Non-Linear Electrical Transport in Silver Sulfide

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We have measured the current-voltage characteristics of β-Ag$_2$S layer at the liquid-nitrogen temperature. Samples showed that there is the non-linear evoluation of the electrical current. Our experimental results are consistent with Bishop's theory treating the interacting Brownian particles in a periodic local potential.

§1. Introduction

It is well known that Ag chalcogenides transform to the so-called superionic phase (α-phase) around 150°C. For example silver sulfide is a prototype superionic conductor which undergoes a phase transition at 179°C from monoclinic β-Ag$_2$S to bcc α-Ag$_2$S with a large increase in the ionic conductivity.[1] In β-Ag$_2$S the ionic conductivity is due to thermally activated Ag$^+$ interstitials, while in α-Ag$_2$S the cations diffuse between preferred sites in a very open structure. In brief, in α-Ag$_2$S the Ag$^+$ ions move in a liquid-like fashion through the lattice of the S^{--} ions. There are many methods of statistical mechanics which enable us to describe high mobility of materials on a microscopic level.[2−4] The independent-particle model may qualitatively describe some features of superionic conductors. This description of ionic conduction is based on one ion hopping in the lattice in terms of the random walk theory. It is, however, difficult to give reasonable explanations of extremely fast conduction with extremely low activation energies within the framework of the one particle model. To reconcile this difficulty, a collective excitation of ions has been proposed. One of the most commonly known collective motions of ions adopted in the theory is the interstitial like motion.[5,6] Wang and Pickett[5] has demonstrated that the correlative motions of mobile ions can result in small activation energies for conduction in superionic conductors. Hence the barrier

height of the pinning potential for the correlated hopping of several particles is strongly reduced compared to the barrier height for the single particle hopping, so that the strong coupling between mobile ions can give rise to collective excitations of mobile ions and such small barriers. Wang's interstitial cation model is equivalent to the simple atomic dislocation model introduced by Frenkel and Kontrova,[7] which is used in the plastic deformation of a material. Hereafter we term an interstitial cation on a chain of coupled cations a dislocation simply.

In the plastic mechanical properties of crystalline solids, the low observed values of the critical shear stress can be explained in terms of the motion through the lattice of dislocation. Crystal dislocations destroy the long-range order, and the essential character of the liquid phase is the disappearance of the long-range order characteristic of a solid crystal. Then we may regard a liquid phase as a crystal saturated with crystal dislocations. This consideration leads us a dislocation model of melting of a crystal.[8−11]

If the characteristics of fast ionic conduction are due to the sublattice disorder, the existence of a transformation to a conducting state with temperature means that some structure change or excitations occur with temperature which lead to a phase change. A possible structural change for the disorder which increases the conductivity is an excitation of dislocation, i.e., interstitial cation. In the low temperature, that is T is smaller than the critical temperature

T_c, we can imagine, based on the dislocation model in a crystal, that a small fraction of the ordered conducting cation species becomes thermally promoted to certain interstitial sites and then dislocations are produced thermally on a chain of cations. The dislocations are frozen in an ordered normal ionic crystal. When $T = T_c$, the dislocation does not find the stable equilibrium position and may propagate freely through a crystal, and hence there occurs the melting of a cation sub-lattice.

Recently, Pasternak *et al.*[12] measured Mössbauer spectroscopy on ^{119}Sn solute in β-Ag$_2$Se at temperatures far below T_c, and they found that there is local Ag hopping and microscopic disorder around the impurity Sn atom within the ordered phase of superionic β-Ag$_2$Se, and they reported that this observation of the local melting is in qualitative agreement with the theory of Rice *et al.*[13] Rice *et al.* showed that the transition can be stimulated by the interaction of interstitial cation defects with the strain field they induce. We interpret Pasternak's result as the dislocation melting effect due to the interaction of dislocations with the impurity atoms. In other words the dislocation model suggests that the phase transition is caused by a transition from "frozen" state with dislocation to "free" state with dislocation around impurity atom. Hence it is possible to occur a local melting transition below T_c.

Dislocation is associated with an excess of one mobile ion's charge q, where q is equal to the magnitude of electron charge. Thus the dislocation, that is interstitial cation on Ag$^+$ ion chain, moves under the influence of an applied electrical field E similar to the movement of a crystal dislocation in a crystal at very low applied stresses. When a dislocation displaces a distance of the lattice constant a, the dislocation gain the energy $a(qE)$ from the electrical field E. If the energy $a(qE)$ is large compared with the thermal energy $k_B T_c$ (k_B Boltzmann constant), the dislocation may move to a neighboring cell and then may move freely through a sub-lattice. Hence the cation sub-lattice becomes melting. It is immediately clear that the critical field may be given as $E_c = k_B T_c / aq$. For $a = 1.5$ Å and $T_c = 170°$C, $E_c = 2.5 \times 10^7$ N/C. More detail explanation of the critical field was discussed by Bishop[14] in terms of collective excitation of cation particles.

Bishop considered a one-dimensional system of interacting Brownian particles in a periodic local potential to be applied to the problem for mobile ions in a superionic conductor and predicted that there exists the critical field E_c. At this point the mobility of mobile ions increases strongly. The critical field E_c is about 2.7×10^7 N/C for Ag$_2$S. If we make an Ag$_2$S thin film of an thickness of 1000 Å, we can generate the critical field E_c in the layer using D.C. voltage supply of 2.7 V and may observe a high non-linear electrical current. So we made Ag$_2$S thin film with help of evaporations and observed I-V behavior of samples. We report in the paper our experimental results.

§2.   Experimental Procedure and Results

The fabrication procedure of samples is consisted of a sequence of evaporations. The top and bottom electrodes for an Ag$_2$S thin film are Al (or Ag) films. The silver thin film
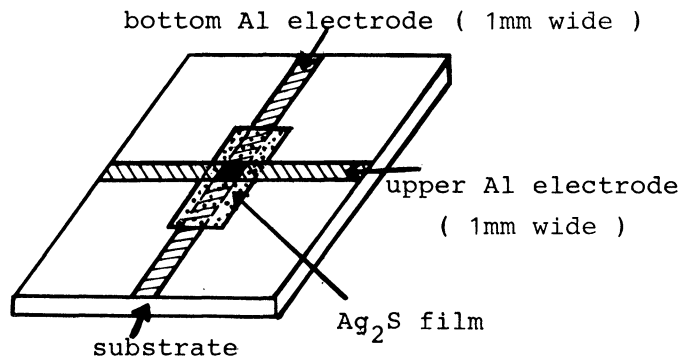

Fig. 1.   Configuration for an Al–Ag$_2$S–Al thin film sample.

(about 1000 Å) has been deposited on the bottom Al electrode. Subsequently the clean Ag film was exposed to SO_2 gas and then an Ag_2S layer was made. Its active area is 1 mm². We show the configuration for samples in Fig. 1. The Ag_2S film produced coares the silver surface. In order to observe the crystallization of a Ag_2S film, the X-ray diffraction patterns are employed for structural analysis of thin films. Cu–Kα ($\lambda = 1.54$ Å) radiation with a Ni filter has been used for the measurement. The results are shown in Fig. 2. With increasing the thickness of a sulfide film on the sample the peaks in the diffraction pattern of Ag which are reflected from the planes (111) and (200) of a single crystal are decreased. There are the extra lines on the pattern given by the structure of an Ag_2S single crystal which arise from the planes ($\bar{1}$22) and (002). These peaks increase with the reaction. The X-ray lines are sharp, so that the crystalline size in the specimen is large. Hence we may consider the large part of the Ag_2S layer to be crystallized.

Measurement of the I-V characteristics was carried out with use of the standard four-probe arrangement. For a specimen with excess Ag, the principal current carriers are interstitial cations. Such an interstitial is identical to a dislocation in which $N+1$ ions are shared among

N lattice sites. To build the critical field in a specimen it is necessary to apply an external electric field $E_c = 10^7$ N/C, which corresponds to an electric field comparable to typical electric beak down fields. Furthermore, interstitial velocities comparable to the sound velocity are equivalent to enormous current densities. For example, when the melting is occurred, the dislocation density is estimated to be about $10^{14}/cm^2$, so that the interstitial concentration is about $10^{21}/cm^3$ and then the current density would be of the order of 10^6 A/cm². Clearly, in accelerating the interstitial up to such high velocity in an electric field, the sample would almost certainly be destroyed by such high current long before we reach the critical field regime. In fact, at room temperature an Ag_2S film shows the electrical breakdown for relatively small applied voltage. To avoid the destructive breakdown we immersed samples in a liquid nitrogen bath. We could observe the non-linear behaviour of the electrical current. The I-V characteristic for an Al(Ag)–Ag_2S–Ag system is shown in Fig. 3. The (Ag) means the surplus Ag on the bottom Al electrode. Measurements were made at the frequency of 0.01 Hz, i.e., the voltage was swept at a rate of 100 sec. At the same time the dynamical conductivity of the samples is shown in Fig. 3. The
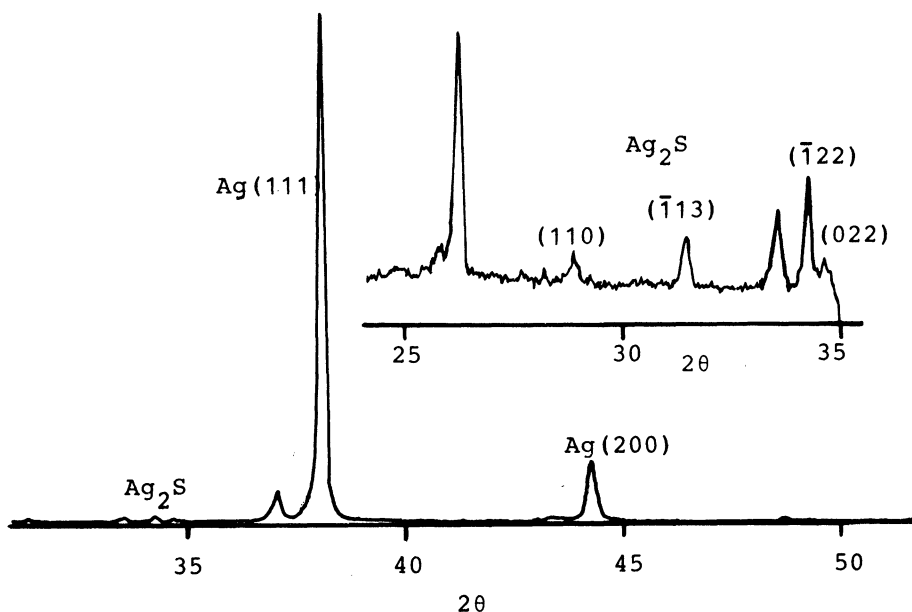

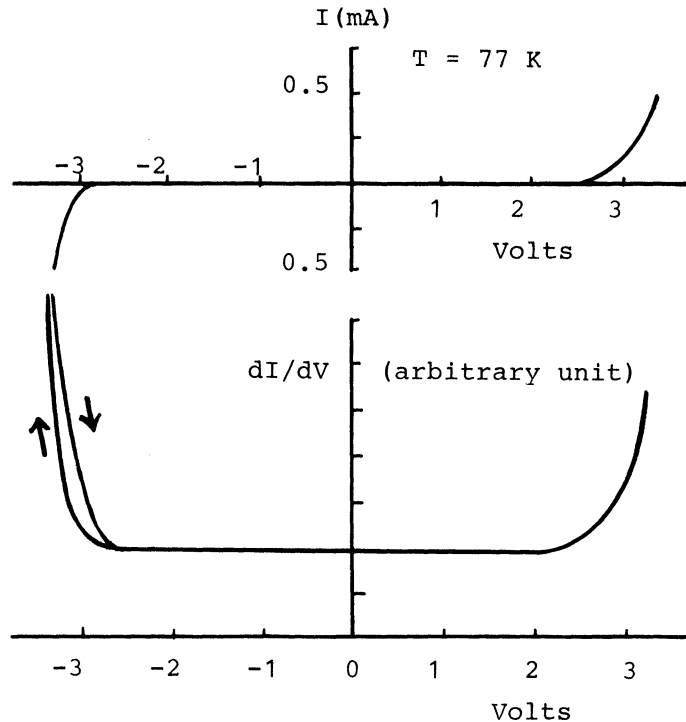Fig. 2.   X-ray diffractions pattern of a sulfide film.

Fig. 3. I-V characteristics and dynamical conductivity for an Al(Ag)–Ag$_2$S–Ag sample.

first derivatives, i.e., the dynamical conductivity, is observed by 300 Hz signal through an impedance to the junction and measuring the in-phase voltage developted with a lock-in amplifier. The output of the lock-in amplifier then gives dI/dV directly.

For Al(Ag)–Ag$_2$S–Al the Ag$_2$S layer is weak electrically for large voltages of the positive polarity, so that we measured only the reverse current for the negative polarity. The positive polarity corresponds to the case in which the bottom electrode is positively biased. As there was hysteresis for large voltages,[15] we measured the I-V characteristics for Ag$_2$S layer by a D.C. method. The results are shown in Fig. 4. For small voltages the current is proportional to voltages. At higher voltages, there is a strong non-linear increasing of the current and there is a threshold voltage ($V_c = 5$ V). The Ag$_2$S thin film thickness is 1000 Å. The current changes its magnitude by four orders around the critical voltages.

We investigated on the effect of combined application of a bias D.C. voltage and an A.C. excitation in the non-linear region of the

electrical properties of an Ag$_2$S layer. In the experimental results said above the resistivity of a specimen is observed to drop considerably when the electric field exceeds the critical field. The anomalous behavior of the resistivity suggests that the dislocation model may explain the transport properties. The application of a large D.C. electric field leads to the possibility of depinning fixed dislocations, so that there exists the creation of current-carrying excitations made up freely moving dislocation (see Figs. 3 and 4). On the other hand, in the case of a low field the pinning dislocations oscillate around their equilibrium positions. This vibrational motion of the pinned dislocations may interpret the observation of the frequency-dependent conductivity in an Ag$_2$S layer. Sample resistances are measured over the frequency range of 10 to 10^4 Hz, using a lock-in amplifier. Input voltages are 10 mV to 50 mV, but no voltage dependence has been detectable. A strong dependence of the conductivity on frequency are observed as shown in Fig. 5. The conductivity smoothly increases from the D.C. limit to 10^4 Hz and saturates
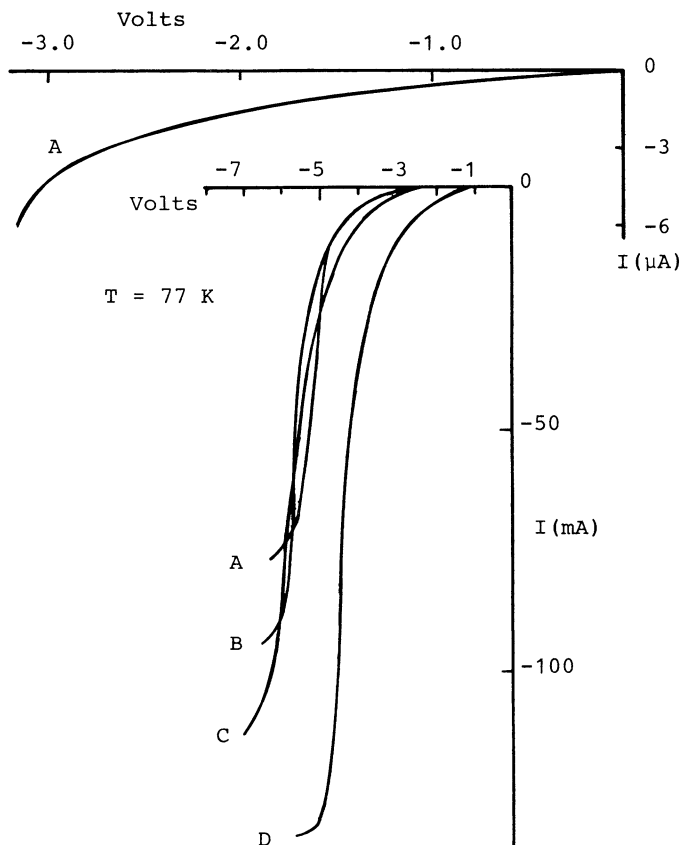
Fig. 4. I-V characteristics for Al(Ag)–Ag$_2$S–Al samples. The critical voltage is about 5 V for the samples of A, B and C.
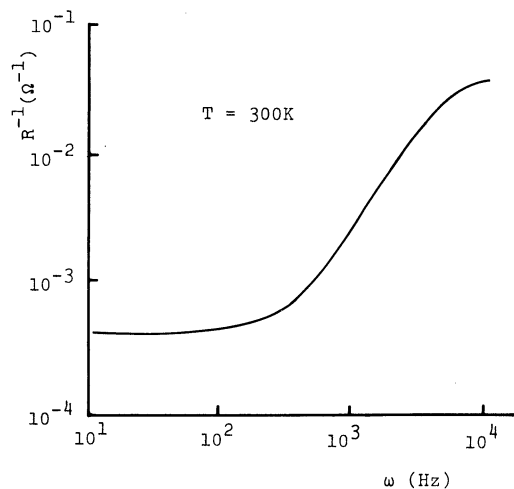
Fig. 5. Conductivity of Ag$_2$S as a function of applied frequency.

above 10^4 Hz.

As the application of a large D.C. voltage depins dislocations, an increase of an applied D.C. voltage should lead to a suppression of the A.C. conductivity drastically. To investigate the dependence of the A.C. conductivity on a D.C. applied voltage, we have performed the same measurements as the measurements in Fig. 3 (the results in Fig. 3 corresponds to the case of a low D.C. voltage). In the measurements a bias D.C. voltage across a specimen and a sinusoidal signal voltage are summed up, and the combined voltage is provided as a signal. A small A.C. voltage as low as about 10 mV has been used. To know the dependence of an alternating current through a specimen on a D.C. bias voltage, it is clear that we need only provide a means of measuring separately and simultaneously the D.C. and A.C. amplitudes. By measuring a voltage across a resistance connected by a specimen by using a lock-in amplifier, we obtain the A.C. current through a specimen as a function of a bias D.C. voltage for typical specimens at the liquid
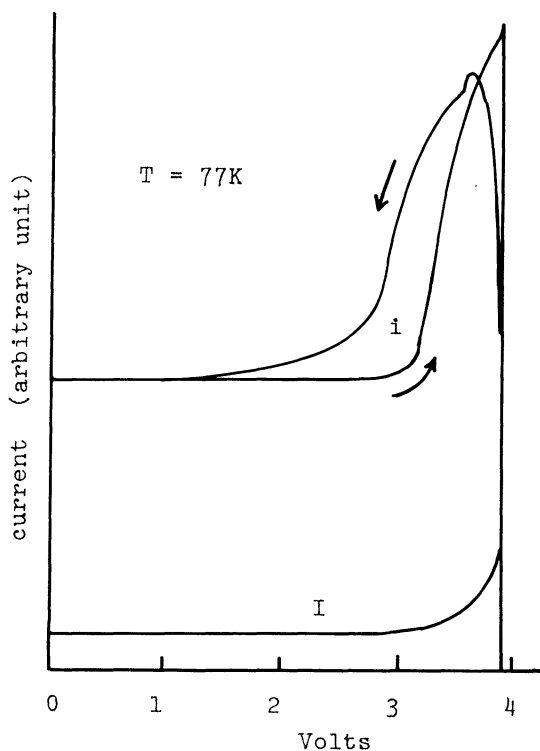
Fig. 6. The dependence of the A.C. current on a D.C. applied voltage. I: I-V characteristics of Ag₂S. i: A.C. current as a function of a D.C. applied voltage. The sinusoidal signal is 5 mV and its frequency is 3 kHz.
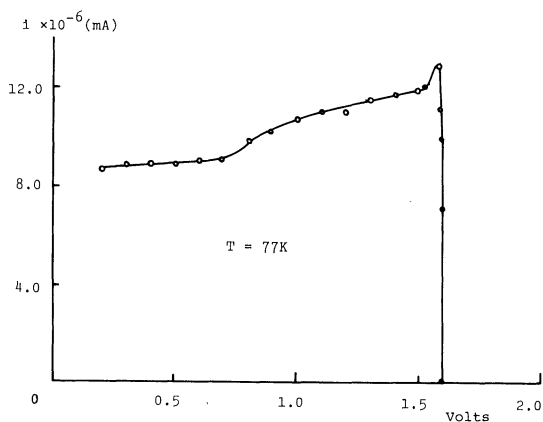

Fig. 7. A.C. current of Ag₂S as a function of a D.C. applied voltage. The A.C. signal voltage is 10 mV and its frequency is 1 kHz.

nitrogen temperature. Figure 6 corresponds to the case of the D.C. voltage swept at a rate of 100 sec. The voltage of A.C. signal is 5 mV and its frequency is 3 kHz. The results shown in Fig. 7 are measured by D.C. method, and

the A.C. signal voltage is 10 mV and its frequency is 1 kHz. These figures show the plots of the A.C. current versus the bias D.C. voltage. The suppresion of the alternating conductivity of the specimen has been achieved by appling a large D.C. electric field. This anomalous behavior of the A.C. conductivity of Ag₂S layer is apparent on considering the fact that the high D.C. voltage releases fixed dislocations at the threshold voltage. Such freely moving dislocation under high electric field can get a high velocity, so that it can not respond to a small applied A.C. signal (about 10 mV) because of the large mass of ion unlike electron. Hence the A.C. conductivity of the specimen becomes zero at the large applied D.C. voltage above the threshold voltage.

§3. Discussion

In the previous section we showed the typical non-linear conductivity of Ag₂S speciments. The non-ohmic behavior of an Ag₂S layer also had been investigated by Sharma and Thomas.[16] They observed the electrical breakdown to Ag₂S in the Au–Ag₂S–Ag system at room temperature and found that the voltage breakdown is strongly affected by silver ion mobility and becomes polarity dependent. However, their experiments can not directly compare with our results.

Bishop considered theoretically a one dimensional system of interacting Brownian particles in periodic local potential to be applied to the problem for mobile ions in a superionic phase. The Langevin equation for mobile ions in a superionic conductor is equivalent to the Brownian motion problem for a one-dimensional array of coupled non-linear pendula.[17,18] According to these theories, there are strong non-linear effects if the field tilts the potential so such an extent that the maxima of potential disappear. At this point the mobility increases strongly. The critical field E_c is given by $E_c = m\omega_0^2 a/2\pi q$. The m is mobile ion's mass, q its charge and ω_0 characteristic frequency of mobile ions. The low temperature ionic current is proportional to applied field E at low field $E \ll E_c$. At high field $E \gg E_c$, the current is again proportional to the field and is due to the field driving the chain of mobile ions uniformly against the viscous force.

Hence, we can expect the saturation of an ionic current. For an ionic conductor such as Ag_2S the critical field E_c is estimated by using the above equation. The mass of Ag^+ ion and its charge are 1.8×10^{-25} kg and 1.6×10^{-19} C, respectively. Far-infrared measurements[19] show that the vibrating frequencies of mobile ions in α-AgI may be of the order of 10^{12} sec^{-1}, which is not higher than those in regular ionic crystal. We use this value for the vibrational frequencies of mobile ions. We assume the interionic distance of a mobile ion to be 1.5 Å. Hence, $E_c = 2.7 \times 10^7$ N/C. This field is too high, so that the strong threshold of ionic current may not be observed in ordinary ionic crystals. But, when we make Ag_2S thin film of an thickness of 1000 Å, we can generate the critical field in the layer using D.C. voltage supply of 2.7 V.

There are some points of agreement between our experimental results and Bishop's theoretical results. (1) There is the strong non-linear electrical conduction and the critical field E_c. When the thickness of Ag_2S film is about 1000 Å, the critical field is $E_c = 5 \times 10^7$ N/C for the threshold voltage $V_c = 5$ V. This value is consistent with the theoretical value. (2) There is the saturation of the current. (3) The theory prodicted that the current changes its magnitude by about 10^4 at the critical field for low temperatures. This value is 10^4 for our experimental results.

Riskin and Vollmer[20] analyzed the diffuse motion of independent particles in a periodic potential and obtained an analytical result for mobility for small friction. There are strong non-linear mobility. The same conclusion was also obtained by Matkowsky and Schuss.[21] But their theory does not predicted the saturation of the current. Bishop's theory is limited to one spatial dimension. Higher dimensions can introduce higher-dimensional correlated motions of mobile ions. However, in our experiments one-dimensional behavior is encouraged by an applied field, and further Dixon and Gillan[22] showed by a molecular dynamics simulation for CaF_2 that the collective excitations are primarily one-dimensional so that transverse coupling arised from two-dimensional might be included crudely as an extra damping contribution. So we think that

Bishop's theory may apply to the case of a high-dimensional conducting material such as Ag_2S.

Vouros and Masters[23] made the vacuum-deposition AgI film and found that the film suffered from a high D.C. internal resistance ($\sim 10^7$ Ω). They considered the high resistance to be due to the presence of high contact resistance between the halide film and the electrode interfaces. The resistance consists basically of the sum of the resistance of the electrolyte and the resistance at the two electrode-electrolyte interfaces. The conductivity at low fields is Ohmic down to the lowest field as seen in Fig. 3. It is therefore concluded that the contacts are Ohmic and the contact resistance is negligibly small. Furthermore, to know whether the main sources of total resistance in our thin film specimen arises from electrolyte resistance or not, we measured the temperature dependence of the resistance of a Al(Ag)–Ag_2S–Al thin film system between 100°C and 170°C. β-silver sulfide below 177°C is an n-type semiconductor with a band gap of 1.3 eV. In this semiconductor phase the conductivity σ is described by $\sigma = A \exp(-E_0/2k_BT)$, where E_0 is the value of the energy gap extrapolated to 0 K and k_B is the Boltzmann constant. The activation energy of our specimen is $E_0 = 1.4$ eV, and this value is about 0.1 eV higher than the activation energy reported by Junod et al.[24] As the temperature dependence of a sample is similar to the behavior of a semiconductor phase, we may say that the large part of the resistance of a specimen lies in the Ag_2S electrolyte.

In β-silver sulfide, just below the transition temperature of 177°C, the fraction of the conductivity due to silver ions is 0.016 for a specimen with excess Ag.[25] The electronic conductivity at room temperature is larger than the ionic conductivity thus making the material imperfect ionic conductors. However, there is some evidence that the fraction value is almost independent of temperatures from 60°–177°C.[26] If we assume this evidence to be valid at more reduced temperatures, we may show that the ionic conductivity is many orders of magnitude greater than the electronic conductivity at the liquid nitrogen temperature because of the high electronic activation en-

ergy as said above, and we may conclude that the total conductivity of a specimen at liquid nitrogen temperature is attributed to the ionic conductivity alone.

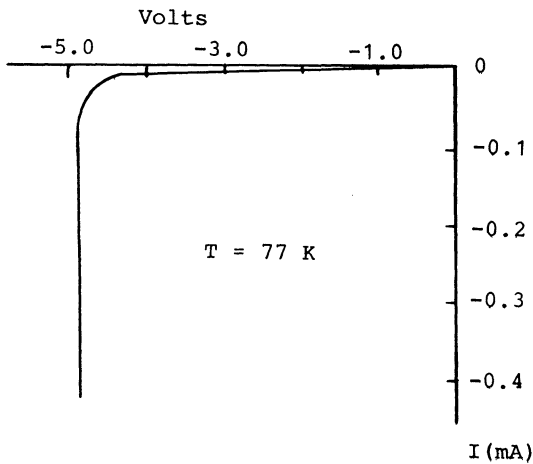AgI is considered to be a purely ionic con-

Fig. 8. I-V characteristics for Ag–AgI–Ag.

ductor in which Ag ions are mobile, so that it is expected the stronger non-linear conductivity to be occurred in AgI because of no existence of the electronic conductivity. We performed the measurement of the I-V characteristics for Ag–AgI–Ag and show the results in Fig. 8. The AgI thin film thickness is about 1000 Å and the threshold voltage is about 5 V. Hence, the critical fields of AgI is nearly equal to that of Ag_2S.

In the previous section we showed the non-linear behavior of I-V properties. The strong non-linear current also may be considered to be due to the space-charge-limited currents in an insulator with traps.[27] If there are neither thermally carriers nor traps in the insulator, the current is space-charged limited current and proportional to the square of the applied voltage, which is usually referred as Child's law. Actually there are thermally generated carriers and traps in an insulator. For lower voltage the current-voltage char-
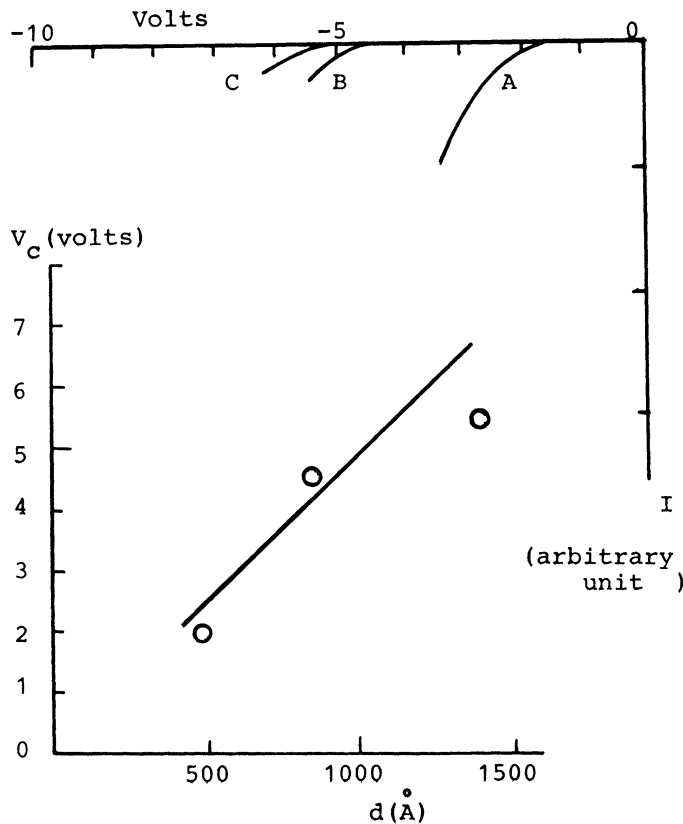
Fig. 9.   Critical voltage versus thickness of an Ag_2S thin film. A = 530 Å, B = 830 Å and C = 1390 Å.

acteristics is Ohm's law and the injected charges may fill the traps. When all traps are filled with electrons, the I-V curve changes suddenly to Child's law and there occurs the strong non-linear current. We said that the critical turn-voltage in our experimental results occurs because of a critical field condition and is not due to the traps effect. If this argument is right, we may expect the different threshold voltages for samples with the different width of the thin film. A plot of the threshold voltage versus the thickness of an Ag_2S thin film is shown in Fig. 9. The threshold voltage increases with increasing separation distance. Hence, we may say that the non-linear condition is not due to the traps effect, but to the critical field condition.

In the above we show the non-linear behavior of I-V properties not to be due to the electrode effect. But it is not possible to rule out the possibility that they might simply be ascribable to an artifact resulting from the use of an imperfect, blocking electrode on the samples. Lines[28] discussed the effect of electric-induced local fields on the dielectric response of ionic conductors. He considered the presence of completely blocking contact through which no itinerant ions can escape or enter the material. As the applied frequency decreases, interfacial charge distribution develops in the boundary layer at the electrodes. This layer progressively screens the bulk material and causes the field in the bulk volume to decrease with decreasing frequency until it approaches zero at $\omega = 0$. At the low frequency ($\omega = 10^2$ Hz), where the capacitance saturates to give a frequency independent "fully blocked" dielectric constant, the conductivity varies quadratically with frequency. However our measured conductivity for Ag_2S as a function of frequency shows the conductivity to be independent of frequency in the same region (see Fig. 5). Our results therefore suggest that the frequency dependence of the conductivity may not originate from the blocking effects.

All evidences from measurements of the electrical properties of a Ag_2S specimen and of a AgI specimen, which is a purely ionic conductor, show that the non-linear Ohmic mechanism may be explained as a result of motion of Ag ions in a layer. Furthermore,

this would suggest the dislocation[29] to present the most appropriate one.

§4. Conclusion

Bishop's theory predicts that there exists the threshold voltage, when cooperative motion exists in ionic conduction. In order to detect highly non-linear electrical conduction and the saturation of its current, we made Ag_2S thin films and AgI thin films. We observed the critical field and the saturation of the current in those specimens. Our experimental results are consistent with Bishop's theory treating a one-dimensional system of interacting Brownian particles in a periodic local potential. But his theory is limited to one dimension, so that the theory is required to extend to the three dimension. Furthermore, the theory predicts that the charges are carried with thermal activated solitons. But we can not decide the existence of the solitons in a chain of coupled mobile ions under the present experimental results, and we are required further experiments to be performed in order to know whether solitons exist or not.

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