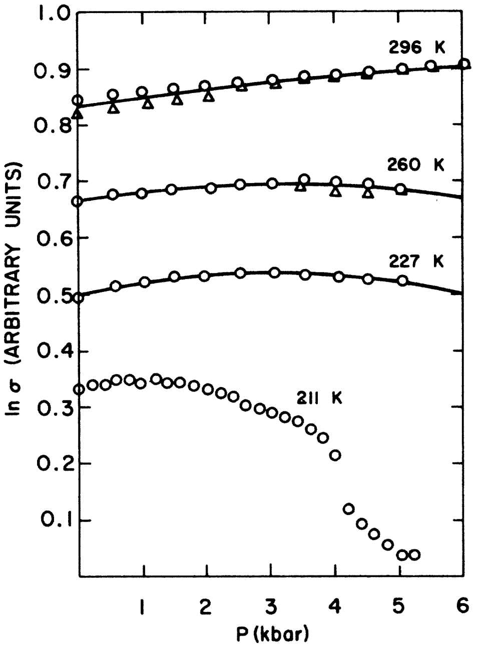

FIG. 2. Effect of pressure on the ionic conductivity of single crystal α-$RbAg_4I_5$. Circles, increasing pressure; triangles, decreasing pressure. Runs have different arbitrary units.

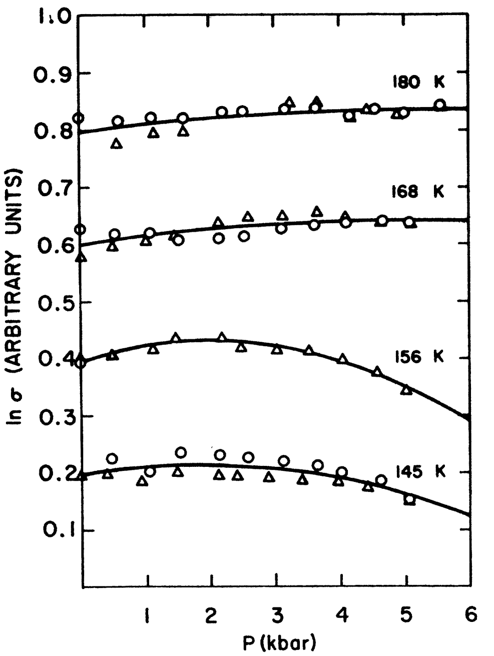

FIG. 3. Effect of pressure on the ionic conductivity of single crystal β-$RbAg_4I_5$. 156-K run was made with bridge.

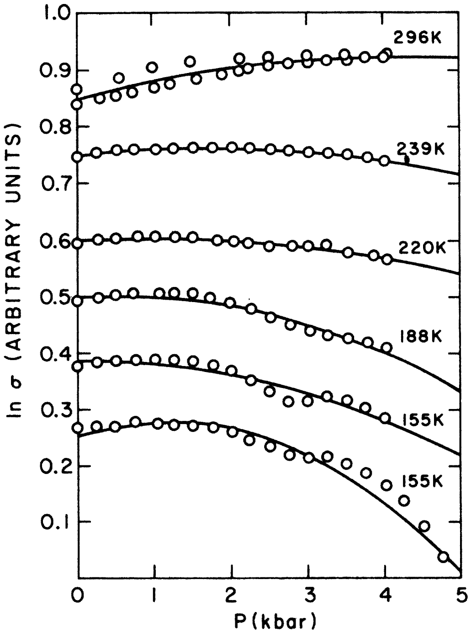

FIG. 4. Effect of pressure on the ionic conductivity of pellet α- and β-$RbAg_4I_5$. Runs have different arbitray units.

Sec. IV.

Figure 4 shows the results for pressure runs, corrected for compressibility, on pellets above and below the 208-K transition. The data were taken on increasing pressure because they were found to be more reproducible. Data on the pellet and single-crystal samples are qualitatively alike, although the curvature seems more pronounced for the low-temperature pellet runs. All three of these low-temperature runs have a weak inflection point at about 2.5 kbar, which is also noticeable in the 220-K pellet data as well as in the 211- and 156-K single-crystal data. The scatter in the data points makes its identification somewhat dubious in the other runs.

The effect of pressure on the jump frequency and lattice parameter must be subtracted from the linear term to calculate the activation volume, as shown in Eq. (7). In this case, using the above value of the bulk modulus and a Grüneisen constant $\gamma = 1.49$,[32] the necessary correction is nearly as large as the effect (0.17 cm^3/mole at 296 K). The activation volumes are given in Table I. Because of the nonlinearity of the data, their scatter, and the approximate nature of the correction term (the Grüneisen approximation may not accurately describe the effect of pressure on the optical modes important for diffusion in ionic crystals), the errors are estimated to be 0.1 and 0.2 cm^3/mole for the α and β phases.

Four different cyrstals were used to measure

TABLE I. Activation volumes for α- and β-$RbAg_4I_5$.

Sample	ΔV^a (cm^3/mole)
Single crystal α phase	-0.4 ± 0.2
β phase	-0.2 ± 0.1
Pellet α phase	-0.4 ± 0.2
β phase	-0.2 ± 0.1

[a]Average volumes over the runs in each category; errors are too large to discern any temperature dependence.

the effect of pressure on the order-disorder transition temperature. The average 1-bar T_c, after applying the thermocouple correction, was 208.6 K, in agreement with other determinations.[17] The results are plotted in Fig. 5 together with a least-squares quadratic fit. There is a small linear term consistent with the second-order nature of the transition and an unexpected, large quadratic term that quickly dominates after 1 kbar.

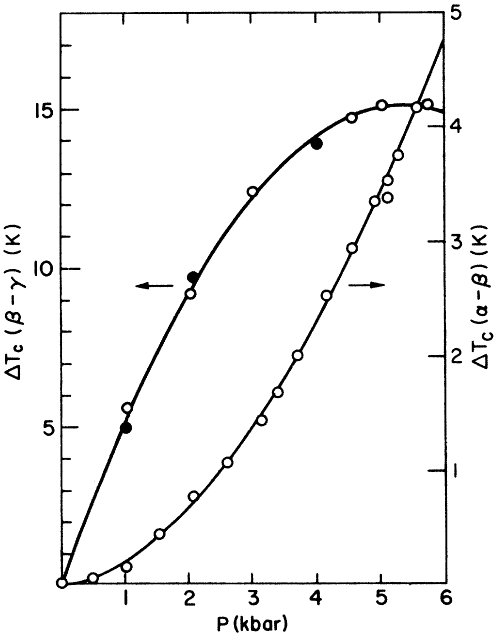

FIG. 5. Effect of pressure on the 122- and 208-K transition temperatures in $RbAg_4I_5$. Solid lines are least-squares fits to the data. $T_c(\alpha-\beta)$(K) = 0.141 P(kbar) + 0.111 P^2(kbar^2); $T_c(\beta-\alpha)$(K) = 5.65 P(kbar) − 0.53 P^2 (kbar^2).

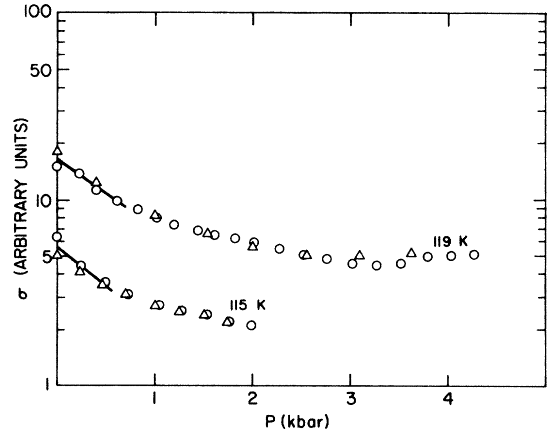

FIG. 6. Effect of pressure on the ionic conductivity of two pellet samples of $\gamma-RbAg_4I_5$. Circles, increasing pressure; triangles, decreasing pressure. Solid lines represent estimates of the initial slope.

Data on γ-$RbAg_4I_5$ could only be taken down to 97 K after which the conductance became too small to measure accurately. Figure 1 also shows the temperature dependence of this phase. Between the β-α transition and 110 K, the data follow a simple exponential behavior with an activation energy of $\Delta E_\gamma = 0.31 \pm 0.02$ eV; below this, the slope begins to flatten gradually. This decrease in activation energy could be interpreted as an extrinsic defect region. However, in view of the substantial disorder still present in the γ phase,[13] it is more likely the result of grain-boundary conduction, such as is found in pressed pellets of β-AgI,[41] or the result of changes in site occupancy.

The effect of pressure on the conductivity of the γ phase, for two samples at 115 and 119 K, is shown in Fig. 6. The data exhibit an activation volume that decreases with pressure in a manner similar to the activation energy in the temperature data. This can be interpreted as pressure driving the sample into the lower-temperature region. Activation volumes can be calculated from the initial slopes, using the bulk modulus and Grüneisen constant from the α phase. The results are $\Delta V = 8 \pm 1$ cm^3/mole at 115 K, and $\Delta V = 9 \pm 1$ cm^3/mole at 119 K.

The variation of the first-order transition temperature with pressure was measured on two pellet samples. The first sample had a transition temperature of 123.0 K (the average of T_c on cooling, 122.0 K, and T_c on heating, 123.9 K); the second had a transition temperature of 125.0 K. The change in T_c, ΔT_c, is plotted in Fig. 5 with a least-squares quadratic fit. The behavior of T_c can be explained as follows: the molar volume of the β phase is larger than that of the γ phase; however, the β phase is also softer than the γ phase and, as the pressure is increased, the volume of the β phase decreases, eventually becoming less than that of the γ phase. From the Clausius-Clapyron equation,

$$\frac{dT_c}{dP}=\frac{V_\beta - V_\gamma}{S_\beta - S_\gamma}=\frac{[(V^0_\beta - V^0_\beta K_\beta P)-(V^0_\gamma - V^0_\gamma K_\gamma P)]}{\Delta S}$$

$$=[(V^0_\beta - V^0_\gamma)-V^0_\beta(K_\beta - K_\gamma)P]/\Delta S\,, \qquad (11)$$

where V_β and V_γ are the molar volumes, K_β and K_γ are the isothermal compressibilities, and ΔS is the molar entropy change. Using the experimentally determined linear and quadratic pressure coefficients, the molar entropy change measured by Johnston *et al.*, $\Delta S = 1.56$ cal/mole K,[15] and the compressibility from Graham and Chang, $K_\beta \approx 0.92 \times 10^{-11}$ cm^2/dyn,[33] the following results are obtained: $V^0_\beta - V^0_\gamma = 0.37 \pm 0.01$ cm^3/mole and $K_\beta - K_\gamma = (0.033 \pm 0.001) \times 10^{-11}$ cm^2/dyn. The molar volumes are nearly the same, and the β phase is 3.6% softer than the γ phase.

The $\beta-\gamma$ transition is reported to occur at 121.8 K.[15] A mass spectrographic analysis following the experiment revealed that the AgI starting material (allegedly 99.999% pure) contained 2-wt% (within a factor of 5) K. The $RbAg_4I_5$ powder used to make the pellets was then analyzed by flame emission and electrodeposition. The single crystals were grown using different AgI chemical and had no detectable K. However, the flame emission results indicated that the pellet samples contained a substantial amount of *K*. We prefer the indirect evidence from the quantitative electrodeposition assay: since *K* enters substitutionally for the Rb, the measured Ag to Rb ratio of 5 implies a K to Rb ratio of 0.25. Furthermore, since the technique overestimated the Ag to Rb ratio for the single crystals, we conclude that the ratio of K to Rb is 0.20 ±0.05. This is supported by the size of the shift in the first-order transition temperature which gives a K to Rb ratio <0.16. Fortunately, $RbAg_4I_5$ and KAg_4I_5 are isostructural and have nearly identical conductivities in the α and β phases. In addition, since the data from two samples having different transition temperatures can be superposed in Fig. 5, the low-temperature structure must remain unaffected by the substitution of small amounts of K.

B. AgI

The results of temperature runs made on α-AgI samples with both Ag and Pt electrodes are shown in Fig. 7. Also included is a run made with relatively K-free AgI (<1000 ppm) to verify the other results; evidently, the K impurity had no detectable effect. The deviation of the conductance of the Pt electrode sample from a straight line at low temperatures and its steeper slope can be attributed to electrode blocking. The reason for the deviation of all the runs at high temperature is obscure but may be the result of annealing. Repeated temperature cycles on the sample that was heated to 740 K followed a reproducible curve of the same features as the first increase, but with 20% decrease in conductance. The activation energies derived from the straight-line portions of each plot are: 0.10 ±0.01 eV for the Ag-electrode samples and 0.14 ±0.01 eV for the Pt-electrode sample. Kvist and Josefson's data[23] yield a value of 0.10 eV in good agreement with the former.

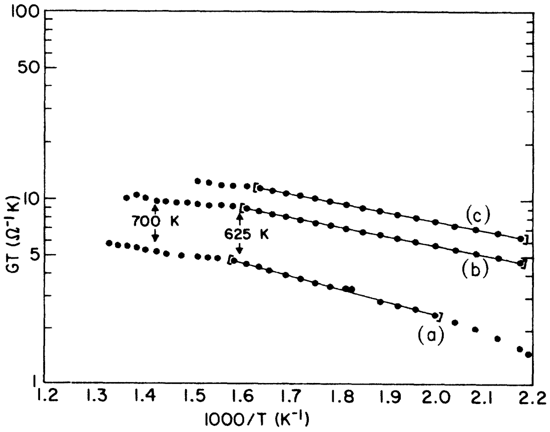

FIG. 7. Conductance of three α-AgI pellet samples as a function of temperature. (a) Pt electrodes; (b) Ag electrodes; (c) Ag electrodes, K-free AgI. Brackets indicate region of fit. All points taken on increasing temperature.

Figure 8 shows the results of four pressure runs, all made with Ag electrodes. The 501-K run was made with the K-free AgI. The lines are least-squares fits to the data. Points below 1 kbar and all the decreasing pressure points from the 556-K run have been ignored in the fits. The sharp initial increase in conductivity was probably caused by the compression of AgI around the electrode wires. Corrections for the compressibility were made using the bulk modulus for α-$RbAg_4I_5$ since elastic-constant data are unavailable for α-AgI. The largest decrease in conductivity amounts to only 3% in 4 kbar. The activation volumes calculated from these data, corrected using the α-$RbAg_4I_5$ bulk modulus and Grüneisen constant, are listed in Table II. Once again, the correction is the same size as the effect; only in this case, they are in the same sense. This introduces considerable uncertainty in the values since the correction can only be estimated. The activation volumes appear to increase with temperature (this is unaffected by errors in the correction term which is proportional to *T*).

The conductance in the temperature region

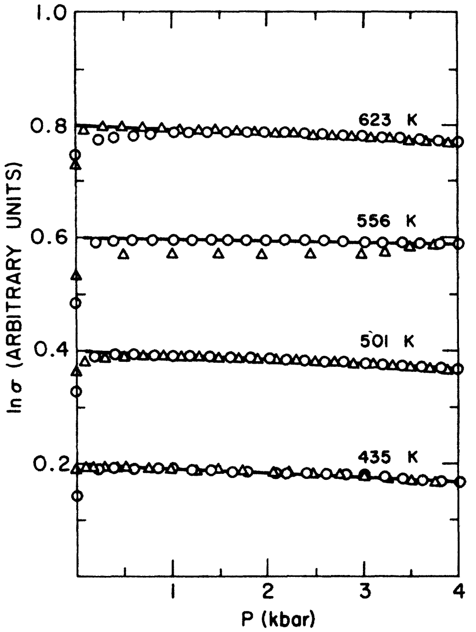

FIG. 8. Effect of pressure on the ionic conductivity of pellet α-AgI. 501-K sample was made from K-free AgI. Circles, increasing pressure; triangles, decreasing pressure. Points below 1 kbar and all decreasing points from the 556-K run have been ignored in the fits. Runs have different arbitrary units.

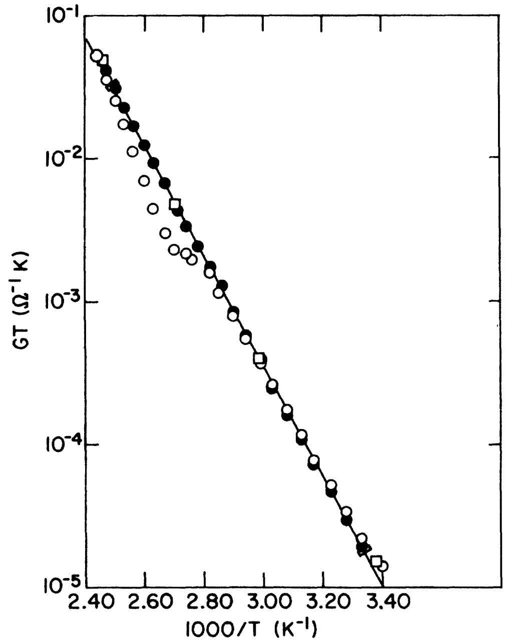

FIG. 9. Temperature dependence of the conductance along the c axis in a single crystal of β-AgI. Open circles, increasing temperature, 1 kHz; squares, increasing temperature, 10 kHz; closed circles, decreasing temperature, 1 kHz. Brackets indicate region of fit to decreasing temperature data.

around 700 K was carefully explored to search for an inflection, characteristic of an order-disorder transition. No evidence for the transition was found. Pt electrodes were tried in an attempt to preserve sample stoichiometry. However, chemical analysis by electrodeposition on a dummy sample, heated to 770 K with no electrodes, indicated an increase of 0.5% in Ag concentration. Therefore, the absence of the transition might still be ascribed to loss of stoichiometry.

Figure 9 shows the temperature dependence of the conductivity along the c axis for a β-AgI single crystal with Ag paint contacts. Some electrode blocking occurs on increasing temperature that could be overcome using a 10-kHz signal. After the sample was taken up in temperature, the contacts behaved well at 1 kHz. There is a slight curvature in the data; the activation energy calculated from the decreasing temperature points, as shown, is 0.78 ±0.02 eV. Least-squares analyses on a graphite-electrode sample yielded 0.80 ±0.02 eV for the high-temperature region. Cochrane and Fletcher[36] obtained 0.79 eV for conduction along the c axis while Schock and Hinze[41] obtained a much higher value of 0.96 eV.

TABLE II. Activation volumes for α-AgI.

(K)	$-10^3\left(\frac{\partial \ln\sigma}{\partial P}\right)_T$ (kbar^{-1})	$RT(\gamma-\frac{2}{3})K$ (cm^3/mole)	ΔV (cm^3/mole)
435	8.5 ±0.9[a]	0.25	0.56 ±0.1
501	8.5 ±0.7	0.29	0.65 ±0.1
556	3.6 ±1.2	0.32	0.5 ±0.1[b]
623	8.2 ±1.1	0.36	0.8 ±0.1

[a] Standard deviation from least-squares analysis.

[b] This value is suspect because the run did not reproduce on decreasing pressure.

The effect of pressure on the conductivity along the c axis is shown in Fig. 10. All samples (one for each temperature) had Ag-paint electrodes. Corrections were made using the linear compresibilities β_c(z direction) = (1.1×10^{-12}) cm^2/dyn and β_a(basal plane) = (1.5×10^{-12}) cm^2/dyn.[34] The conductivity increases with pressure until about 1 kbar where there is a discontinuous drop, probably due to a transformation to the cubic zinc-blende structure, γ phase. A discontinuity in the elastic constants has also been observed at this pressure.[34] As the pressure is decreased, the conductivity returns along a different path to a lower value. The activation volumes derived from

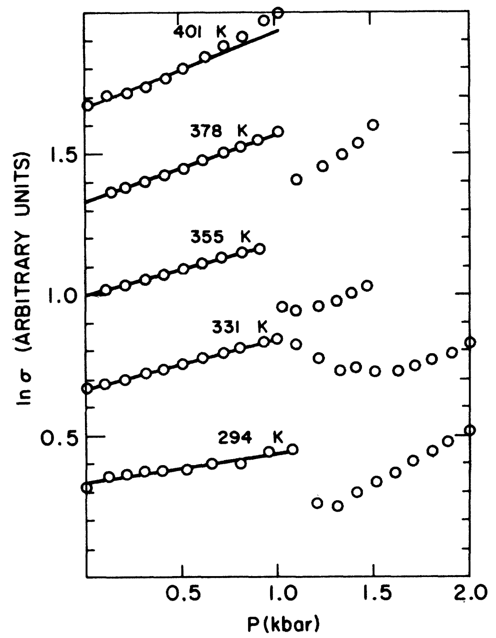

FIG. 10. Effect of pressure on the ionic conductivity along the c axis in single crystal β-AgI. Data taken on increasing pressure.

least-squares fits to the data in Fig. 10 are plotted in Fig. 11. The correction term has been estimated using $K=\beta_c+2\beta_a$ and $\gamma=-2$.[49] The activation volumes are seen to become increasingly negative with increasing temperature.

The dependence of the β-α transition on pressure has been known for some time.[50] Our measurements on a single crystal yield $T_c(\mathrm{K})=420.7-15.66\,P(\mathrm{kbar})$.

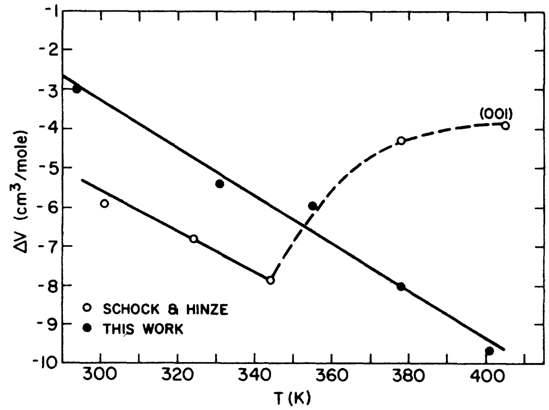

FIG. 11. Activation volume for conduction along c axis in β-AgI as a function of temperature. Closed circles, this work; open circles, work of Schock and Hinze (Ref. 41).

Using the entropy change of the transition, 3.5 ±0.03 cal/mole K,[51] the volume change of the transition can be found from the Clausius-Clapyron equation [Eq. (11)]. The result is a volume decrease from the β to α phase 2.3 ±0.2 cm^3/mole, or a decrease of 5.6% (molar volume of the β phase is 41.3 cm^3) in good agreement with previous determinations.

IV. DISCUSSION

A. Superionic activation volumes

The most salient feature of the results in Tables I and II is the small size of ΔV. The values are unusually low even for interstitial diffusion in AgCl and AgBr, although they have similar activation energies. Table III compares their diffusion parameters and the ratio $\Delta V/\Delta E$ to the parameters found in this experiment. The largest ratio for α-AgI is still a factor of 2 lower than the smallest ratio for the normal silver halides. This would seem to indicate that interstitial diffusion in superionic $\mathrm{RbAg_4I_5}$ and AgI is qualitatively different from diffusion in normal salts. This result also almost certainly rules out the possibility of a diffusion mechanism requiring large-scale domain motion, which should be characterized by a large ΔV.

The results obtained for $\mathrm{RbAg_4I_5}$ can be compared to the predictions of the strain-energy model.[27,28] Equation (9) can be rewritten in terms of the Grüeisen constant associated with the shear modes,[28]

$$\Delta V=2(\gamma_s-\tfrac{1}{3})K\Delta G\,, \qquad (12)$$

where K is the isothermal compressibility. γ_s can be found from the elastic-constant data of Graham and Chang[33] and is equal to 1.05. The model predicts a $\Delta V=1.4$ cm^3/mole for the α phase and $\Delta V=2.3$ cm^3/mole for the β phase. Not only are these values of the wrong sign, but they are too large by a factor of 4 to 10. Apparently, either the migration energy cannot be related to macroscopic elastic properties in this material, or γ_s markedly overestimates the effect of pres-

TABLE III. Interstitial diffusion in the silver halides.

Substance	ΔE_m (eV)	ΔV_m (cm^3/mole)	$\Delta V_m/\Delta E_m$	Reference
AgCl	0.16	3.2	20	52
AgBr	0.20	3.6	18	53
α-AgI	0.10	0.6–0.8	6–8	Present work
α-$\mathrm{RbAg_4I_5}$	0.12	−0.4	−3.3	Present work
β-$\mathrm{RbAg_4I_5}$	0.17	−0.2	−1.2	Present work

sure on the modes important for diffusion. Unfortunately, similar elastic-constant data are unavailable for AgI.

From the standpoint of the dynamical theory,[26] in which the activation volume is proportional to a pressure derivative of a mode frequency [see Eq. (10)], a weak pressure dependence of that frequency would also qualitatively explain the small activation volumes.

The negative activation volume of $RbAg_4I_5$ can be interpreted in three ways: (i) in the spirit of Flygare and Huggins' analysis[4] of ionic transport through crystallographic tunnels, the silver ions may be slightly smaller than the optimal size, yielding a higher conductivity for a decrease in the lattice parameter; (ii) ion-ion interactions are more important at the interstitial sites than at the saddle points,[19] and pressure may increase the interaction enthalpy, effectively raising the bottoms of the potential wells; (iii) a decrease in the lattice parameter may change the relative occupation of the interstitial sites in such a way as to increase the conductivity.

Although none of the above explanations can be rejected outright, we prefer the second. Flygare and Huggins conclude that the Ag-ion radius is actually slightly larger than the optimal size, at least for the α-AgI lattice. As for the third explanation, it is unlikely that pressure would change the relative occupancy where temperature would not. If temperature did effect the occupancy substantially, an Arrhenius plot of the conductivity would be curved rather than straight as observed. Also, Geller[13] has determined that the occupancies of the sites in the β phase corresponding to the sites in the α phase are nearly the same. This leaves the second explanantion, which arises because an ion at the saddle point must be adjacent to an unoccupied site, if it is to complete its jump. It is, therefore, less influenced by the Coulomb interactions between the diffusing ions than an ion at a regular site. These Coulomb interactions increase with pressure, thus lowering the activation enthalpy and giving the appearance of a negative activation volume. In the case of AgI, this effect is probably dominated by the usual expansion of the saddle point, resulting in a small positive activation volume. The molecular-dynamics study[11] indicates that significant correlations between the velocities of the Ag ions do exist in α-AgI. As will be shown later, the interactions between the ions can have a significant effect on the activation in $RbAg_4I_5$.

The activation volumes for α-AgI are observed to increase by nearly 50% over 200 K. This could be the result of mode softening with increasing temperature; the lattice is able to relax outward more as the ions move through the saddle point. It is noteworthy that the mean atomic displacement of the silver and iodine atoms, as deduced from x-ray measurements, increases from 0.2 to 0.4 Å over the same temperature range.[32]

B. Anomalous pressure effects in α- and β-$RbAg_4I_5$

Perhaps the most puzzling result of this investigation is the large quadratic-pressure dependence of the 208-K critical temperature. A small linear dependence is expected because the transition is not first order. However, it is difficult to understand what makes the zero-pressure lattice parameter unique. From the Ising model, [Eq. (1)]:

$$kT_c = qJ\,, \tag{13}$$

where J is an interaction energy between the pseudospins, and q is a factor of order unity. The quadratic dependence of T_c means that J is essentially at a minimum at zero pressure, as can be seen from its expansion about a_0, the zero-pressure lattice parameter.

$$\begin{aligned} J(a) &= J(a_0) + \frac{dJ}{da}(a-a_0) + \frac{1}{2}\frac{d^2J}{da^2}(a-a_0)^2 \\ &\approx J(a_0) + \frac{1}{2}\frac{d^2J}{da^2}(a-a_0)^2\,. \end{aligned} \tag{14}$$

In this connection, it would be interesting to know the effect of pressure on T_c in the related compounds $NH_4Ag_4I_5$ and KAg_4I_5. They have T_c's that are several degrees lower[52] and may have J's that are farther from the minimum. However, the transition temperatures of these three isostructural compounds decrease with their respective a_0's, making the situation even less clear.

Although considerable progress has been made explaining the Ising-like properties of this system in terms of coupling between the pseudospins via phonons, not enough is known about the detailed lattice dynamics to be able to predict T_c. Therefore, it seems unlikely that the pressure dependence of T_c can now be simply understood.

The $\ln\sigma$ versus P plots for superionic $RbAg_4I_5$ are not linear as expected for normal activated processes. Instead, there is a pronounced curvature that can be fit fairly well to a quadratic. This is almost certainly related to the quadratic-pressure dependence T_c. The following is a model for this connection.

The interactions between the ions leading to the ordering at 208 K contribute to the activation enthalpy, which can be written as

$$\Delta H_\alpha = \Delta H_0 + \lambda_\alpha J \tag{15a}$$

for the α phase and

$$\Delta H_\beta = \Delta H_0 + \lambda_\beta J \tag{15b}$$

for the β phase. ΔH_0 contains the unperturbed activation enthalpy between the lattice site and the saddle point, and it includes all ion-ion interactions that do not lead to ordering. J is the Ising-spin coupling energy, and the λ's are a measure of the contribution J makes to the activation enthalpy. In the α phase, the existence of short-range order causes λ_α to be nonzero. As the crystal is cooled through the transition, long-range order sets in, and the ordering enthalpy increases, manifested by a larger λ_β. The important point here is that the activation enthalpy samples both the short- and long-range order. In a sense, there is a mean-field contribution to λ_β, while there is none to λ_α. Vargas *et al.*[19] have shown that it is just this increase in local order that accounts for the singularities in the slope of the resistivity and the specific heat.

The difference in activation enthalpies across the transition is

$$\Delta H_\beta - \Delta H_\alpha = J(\lambda_\beta - \gamma_\alpha) . \tag{16}$$

The ordering enthalpies can then be written in terms of $f = \lambda_\beta/\lambda_\alpha$.

$$\lambda_\alpha J = \frac{1}{f-1}(\Delta H_\beta - \Delta H_\alpha) , \tag{17a}$$

$$\lambda_\beta J = \frac{f}{f-1}(\Delta H_\beta - \Delta H_\alpha) . \tag{17b}$$

Note that f must be greater than 1.4, the value at which $\Delta H_\alpha = \lambda_\alpha J$. Using

$$J = kT_c/q \tag{18}$$

in Eqs. (15) and (17), and assuming ΔH_0 has no appreciable quadratic-pressure dependence, we find

$$-T\left(\frac{\partial^2 \ln\sigma}{\partial P^2}\right)_T = \frac{1}{f-1}\,\frac{(\Delta H_\beta - \Delta H_\alpha)}{kT_c}\,\frac{\partial^2 T_c}{\partial P^2} \tag{19a}$$

$$-T\left(\frac{\partial^2 \ln\sigma}{\partial P^2}\right)_T = \frac{f}{f-1}\,\frac{(\Delta H_\beta - \Delta H_\alpha)}{kT_c}\,\frac{\partial^2 T_c}{\partial P^2} \tag{19b}$$

for the α and β phases, respectively. Upon inserting the values for the enthalpy change (0.05 eV) and the quadratic-pressure derivative of T_c (0.222 K/kbar^2), we have

$$-T\left(\frac{\partial^2 \ln\sigma}{\partial P^2}\right)_T = \frac{1}{f-1}0.62\left(\frac{\mathrm{K}}{\mathrm{kbar}^2}\right) \quad (\alpha \text{ phase}) \tag{20a}$$

$$-T\left(\frac{\partial^2 \ln\sigma}{\partial P^2}\right)_T = \frac{f}{f-1}0.62\left(\frac{\mathrm{K}}{\mathrm{kbar}^2}\right) \quad (\beta \text{ phase}) \tag{20b}$$

This leaves one adjustable parameter to fit the data for the two different phases. Table IV compares the experimental single-crystal and pellet values with the theoretical values using optimized f's. Agreement is within experimental error. Although the pellet data appear to fit the theory better, they give an unrealistically low value of 1.5 for f, which implies a value of 0.02 eV for ΔH_0. For this reason, we prefer the results of the single-crystal runs, which give the more sensible values of 2.74 for f and 0.09 eV for ΔH_0.

If the critical amplitudes of the specific heat are used as the ratio of the contributions of short- and long-range order to the activation enthalpy (this is a reasonable assumption because the singular part of the specific heat is proportional to the singular part of the derivative of the interaction enthalpy),[17]

$$f = A^-/A' = 2.17 . \tag{21}$$

Using this value of f in Eq. (17), we obtain $\Delta H_0 = 0.08$ eV, $\lambda_\alpha J = 0.043$ eV, and $\lambda_\beta J = 0.093$ eV, close to the single-crystal results.

It is evident from these results that a significant fraction of the activation enthalpy is due to the ordering enthalpy. The linear dependence of T_c on pressure is small enough to be neglected in its contribution to the activation volume. Nevertheless, ΔH_0 contains interaction terms that are roughly the same size as the ordering enthalpy, and could well account for the observed negative activation volume.

TABLE IV. Comparison between experimental and theoretical quadratic pressure coefficients.

Sample	$-T\left(\frac{\partial^2 \ln\sigma}{\partial P^2}\right)_T$ (expt) (K/kbar^2)	$-T\left(\frac{\partial^2 \ln\sigma}{\partial P^2}\right)_T$ (theory) (K/kbar^2)	f	λJ (eV)
Single crystals α phase	0.66 ± 0.3[a]	0.35	2.74	0.029
Single crystals β phase	0.66 ± 0.3	0.97	2.74	0.079
Pellets α phase	1.09 ± 0.3	1.23	1.50	0.10
Pellets β phase	1.96 ± 0.6	1.84	1.50	0.15

[a] Values are the average of quadratic coefficients in each category; errors are standard errors of the mean.

The inflection point at 2.5 kbar is also a puzzle. Its shape is reminiscent of the larger inflection point at the 208-K transition, an indication that there might be a change in the ordering of the Ag ions. Yet, it does not move with temperature, and this would require that the two orderings fortuitously have almost identical configurational entropies.

C. Low-conductivity phases

In γ-$RbAg_4I_5$, the effect of pressure on the conductivity appears to confirm the formation of Frenkel defects. Since the initial slope is a measure of both components of the activation volume, it yields the sum $\Delta V = \Delta V_m + \frac{1}{2}\Delta V_f$. The values found were 8–9 cm/mole; this compares favorably with the combined volumes for interstitial diffusion in AgBr ($\Delta V = 10.6$ cm^3/mole) and in AgCl ($\Delta V = 11.6$ cm^3/mole).[53,54] However, the combined activation energy in this region, $\Delta E = \Delta E_m + \frac{1}{2}\Delta E_f$, is measured to be 0.31 eV, which is substantially lower than the corresponding values in AgBr ($\Delta V = 0.74$ eV) and in AgCl ($\Delta E = 0.8$ eV).[55] The migration energy is not likely to be less than 0.1 eV since it is 0.17 eV in the β phase. This implies a maximum ΔE_f of 0.4 eV which is unusually small for a formation energy.

Another explanation is possible. A small formation energy is consistent with other evidence that the γ phase is not ordered, namely, Geller[13] had determined that none of the possible ordering schemes are exactly corroborated by his x-ray data, and Johnston *et al.*[15] have observed an excess specific heat, attributed to configurational disorder, down to 50 K. In fact, if the γ phase is disordered, it makes little sense to separate activation volumes and energies into terms due to formation and motion. The curved Arrhenius and activation volume plots in Figs. 1 and 6 may reflect the promotion of Ag ions from lower-lying sites to higher ones having smaller Gibbs energies of migration. At temperatures just below 122 K, all the ions in the higher sites are involved in the conduction process, and any increase in the conductivity must come from the ions in the lower sites. This situation is analogous to having intrinsic and extrinsic regions, except that in this instance the occupation of higher lying sites is inherent in the disorder of the low-temperature region instead of being caused by impurities. If this explanation is correct, migration from the higher-lying sites has an activation energy of ~0.13 eV and an activation volume that is sensibly zero. Yet, it is difficult to account for the large volume of promotion in this model, and the possibility that the low-temperature and high-pressure portions of the data are the result of grain-boundary conduction cannot be discounted.

The activation volumes found for β-AgI disagree with those of Schock and Hinze[41] in two respects. First, for $T < 340$ K, their negative volumes are larger by a factor of 2, and second, they find a sudden increase to less negative values at $T > 340$ K. The data are compared in Fig. 11. Their observation of a sudden change at 340 K and the absence of one in our data is partially explained by their conductivity data having a knee at that temperature while ours has none. Cochrane and Fletcher[36] do observe a knee, but at 290 K, which is below our lowest temperature points. The shift in the position of the knee could be ascribed to varying levels of impurities affecting the extent of the extrinsic region were it not for the differences in observed activation energies. It may be that the conductivity is sample dependent because of a nonequilibrium concentration of defects or a combination of impurities and more than one kind of diffusion mechanism. In any event, the feature of a large negative activation volume is clearly reproducible.

Since ΔV was measured in the intrinsic region, it is the sum $\Delta V = \Delta V_m + \frac{1}{2}\Delta V_f$. ΔV_m is assumed to be small and positive although this has not been proven. The large negative formation volume accounts for the negative thermal expansion and, through the strain-energy model, for the negative Grüneisen constant.[41]

Finally, it should be pointed out that both β-AgI and γ-$RbAg_4I_5$ have $|\Delta V| \sim 9$ cm^3/mole just before the first-order transition into the superionic phase. This lends some support to the idea of Rice *et al.*[25] who conclude that transitions to the superionic phase require large interstitial formation volumes.

ACKNOWLEDGMENTS

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[1] G. Eckold, K. Funke, J. Kalus, and R. E. Lechner, J. Phys. Chem. Solids 37, 1097 (1976).

[2] J. B. Boyce, T. M. Hayes, W. Stutius, and J. C. Mikkelsen, Jr., Phys. Rev. Lett. 38, 1362 (1977).

[3] M. J. Rice and W. L. Roth, J. Solid State Chem. 4, 294 (1972).

[4] W. H. Flygare and R. A. Huggins, J. Phys. Chem. Solids 34, 1199 (1973).

[5] W. J. Pardee and G. D. Mahan, J. Solid State Chem. 15, 310 (1975).

[6] G. D. Mahan and W. J. Pardee, Phys. Lett. A 49, 325 (1974).

[7] W. van Gool, J. Solid State Chem. 7, 55 (1973).

[8] W. van Gool and P. H. Bottelberghs, J. Solid State Chem. 7, 59 (1973).

[9] W. van Gool, in *Superionic Conductors*, edited by G. D. Mahan and W. L. Roth (Plenum, New York, 1976).

[10] W. van Gool, in *Fast Ion Transport in Solids*, edited by W. van Gool (North-Holland, Amsterdam, 1973).

[11] W. Schommers, Phys. Rev. Lett. 38, 1536 (1977).

[12] S. Geller, Science 157, 310 (1967).

[13] S. Geller, Phys. Rev. B 14, 4345 (1976).

[14] W. J. Pardee and G. D.Mahan, J. Chem. Phys. 61, 2173 (1974).

[15] W. V. Johnston, H. Wiedersich, and G. W. Lindberg, J. Chem. Phys. 51, 3729 (1969).

[16] W. J. Pardee and G. D. Mahan, J. Solid State Chem. 15, 310 (1975).

[17] F. L. Lederman, M. B. Salamon, and H. Peisl, Solid State Commun. 19, 147 (1976).

[18] M. B. Salamon, Phys. Rev. B 15, 2236 (1977).

[19] R. Vargas, M. B. Salamon, and C. P. Flynn, Phys. Rev. Lett. 37, 1550 (1976).

[20] G. Burley, Acta Crystallogr. 23, 1 (1967).

[21] C. M. Perrot and N. H. Fletcher, J. Chem. Phys. 50, 2770 (1969).

[22] W. Jost, J. Chem. Phys. 55, 4680 (1971).

[23] A. Kvist and A. Josefson, Z. Naturforsch. A 23, 625 (1968).

[24] A. M. Josefson, A. Kvist and R. Tarneberg, in *Atomic Transport in Solids and Liquids*, edited by A. Lodding and T. Tarneberg (Springer, Tubingen, 1971).

[25] M. J. Rice, S. Strassler, and G. A. Toombs, Phys. Rev. Lett. 32, 596 (1974).

[26] C. P. Flynn, *Point Defects and Diffusion* (Clarendon, Oxford, 1972).

[27] C. Zener, in *Imperfections in Nearly Perfect Crystals* (Wiley, New York, 1950).

[28] R. W. Keyes, in *Solid under Pressure*, edited by W. Paul and D. M. Warschauer (McGraw-Hill, New York, 1963).

[29] S. A. Rice, Phys. Rev. 112, 804 (1958).

[30] N. B. Slater, *The Theory of Unimolecular Reactions* (Cornell University, Ithaca, 1959).

[31] G. Burley, J. Chem. Phys. 38, 2807 (1963).

[32] S. Hoshino, J. Phys. Soc. Jpn. 12, 315 (1957).

[33] L. J. Graham and R. Chang, J. Appl. Phys. 46, 2433 (1975).

[34] T. A. Fjeldy and R. C. Hanson, Phys. Rev. B 10, 3569 (1974).

[35] B. Owens and G. Argue, Science 157, 308 (1967).

[36] G. Cochrane and N. H. Fletcher, J. Phys. Chem. Solids 32, 2557 (1971).

[37] W. Buhrer and P. Brüesch, Solid State Commun. 16, 155 (1975).

[38] D. Galagher and M. V. Klein, J. Phys. C 9, L687 (1976).

[39] G. Burns, F.H. Dacol, and M. W. Shafer, Solid State Commun. 19, 291 (1976).

[40] H. Hoshino and M. Shimoji, J. Phys. Chem. Solids 33, 2303 (1972).

[41] R. N. Schock and E. Hinze, J. Phys. Chem. Solids 36, 713 (1975).

[42] P. C. Allen, Ph.D. thesis (University of Illinois, 1977) (unpublished).

[43] M. R. Manning, C. J. Venuto, and D. P. Boden, J. Electrochem. Soc. 118, 2031 (1971).

[44] B. B. Owens, in *Advances in Electrochemistry and Electrochemical Engineering*, edited by P. Delaney and C. W. Tobias (Wiley, Sussex, 1971), Vol. 8.

[45] H. C. Montgomery, J. Appl. Phys. 42, 2971 (1971).

[46] B. F. Logan, S. O. Rice, and R. F. Wick, J. Appl. Phys. 42, 2975 (1971).

[47] M. E. Hills, Naval Weapons Center TP 4806 (1969).

[48] V. M. Cheng, P. C. Allen, and D. Lazarus, Appl. Phys. Lett. 26, 6 (1975).

[49] R. T. Payne and A. W. Lawson, J. Chem. Phys. 34, 2201 (1961).

[50] A. I. Majumdar and R. Roy, J. Phys. Chem. 63, 1858 (1959).

[51] C. M. Perrot and N. H. Fletcher, J. Chem. Phys. 48, 2143 (1968).

[52] R. Vargas, Ph.D. thesis (University of Illinois, 1977) (unpublished).

[53] A. E. Abey and C. T. Tomizuka, J. Phys. Chem. Solids 27, 1149 (1966).

[54] S. Lansiart and M. Beyeler, J. Phys. Chem. 36, 703 (1975).

[55] P. Süptitz and J. Teltow, Phys. Status Solidi 23, 9 (1967).