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# Electrical Transport and Structural Properties of Bulk As-Te-I, As-Te-Ge, and As-Te Chalcogenide Glasses*

C. H. Seager, David Emin, and Rod K. Quinn
*Sandia Laboratories, Albuquerque, New Mexico 87115*

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A variety of compositions of glass in the As-Te-I, As-Te-Ge, and As-Te chalcogenide series have been prepared and structurally analyzed. The analytical techniques included x-ray powder diffraction, density determinations, and differential-scanning-calorimetry experiments. The temperature dependence of the Hall mobility, Seebeck coefficient, and dc conductivity was determined for six representative alloy compositions. The Hall mobility was found to be *n*-type, low, and activated with nearly equal activation energies in each case. The conductivity mobility was deduced from the *p*-type Seebeck coefficients and the conductivity measurements to have an activated character with a characteristic energy of $0.19 \pm 0.02$ eV for all the measured compositions. These results appear to be inconsistent with the familar Cohen-Fritzsche-Ovshinsky (CFO) picture for transport in amorphous semiconductors, and a new model for conduction in these glasses is proposed. This model involves the hopping of holelike small polarons between sites associated with a common As-Te structural entity which is postulated to be present in all the alloys measured here. The sign, magnitude, and temperature dependence of the dc conductivity, Seebeck coefficient, and Hall mobility are all consistent with this model.

## I. INTRODUCTION

Semiconducting chalcogenide glasses have recently come under scientific scrutiny because of their possible commercial applications. A reasonably complete understanding of electrical transport properties is, therefore, a goal quite germane to further practical utilization. With this in mind we have prepared, characterized, and measured the low-electric-field transport properties of a series of As-Te-I, As-Te-Ge, and As-Te alloys as a function of temperature. Furthermore, a model for conduction in these glasses has been developed which appears to be reasonably successful in its predictions of the magnitude, temperature dependence, and compositional dependence of the data obtained here as well as those obtained by other workers on similar amorphous chalcogenide systems.

### A. CFO Model

The principal categorization of the electronic properties of these glasses has been provided by the model of Cohen, Fritzsche, and Ovshinsky (CFO).[1] This model envisions the disordered material as possessing an essentially *rigid* atomic structure with the electronic states of these materials being so-called extended states at the center of the valence and conduction bands[2] and being spatially localized states in the tails of these bands. In some (but not necessarily all) cases the tails of localized states from the valence and conduction bands may overlap, giving rise to a significant density of states at the Fermi energy. A major feature of the CFO picture, and the one which ensures semiconducting behavior, is the postulation of a mobility edge. This suggestion is that at some energy on the shoulders of the band the nature of the charge transport associated with the electronic states changes from that which is presumed characteristic of motion involving localized states to that which is related to motion involving the extended states of the relevant band.

Specifically, the electrical transport which is associated with the localized states is characterized by the low-mobility ($< 0.01$ cm$^2$/V sec at $\sim 300$ K) thermally activated hopping of charge carriers,[3] while that which involves the extended states is associated with much higher (nonactivated) mobilities (5–100 cm$^2$/V sec at $\sim 300$ K).[4] This implies the observance of thermally activated conductivity over a considerable range of temperature.

Rather than pursue a lengthy discussion of the theoretical justifications of the CFO model,[5] let us consider the predictions of this model regarding a number of commonly measured transport coefficients. The conductivity in this picture would be expected to vary as $\sigma_0 e^{-E_\sigma/kT}$ for the chalcogenide glasses. For conduction involving the extended states, the activation energy $E_\sigma$ would be the energy difference between Fermi energy and the mobility edge of the band associated with the carriers which provide the dominant contribution to the electrical current. The value of $\sigma_0$ would range roughly from 10 to $10^3$ mho/cm depending on the estimates of the values of the carrier mobility and density of states near the mobility edge. A measurement of the thermoelectric power would also be expected to yield directly the energy difference (defined here as $E_S$) between the mobility edge and the Fermi level in the likely case where two carrier effects are not predominant. In this case the formula for the Seebeck coefficient associated with the motion of a single species of carrier in a nondegenerate semiconductor,

$$S=(k/e)[(E_S/kT)+A], \qquad (1)$$

should be applicable. A measurement of the thermoelectric power then yields $E_S$ directly in the cases where $S$ is found experimentally to vary as $1/T$ (here $A$ is a constant depending on the carrier scattering mechanism). Calculations (using the random-phase-model suggested by the CFO picture) of the carrier mobility above the mobility edge[6] confirm that it decreases slowly with increasing temperature. Thus, $E_\sigma$ should be composed entirely of the energy required to excite a carrier to the mobility edge and should therefore equal $E_S$.

A calculation by Friedman within the random-phase-model[6] has shown that the Hall mobility $\mu_H$ associated with the "diffusive" extended-state motion is low (of the order 0.5 $cm^2/V$ sec or greater), temperature independent, and has the sign of electrons in the case where the majority of the current is carried by holes in threefold coordinated glasses. This sign anomaly is, in fact, expected (for holes) whenever the equivalent hopping sites are arranged in a triangular array (in the plane perpendicular to the applied $B$ field).

Thus in principal, accurate measurements of the conductivity, Seebeck coefficient, and Hall effect on a series of chalcogenide glasses should be sufficient to test some of the aspects of the CFO model for these materials. This is particularly true in light of the quite different predictions of the alternative model which we shall describe below.

## B. A Polaron Conduction Model

### 1. General Considerations

A different model for conduction in these materials can be formulated if the possibility is admitted that atomic displacements occurring about an excess charge carrier lead to the formation of a "self-trapped" state (a small polaron). A small polaron is the unit comprised of a localized excess charge carrier and the displacement of the atomic constituents which occurs if the carrier lingers in the vicinity of an atomic site for an ample time for atomic rearrangements to take place. Such a phenomenon is associated with low-mobility materials.[7] The question of small-polaron formation in disordered materials, chalcogenide glasses in particular, is not at odds with the knowledge that has been obtained from studies of low-mobility ($\mu \lesssim 1$ $cm^2/V$ sec) crystalline systems in that there already exists experimental evidence for small-polaron formation in such crystals.[8] In addition, the presence of disorder in noncrystalline compounds generally tends to impede the coherent propagation of an excess carrier through the lattice[9]; it is this "slowing down" of the carrier in addition to a possible reduction of the local stiffness of the material (and/or change of local order) that may make polaron formation more likely in disordered chalcogenide compounds than in their crystalline counterparts.[10,11] Furthermore since holes appear to be more mobile than electrons in a variety of crystalline chalcogenide materials in which the electrons are believed to be self-trapped (orthorhombic sulfur[12] and $As_4S_4$,[13] for example), it is not unreasonable to suspect that self-trapped holes would be more mobile than self-trapped electrons in amorphous chalcogenide substances as well; thus, hole-like small polarons might be expected to dominate the observed conduction processes in these materials.

### 2. Insensitivity of Transport Properties to Composition: The Idea of a Dominant Constituent

If it is accepted, for the moment, that hole-like small polarons are formed in these alloys, it is in some circumstances possible to quantitatively predict the magnitudes and temperature dependences of the resulting transport coefficients. In particular, we believe that the observed insensitivity of the nature of the transport to additions of iodine or germanium to the As-Te binary glass seen here suggests the following, rather simple "local" model of conduction in these alloys.

We first note that the small-polaron charge carrier and the displacement of the atomic constituents of the glass which the carrier's presence induces are essentially localized with a spatial extent of the order of an interatomic spacing. Such a "self-trapped" unit will be capable of moving to a very similar situation about a nearby site provided that there are a sufficient number of nearly equivalent structural entities close to it. In particular, if one assumes (as we will argue that the experimental results suggest) that the "hole-like" small polaron is associated with an As-Te bond within an As-Te structural unit (such as an As atom bonded to three adjacent Te atoms), then the charge carrier may move through the material by hopping between and amongst similar structural entities. Since the small polaron is local in nature, the absence of long-range order may be expected to have little influence upon it or its motion.[7] If hopping between connected As-Te units provides the easiest (most conductive) path for the carrier to move (there being a sufficient number of such units to provide a reasonably well connected regions of As-Te units throughout the glass), then the As-Te structural unit may be said to be the *dominant constituent* of the glass. The transport properties of the glass will then essentially manifest those of this dominant constituent. Glasses having nominally different compositions but possessing the same dominant constituent will be very similar in their electrical transport properties. Thus although the chalcogenide glasses whose study forms the basis of this paper ostensibly are very different, the similarity in their transport properties[8] is consistent with the notion of a dominant constituent existing in all of these As-Te based glasses.

While, the existence of a dominant constituent is *not* equivalent to postulating large scale (20 Å regions or greater) phase separation, the occurrence of phase separation is certainly compatible with this model.

### *3. Specific Predictions of Transport Properties*

Having suggested that charge transport associated with a dominant constituent may be germane to understanding conduction in many chalcogenide glasses, we can proceed to examine the possible nature of a polaronic conduction process within such a constituent. If electrons and holes are self-trapped in the dominant constituent, we may expect, from prior studies of the small polaron[7,14] that both electron and hole states are distributed very densely in energy (the band-narrowing effect). In crystalline materials small-polaron bands are extremely narrow (the order of meV or less). In the case of noncrystalline materials the spread in energy of the local small polaron is simply the so-called "disorder energy." Assuming that the disorder energy is comparable with $kT$, the Fermi level will be strongly pinned in the center of the gap between the very dense electron- and hole-polaron bands.

The electrical conductivity $\sigma$ in the high-temperature semiclassical regime ($kT \gtrsim \frac{1}{3}$ phonon energy) will display an activated character over a wide range of temperature. In this case the activation energy $E_\sigma$ will be the sum of the energy required to generate hole-like small polarons and the energy required for hopping of the carrier from site to site (we denote this energy as $W_H$).[7] The value of $\sigma_0$ can be deduced from small-polaron theory[7] and is found to be

$$\sigma_0 = (Ne^2a^2\nu/kT)p \,. \tag{2}$$

Here $N$ is the density of equivalent sites in the dominant constituent ($\sim 10^{22}$ cm$^{-3}$) $a$ is a typical lattice constant, $\nu$ is a typical lattice vibrational frequency, and $p$ is a factor which in the adiabatic theory of the small polaron[14,15] is unity (in the nonadiabatic theory it is less than 1). The value of $\sigma_0$ should thus be within an order of magnitude of $10^2$–$10^3$ mho/cm (for $p = 1$) and should vary by less than an order of magnitude among glasses having the same dominant constituent.

If, as we have assumed, hole-like small polarons carry the majority of the current in these glasses, measurement of the Seebeck coefficient should yield the energy required to generate these carriers, $E_S$, via the relation[7]

$$S = \frac{k}{e}\left(\frac{E_S}{kT} + A'\right) , \tag{3}$$

where $A'$ is a weak function of temperature, typically less than ~10 which vanishes for $kT \gg$ disorder energy. Thus, the difference between $E_\sigma$ and $E_S$ should yield the hopping energy $W_H$. This quantity should be invariant among glasses whose electrical properties manifest charge motion through the same dominant constituent.

Measurements of the Hall mobility can further elucidate whether or not small polarons dominate the conduction processes in the chalcogenide alloys. Although, the theory of the Hall effect of small polarons[15–17] as well as that of the random-phase model[6] predicts an $n$-type Hall effect (in the case where the holes which contribute to the Hall mobility move among nondegenerate sites which are generally arranged with a three-site geometry),[18] the temperature dependence of the Hall mobility in the two models differs. In the small-polaron model the Hall mobility is predicted to be small (less than 0.1 cm$^2$/V sec) and activated with an energy which is predicted to be essentially $\frac{1}{3}$ of that found for the conductivity mobility, $W_H$:

$$\mu_H = \mu_0 e^{-W_H/3kT} \,. \tag{4}$$

The values of $\mu_0$ (in the adiabatic regime) generally lie in the range 1.0–0.1 cm$^2$/V sec.[7] The random-phase model predicts somewhat larger and *temperature-independent* Hall mobilities.

Having examined the predictions of these two quite different pictures of transport in the chalcogenide alloys, it remains for us to review the data presented here and the data of other workers on similar glass systems.

## II. EXPERIMENTAL

### A. Glass Synthesis and Characterization

The synthesis of As-Te-I glasses has been previously outlined in detail.[19] The As-Te-Ge glasses were prepared from 99.9995% arsenic and 99.9999% germanium and tellurium. Approximately 25 g of the starting materials was crushed, weighed in the desired proportions, and loaded into especially designed quartz ampules (25-mm i.d.).[19] All of these operations were performed in dry, high-purity argon. The samples were heated to (920 ± 3)°C over the length of the ampule and rotated for 4 h; periodically the rotation was interrupted. The sample container was then quenched in ice water while rotating. Samples prepared in this manner were homogeneous and sufficiently free of thermal cracks to allow electrical measurements. The Ge-Te glasses required several procedural modifications: Smaller ampules (6-mm i.d.), longer reaction times (20 h), and faster quenching rates (liquid-nitrogen quench) were necessary to produce homogeneous-glassy material. Although $As_{50}Te_{50}$ glasses could be prepared in the manner described for the As-Te-I system,[19] glass formation became increasingly difficult as the composition of these binary glasses approached the atomic ratio of stoichiometric $As_2Te_3$. The technique used for preparing $As_{40}Te_{60}$ was similar to that used for the Ge-Te glasses except that (a) 3-mm i.d. ampules and subsequently 3×7×25-mm rectangular ampules, were used in order to achieve even faster quench rates, (b) the ampules were rotated with intermittent interruption for 30 h, and (c) the temperature was held at 800 °C. Each sample was routinely analyzed to verify the chemical composition, and these results indicate that the subscripts cited in this work (atomic percent in all cases) are accurate to within 1%.

All samples were examined by x radiation with a Debye-Scherrer powder camera using zirconium-filtered molybdenum and/or nickel-filtered copper radiation. The samples were considered noncrystalline if only diffuse haloes were observed in the powder patterns. Density measurements using a Berman torsion balance were also performed on representative compositions. Thermal properties of the samples were systematically investigated using the techniques of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Both the thermogravimetric balance[20] and the DSC experimental techniques[19] have been discussed previously. Calorimetric scans were made with a Perkin-Elmer DSC-1 calorimeter from room temperature to ~ 500 °C on encapsulated powder and bulk samples at rates of 5 and 20 °C/min. Since a discussion of the TGA data, as well as a detailed presentation of the totality of the structural data, is beyond the scope of this paper, a full discussion of the structural data obtained from the samples used in the transport measurements, as well as others, will be deferred to a future structural paper by one of us (RKQ). However a brief synopsis of some of the results will be given in Sec. II A.

### B. Electrical Transport Measurements

#### *1. Hall Measurements*

Hall mobilities as low as $10^{-3}$ cm$^2$/V sec in these glasses can be measured on samples having impedances as great as $10^7$–$10^8$ Ω. The apparatus used for the present measurements is shown in schematic form in Fig. 1. ac measurements allow the use of phase-sensitive detection techniques which minimize problems resulting from poor signal-to-noise ratio. For a Hall voltage measurement it is required that no current be drawn from the sample in the Hall ($\vec{E}\times\vec{B}$) direction, and hence the preamplifiers shown in Fig. 1 utilized driven shields[21] around the input conductors to reduce their input capacitance to roughly 1–2 pF. This assured input impedances of several hundred MΩ at the frequencies ($10^2$–$10^3$ Hz) used during the measurements. A variable resistor was used to move the ground reference to a line nearly passing through the two Hall probes, thus minimizing both drift and distortion problems in the preamplifiers. The residual offset signal across the Hall probes was cancelled by a small adjustable signal from a phase shifter fed from the main audio oscillator. After processing through a lock-in amplifier the signal was introduced into a small on-line signal-averaging computer. This computer also controlled the magnetic field,[22] sweeping it in a linearly increasing fashion as shown in Fig. 1. The Hall signal corresponding to a given strength of the magnetic field was stored in a particular channel of the computer memory. The full computer print-out thus gave the Hall voltage as a function of magnetic fields (up to 15 kG). A further procedure which minimized error due to drift in the lock-in output was alternation of the direction of magnetic field on each successive sweep cycle. Since each sweep cycle encompassed a 90-sec

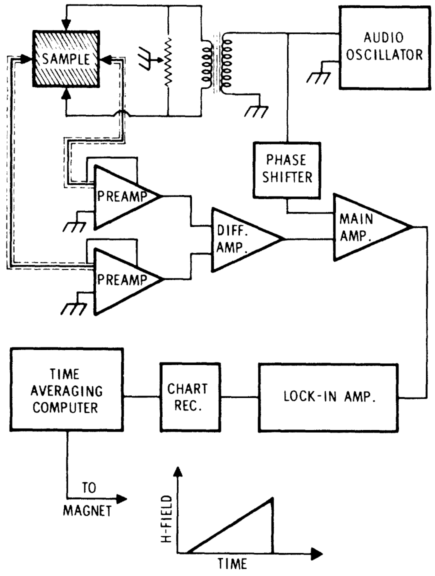

FIG. 1. Schematic diagram of the ac Hall-effect apparatus.

period, several hundred sweeps could be made during a single day of operation, resulting in signal-to-noise improvements exceeding an order of magnitude over the raw lock-in output.

Samples used in the Hall measurements were generally about 1 cm square and 1 mm thick. Electrical contact was made via brass pins which contacted small areas on the edge of the samples wetted with In-Ga alloy. This method provided stable, noise-free, low-resistance contacts over the range of temperatures employed. The impedance of the contacts was verified by the methods discussed in Sec. IIB 3. Control experiments were also carried out to verify that the In-Ga contact patches introduced no spurious effects into the Hall measurements.

In the case where the sample has uniform thickness $d$ and contact areas which are small relative to its total edge area, van der Pauw[23] has shown that

$$\mu_H = \frac{1}{B}\,\frac{V_H}{V_D}\left(\frac{R_d d}{\rho}\right) \tag{5}$$

where $B$ is the magnetic field strength in gauss, and $V_H$ and $V_D$ are the peak-to-peak values of the Hall and drift voltages, respectively. $R_d$ is the impedance of the sample measured between the drift-voltage electrodes in ohms, $\rho$ the sample resistivity in $\Omega$ cm, and $d$ the sample thickness in cm. The factor in parentheses accounts for the actual electric field distribution due to the point contact technique as well as any contact resistances which may be present; it is generally of the order of 1.5–2.0 for nearly square samples having contacts of negligible impedance.

All measurements were carried out with drift fields less than 5 V/cm to minimize sample heating and to avoid the well-known nonlinearities[1] present in current-voltage characteristics that occur in these glasses at higher field strengths. In all cases the observed Hall mobilities were independent of both the electric and magnetic field intensities.

The sample holder was situated in a standard cryogenic Dewar capable of maintaining the sample temperature to within ± 0.05 K over the periods involved in the actual measurement. Sample temperatures were measured by means of two calibrated chromel-*p* constantan thermocouples located in close proximity to the specimen. Determination of the sample temperature, resistivity, drift voltage, and drift impedance $R_d$ was made before and after each measurement of the Hall mobility.

### 2. Seebeck Measurements

The Seebeck-effect sample holder consisted of two small copper blocks, each provided with its own resistance heaters, attached to a Teflon mounting block. The sample had dimensions of roughly $1\times0.2\times0.1$ cm and was suspended lengthwise between the two blocks in vacuo. Thermal contact between the sample and the blocks was provided by a light coating of thermally conducting grease, and the temperature of each end of the sample was measured by calibrated chromel-*p*-constantan thermocouples which were connected in the differential mode for the determination of the actual temperature difference across the specimen. Electrical contact was made via silver paint and phosphor bronze clips in close proximity to the thermocouples at each end of the sample. The actual Seebeck emf was measured with a Keithley model 610R electrometer, thus ensuring negligible current drain from the sample.

The sample holder was contained in a standard helium-nitrogen cryostat which had the capability of maintaining the sample temperature within close limits (± 0.1 K) for long periods of time. During the measurement the Seebeck emf was plotted on an $X$-$Y$ recorder as the temperature gradient across the sample was varied continuously over the range ± 3 K at the rate of roughly 1 K per minute. The resulting plots of emf vs $\Delta T$ were essentially linear, and the slope of these plots is in fact the Seebeck coefficient. The temperature at both ends of the sample and the two-point resistance across it were measured before and after each Seebeck measurement. Typically, the mean temperature of the sample rose about 5 K during the measuring process. Several control experiments varying sample geometry, heating rates, thermocouple locations, etc., were carried out to ensure that this technique provided an accurate measurement of the sample temperature gradient.

### 3. Conductivity Measurements

The dc conductivity of these glasses was measured by the four-probe van der Pauw technique[23] while the samples were in the Hall-effect sample holder. The current through the specimen was measured via calibrated milli- and microammeters and the voltage by a Keithley model 610R electrometer. By comparing two-probe resistances with the actual resistivity of the sample, it was found that the In-Ga alloy patches used for contacts had negligible resistance. Two-probe conductance measurements made in conjunction with the Seebeck experiments were also employed to characterize the temperature dependence of the conductivity of the glasses. All measurements were made in vacuo and in the absence of visible light. No electric field dependence of the conductivity was detected over the range of fields employed (~ 0.1–5 V/cm).

## III. RESULTS

### A. Structural Analysis

#### *1. X-Ray Results*

Although no discreet lines are observed in the x-ray diffraction patterns of these glasses, several haloes are clearly visible and reproducible in position. A densitometric examination of the x-ray data has allowed us to fix the approximate position and relative intensity of the diffuse haloes for all compositions studied. These data are reproducible from sample to sample of equivalent composition as well as for samples of the same boule. It has previously been noted[19] that the haloes in the As-Te and As-Te-I glasses are centered about 3.00 ± 0.05 and 1.82 ± 0.03 Å with the former halo approximately three times more intense than the latter. It is striking that the position and relative intensity was apparently independent of composition for these alloys (despite rather large density variations). This suggests that these glasses contain a common structural unit.

The position of the haloes in glasses containing germanium were found to vary with chemical composition. For glasses with high arsenic content (As, 40–50 at.%; Te, 35–50 at.%), haloes were observed at 3.03 ± 0.02, 1.83 ± 0.02, and 1.18 ± 0.03 Å. However glasses containing little or no arsenic but large amounts of Te showed haloes at 3.17 ± 0.02, 1.88 ± 0.02, and 1.20 ± 0.03 Å. The similarity of Ge-containing glasses with high arsenic content to the As-Te-I glasses supports the notion of a dominant structural entity, presumably associated with As and Te, being present in all of these glasses. Although haloes centered at different positions are observed in the glasses containing only a small amount of arsenic, this does not preclude the presence of an As-Te based structural entity. For example, if all the arsenic in $As_5Te_{80}Ge_{15}$ were involved in an As-Te unit, such units would account for $\lesssim 8$ wt% of the sample. Since this value approaches the minimum limit discernible by x-ray diffraction methods, the very nature of the diffuse patterns makes detection unlikely.

TABLE I. Densities of the various as-prepared chalcogenide alloys.

| Glass composition | $\rho$ (g/cm$^3$) | Glass composition | $\rho$ (g/cm$^3$) |
|---|---|---|---|
| $As_{40}Te_{60}$ | 5.55 | $As_{50}Te_{15}I_{35}$ | 4.68 |
| $As_{50}Te_{50}$ | 5.36 | $As_{40}Te_{50}Ge_{10}$ | 5.34 |
| $As_{50}Te_{48}I_2$ | 5.37 | $As_{50}Te_{45}Ge_5$ | 5.36 |
| $As_{50}Te_{45}I_5$ | 5.30 | $As_{50}Te_{35}Ge_{15}$ | 5.26 |
| $As_{47}Te_{43}I_{10}$ | 5.25 | $As_5Te_{80}Ge_{15}$ | 5.54 |
| $As_{50}Te_{30}I_{20}$ | 5.00 | $Te_{83}Ge_{17}$ | 5.52 |

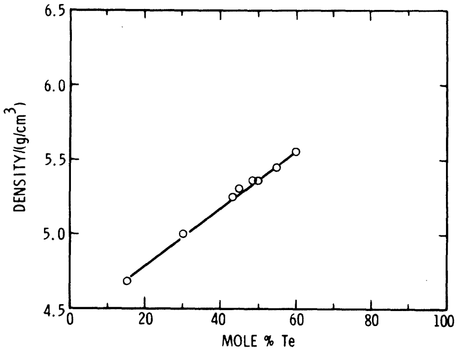

FIG. 2. Density of the various as-prepared chalcogenide alloys versus Te concentration for the $As_{50}Te_{50-x}I_x$ glasses.

#### *2. Density Results*

The densities of several glasses examined in this study are shown in Table I. From these data it can be seen that in general the density increases with Te concentration. The most striking variation of density with composition arises in the As-Te-I system for which the observed experimental dependence is illustrated graphically in Fig. 2. The densities of this glass system show a positive linear dependence on the amount of Te present. Since Te and I have nearly equal atomic weights, this density increase reflects the fact that the structure is becoming more compact as the fraction of Te increases. This presumably results from an increase in As-Te and/or Te-Te bonds.

#### *3. Thermal Results*

Typical thermal analysis results for the As-Te-Ge glasses are displayed in Table II. All DSC data were reproducible to ± 2 °C on redundant samples from the same boule and for the same compositions of different boules. The values listed here show good agreement with that published for similar compositions by Savage[24] and Iizima *et al.*[25] The endothermic melting temperature is almost composition independent and agrees quite well with the eutectic temperature (375 °C) for Te-rich Ge-Te alloys as found in Hansen,[26] whereas $T_g$ and $T_x$ are seen to be composition dependent.

Details of the thermal data for As-Te-I glasses have been discussed previously.[19] These data are reproduced in Table II for comparative purposes. As was noted, for iodine concentrations less than 20 at.%, $T_g = 120 \pm 8$ °C, independent of Te-vs-I composition. Above 20 at.%, $T_g$ decreases to 65–70 °C as iodine increases to 37 at.%. For these same glasses, $T_x$ varies from 210 °C for I = 0 to 230 °C for I = 7 at.%, and for I ≥ 10 at.% the crystallization exotherm becomes indistinguishable from the multiple melting endotherms.

TABLE II. Thermal analysis data, where $T_g$ is the glass transition temperature, $T_x$ the start of exothermic crystallization reaction, and $T_m$ the temperature of melting endotherm.

| Composition | $T_g$(°C) | $T_x$(°C) | $T_m$(°C) |
|---|---|---|---|
| $As_{50}Te_{35}Ge_{15}$ | 243 | 360 | 410 |
| $As_{50}Te_{45}Ge_5$ | 160 | 295 | 363 |
| $As_{40}Te_{50}Ge_{10}$ | 180 | 312 | 375 |
| $As_5Te_{80}Ge_{15}$ | 129 | 228 | 375 |
| $Te_{83}Ge_{17}$ | 133 | 225 | 380 |
| $As_{40}Te_{60}$ | 105 | 160 | 365 |
| $As_{50}Te_{50}$ | 128 | 210 | 365 |
| $As_{50}Te_{48}I_2$ | 120 | 205 | 367 |
| $As_{50}Te_{45}I_5$ | 121 | 225 | 360 |
| $As_{47}Te_{43}I_{10}$ | 120 | 215 | 350 |
| $As_{50}Te_{30}I_{20}$ | 118 | a | 350 |
| $As_{50}Te_{15}I_{35}$ | 67 | a | b |

[a] Crystallization exotherms were not observed for these samples. This is probably due to the complex nature of the chemical reactions and multiple high temperature phases that are possible.

[b] Multiple melting endotherms were observed for this glass. The continuously changing heat capacity suggests several possibilities involving activated processes (cf. Ref. 19).

The uniformity of $T_m$ for the samples containing no germanium (therefore distinguishable from the GeTe eutectic) suggests the existence of common features in the high-temperature structure of these glasses. Several DSC scans of polycrystalline $As_2Te_3$ showed a melting endotherm beginning at 365 ± 3 °C which is very close to the value of $T_m$ obtained in these As-Te and As-Te-I glasses with a single endotherm.

### B. Electrical Transport Measurements

Although a variety of compositions of As-Te-I, As-Te-Ge, and As-Te glasses were synthesized and analyzed, only six representative compositions were fully characterized electrically. Since the transport coefficients appear to vary little with changes in composition, the scope of these studies appears to be wide enough to facilitate an understanding of the nature of conduction in this series of glasses. Efforts have also been made to measure the transport properties of a $Ge_{17}Te_{83}$ glass; the presentation of the preliminary results of this study will be deferred to Sec. IV.

#### 1. Hall Mobility

*a. As-Te-I Glasses.* The Hall mobility was measured on a single sample of two compositions in this series and the results are shown in Fig. 3. The measured mobilities were *n* type. It is seen that the temperature dependence of two glasses can be reasonably well described by an Arrhenius-type behavior with a characteristic activation energy of 0.06–0.07 eV. In the case of the 2-at.% iodine composition, this energy appears to increase somewhat below 240 K. The error bars reflect the accuracy with which the temperature dependence of $\mu_H$ is known, and they were determined from the signal-to-noise ratio present in the computer print-out of the Hall voltage versus magnetic field intensity. Due to the fragility of these glasses some of the specimens could not be prepared with completely uniform thickness *d*, and others had small chips missing from the edges. Thus, the sample geometry was not always identical to the ideal case considered by van der Pauw. For this reason the error bars in Figs. 3–5 do not give the absolute error of each point but rather reflect the accuracy to which the temperature dependence of $\mu_H$ could be determined. The absolute error in $\mu_H$ is estimated at ~ ± 10%. Spot checks were also made for any frequency dependence of $\mu_H$: none was found (from ~ 50–2000 Hz) in any of the chalcogenide alloys reported in this study.

Previous measurements by Peck and Dewald[27] on a glass ($As_{53}Te_{43}I_4$) similar to our low-iodine materials yielded $\mu_H \simeq 0.08$ $cm^2/V\,sec$ at room temperature. This value appears to be consistent with our measurements. Their studies indicated, as do ours, that *n*-type Hall effects occur in this

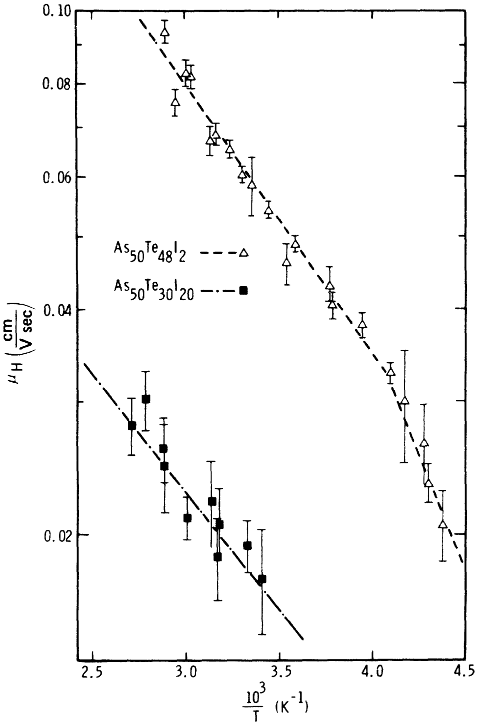

FIG. 3. Hall mobility vs temperature in the As-Te-I glasses.

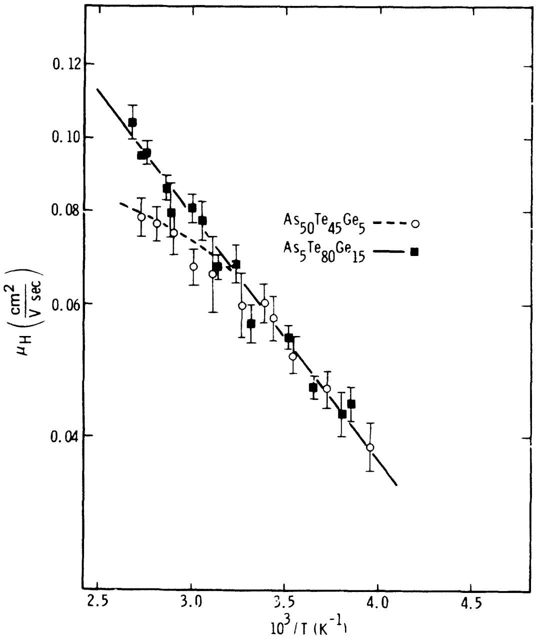

FIG. 4. Hall mobility vs temperature in the As-Te-Ge glasses.

glass system.

*b. As-Te-Ge Glasses.* The Hall mobility was measured on two samples of each of two compositions in this series, and the results for one sample of each alloy are plotted in Fig. 4. As in the case of the As-Te-I glasses, the mobilities were again observed to be *n* type. In general, the second sample of each composition had a temperature dependence identical to the first, but the magnitude of the measured mobilities varied by about 10% in the case of the $As_5Te_{80}Ge_{15}$ samples and 20% in the case of the $As_{50}Te_{45}Ge_5$ samples. This variation in apparent magnitude from sample to sample could result from applying Eq. (3) to specimens which did not possess completely uniform thicknesses.

In general, the temperature dependence of the Hall mobility can be well described as activated with an energy of 0.06–0.07 eV, except in the case of the $As_{50}Te_{45}Ge_5$ samples in which $\mu_H$ appeared to flatten out somewhat above 300 K. As can be seen, the magnitude, sign, and temperature dependence of the observed mobilities were quite similar to those measured in the case of the As-Te-I alloys. Panus *et al.*[28] have measured $\mu_H$ at room temperature on an As-Te-Ge composition which is quite similar to our $As_5Te_{80}Ge_{15}$ material, and their value of 0.053 $cm^2/V$ sec is seen to be in good agreement with our results. They also found the Hall mobility to be insensitive to wide variations in alloy composition; the similarity of all our Hall results agrees with their observation.

*c. As-Te Glasses.* The Hall measurements in the two binary glasses investigated reveal similar behavior to that found for the four ternary alloys (above). The *n*-type Hall mobilities are seen in Fig. 5 to be thermally activated. The activation energies characterizing each curve are $0.05 \pm 0.01$ eV for the $As_{40}Te_{60}$ composition and $0.06 \pm 0.01$ eV for the $As_{50}Te_{50}$ glass. The proper characterization of the 40–60 glass is important because of the possibility that this glass contains more of the most probable As-Te bonding units as a result of its compositional equivalence to the only known As-Te binary compound, $As_2Te_3$. For this reason the Hall mobility was also checked on a second sample of this glass; the second sample displayed behavior very similar to that shown in Fig. 5.

### 2. *Seebeck Measurements*

*a. As-Te-I Glasses.* The measured Seebeck coefficients were, without exception, *p* type and are plotted in Fig. 6. More than one sample of each composition was measured although for clarity the results for only one specimen of each alloy are shown; in general, the Seebeck coefficient was very reproducible within each particular composition. Except for the 20-at.% iodine glass at low temperatures, the data for all the alloys are pro-

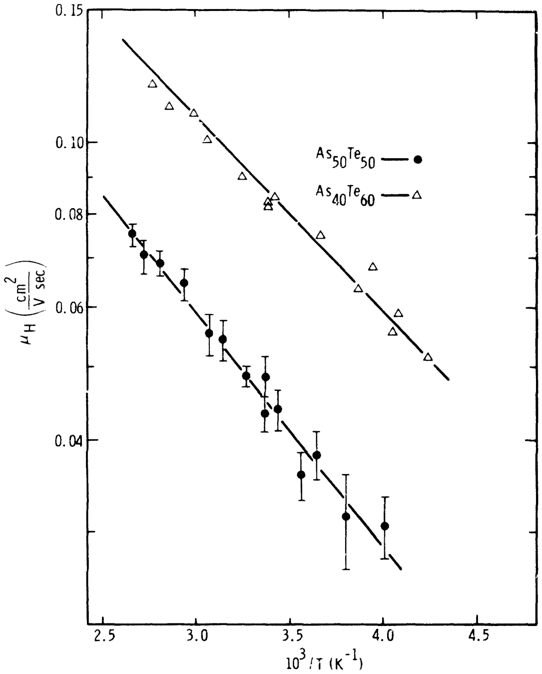

FIG. 5. Hall mobility vs temperature in the As-Te glasses.

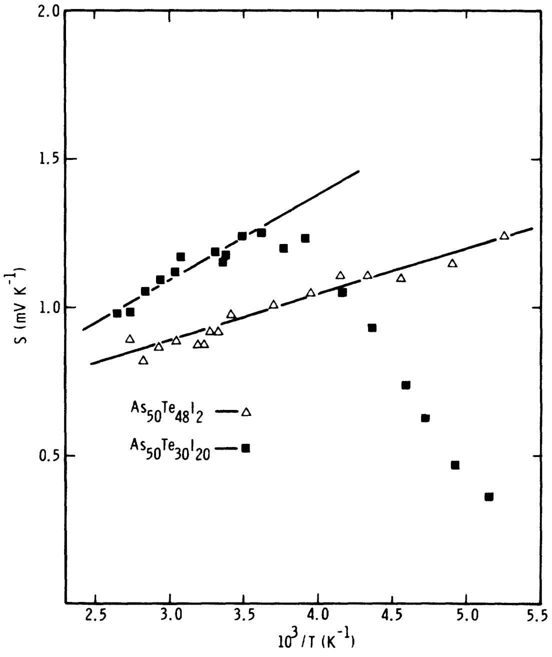

FIG. 6. Seebeck coefficient vs temperature in the As-Te-I glasses.

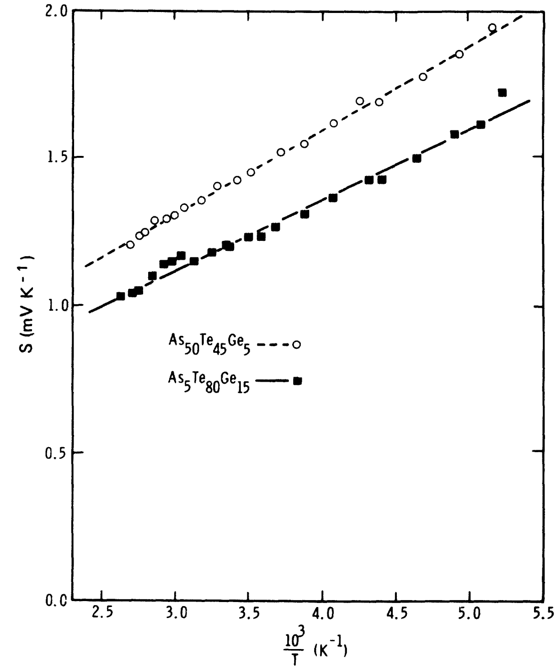

FIG. 7. Seebeck coefficient vs temperature in the As-Te-Ge glasses.

portional to the inverse of the absolute temperature. Applying Eq. (3) to the results, it is found that $E_S = 0.16$ and 0.27 eV for the 2- and 20-at.% (for $T > 260$ K) iodine compositions, respectively. The values of $A'$ deduced from the data lie between 4 and 5 for all the compositions.

*b. As-Te-Ge Glasses.* The Seebeck data for one specimen of each composition are shown in Fig. 7. Again, all the Seebeck coefficients measured were *p* type and appeared to vary linearly with inverse temperature. As in the case of the iodine containing glasses, reproducibility of the Seebeck coefficients within each composition was excellent. These data yield $E_S = 0.24$ and 0.29 eV for $As_5Te_{80}Ge_{15}$ and $As_{50}Te_{45}Ge_5$, respectively. As in the As-Te-I glasses, the values of $A'$ are roughly 4.

*c. As-Te Glasses.* The *p*-type Seebeck coefficients found for both compositions are plotted in Fig. 8. Applying Eq. (3) to the $As_{50}Te_{50}$ data, we find that $E_S \simeq 0.25$ eV and $A' \simeq 4$. For the particular $As_{40}Te_{60}$ sample whose data are shown in Fig. 8, $E_S = 0.27$ eV and $A' = 2.1$. A similar series of measurements on a second sample yielded $E_S = 0.30$ eV and $A' = 2.2$. Since the errors in determining $E_S$ for each sample appeared to be about the same as the observed sample-to-sample variation, we conclude that $E_S \simeq 0.29 \pm 0.02$ and $A' \simeq 2.1 \pm 0.1$. Measurements by Rockstad *et al.*[29] on thin-film $As_2Te_3$ also yield a $1/T$ dependence of $S$ with $E_S = 0.29$ eV. Thus, our Seebeck measurements on bulk $a$-$As_2Te_3$ appear to be in good agreement with the thin-film measurements of

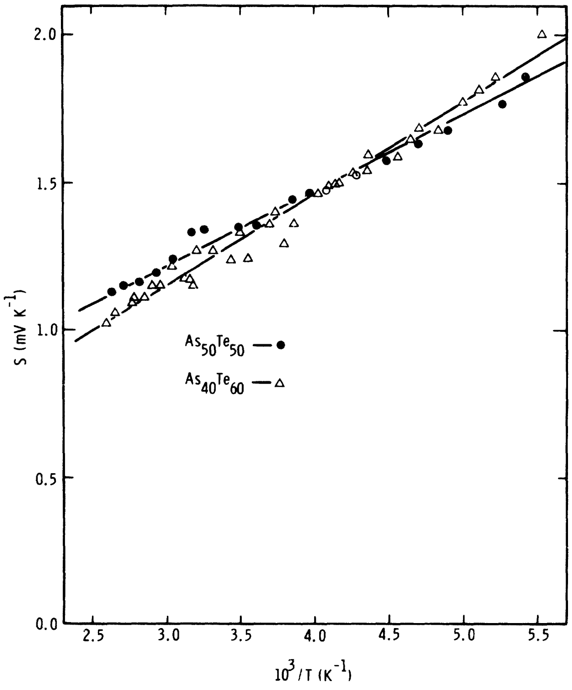

FIG. 8. Seebeck coefficient vs temperature in the As-Te glasses.

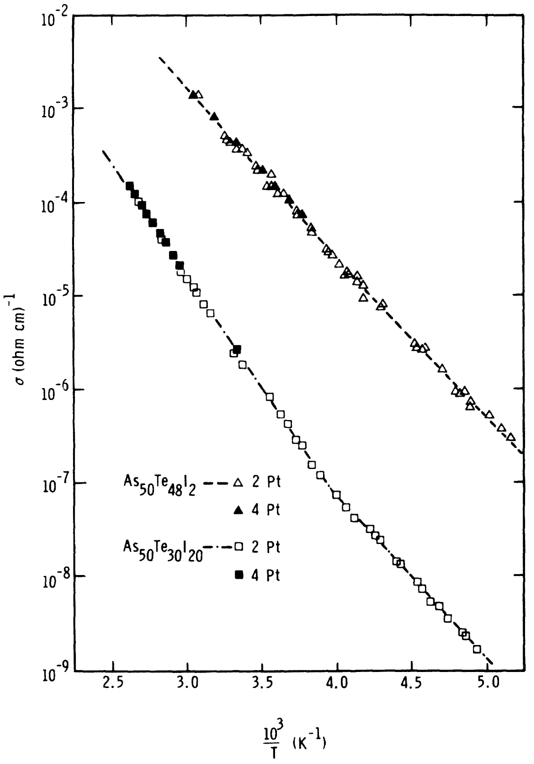

FIG. 9. Conductivity vs temperature in the As-Te-I glasses.

other workers.

### 3. Conductivity Measurements

*a. As-Te-I Glasses.* The results of four-probe conductivity measurements made in conjunction with the Hall experiments and normalized two-probe conductance data coincidentally with the Seebeck measurements are shown in Fig. 9. All the compositions appear to have their conductivities depend nearly exponentially on inverse temperature. The conductivity activation energies for the 2, and 20-at.% iodine alloys are 0.36 and 0.45 eV (above $T = 260$ K), respectively.

*b. As-Te-Ge Glasses.* The conductivity data for these materials are shown in Fig. 10. Again, $\sigma$ appears to behave in an activated fashion although some slight curvature of the data is evident on this Arrhenius-type plot. For these compositions $E_\sigma = 0.43$ eV (above 260 K) and 0.46 eV for the $As_5Te_{80}Ge_{15}$ and $As_{50}Te_{45}Ge_5$ glasses, respectively. All conductivities measured were sample independent within each composition and were not affected by thermal cycling between ~150 and 390 K.

*c. As-Te Glasses.* Although some curvature is evident, both compositions display a roughly activated behavior with temperature. For the $As_{50}Te_{50}$ glass $E_\sigma = 0.44$ eV and for $As_{40}Te_{60}$, $E_\sigma$ (above room) $\simeq$ 0.46 eV. This latter value is in excellent agreement with the value obtained by Weiser and Brodsky[30] on thin films of $a$-$As_2Te_3$. It is also consistent with the results reported by Hruby and Stourac[31] on bulk $a$-$As_2Te_3$.

## C. Summary

Table III gives a summary of the Hall-mobility activation energies, the energies $E_S$ [see Eq. (3)] associated with the Seebeck coefficients, and the conductivity activation energies associated with each of the six compositions. All energies are given in eV.

## IV. DISCUSSION

The most striking feature of the transport data presented in Sec. III is the relative composition independence of values of (a) the Hall-mobility activation energies (and, in most cases, magnitudes as well), (b) the energy differences between the Seebeck and conductivity energies, and (c) the values of the $\sigma_0$'s; these similarities suggest some common feature characterizing all six of these glasses. In this section we will discuss the possibility that this commonality may be related to similarities in the microscopic structure of all of these As-Te based chalcogenide glasses. In

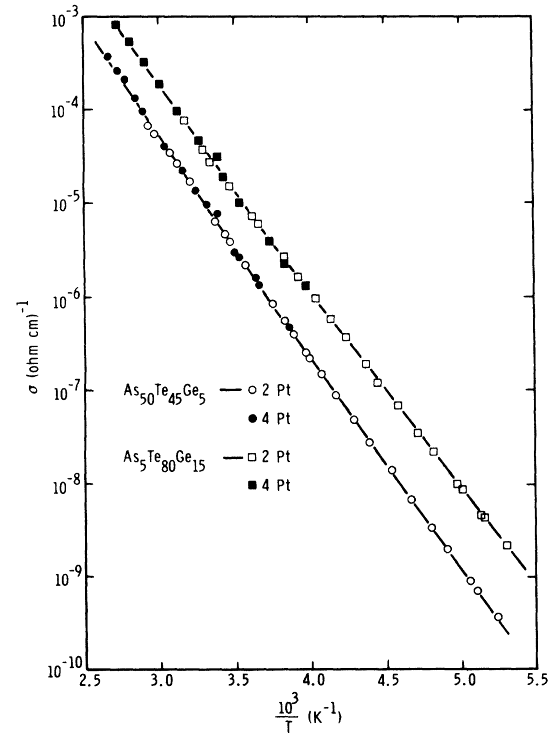

FIG. 10. Conductivity vs temperature in the As-Te-Ge glasses.

agreement with prior theories of conduction in inhomogeneous materials,[32–37] we suggest this common feature is the occurrence of a conductive substructure in these glasses which carries most of the current and over which much of the voltage is dropped. Furthermore it will be shown that our results are consistent with the view that the charge carriers are hole-like small polarons moving within this *dominant constituent* and are at variance with the standard CFO predictions based on rigid-lattice calculations.

Although we have observed a constancy of the positions of our Debye-Scherrer x-ray haloes from composition to composition, this does not necessarily imply any large-scale segregation of the glass into separate glassy (or crystalline) phases. What this constancy does indicate is the occurrence of certain commom chemical bonding configurations. One possible configuration is an arsenic atom linked to three neighboring tellurium atoms. We note that a number of authors have argued that the chalcogenide glasses do have a tendency to exist in a heterogeneous di- or multiphasic structure on a microscopic scale. Based on observations from a variety of techniques including scanning electron microscopy and electron diffraction, Chaudhari and Herd[38] and Roy and Caslavska[39] have reported phase separation in the As-Te-Ge system. The latter investigators have also reported evidence of the same phenomenon in the As-Te-I alloys. Other investigations on the As-Te-Ge-Si,[40] Ge-Te,[41] As-Te-Se,[42] and As-S[43] systems have suggested that chalcogenide alloys form microscopically heterogeneous glasses. These inhomogeneities have even been inferred solely from electrically (eddy current) measurements on $As_2Te_3Tl_2Se$ glasses by Strom and Taylor.[44] Other workers such as deNeufville[45] have argued against phase separation on the basis of thermal data. Thus, the issue of phase separation and the scale on which it might exist is clearly unresolved at present. The similarities in our transport data from composition to composition could occur independently of whether phase separation does or does not occur in these glasses. In other words, the suggestion of a dominant constituent does not rely on the existence of large regions of a single phase. Rather, we envision a transport mechanism (hopping) which only requires the motion of a carrier through regions formed by frequently recurring chemical bonding configurations. The scale of the structural unit associated with phase separation is larger than that required for the existence of this dominant constituent.

TABLE III. Conductivity activation energy $E_S + W_H$, the thermoelectric power energy $E_S$ (both accurate to ±0.01 eV), the deduced hopping energy $W_H$, and the Hall-mobility activation energy $E_\mu$, all in eV.

| | $E_S + W_H$ | $E_S$ | $W_H$ | $E_\mu$ |
|---|---|---|---|---|
| $As_{50}Te_{48}I_2$ | 0.36 | 0.16 | 0.20 | 0.06 |
| $As_{50}Te_{30}I_{20}$ | 0.45 | 0.27 | 0.18 | 0.06 |
| $As_{50}Te_{45}Ge_5$ | 0.46 | 0.29 | 0.17 | 0.06 |
| $As_5Te_{80}Ge_{15}$ | 0.43 | 0.24 | 0.19 | 0.06 |
| $As_{50}Te_{50}$ | 0.44 | 0.25 | 0.19 | 0.07 |
| $As_{40}Te_{60}$ | 0.46 | 0.29 | 0.17 | 0.05 |

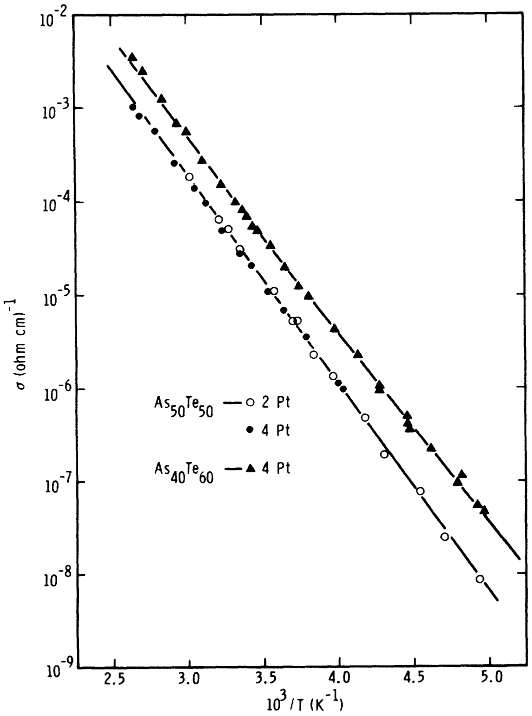

FIG. 11. Conductivity vs temperature in the As-Te glasses.

If in fact As-Te units comprise a significant fraction of the material of all of our glasses, it remains to specify the circumstances in which transport measurements primarily reflect the properties of such a constituent. Certainly if we consider essentially parallel paths of varying conductivities which traverse the sample, the bulk of current will pass through the high-conductance paths. If the conductivity, Hall mobility, and drift mobility associated with motion amidst and among the As-Te units are relatively high, then the current in the glasses will pass primarily through this constituent provided that the conductive regions are sufficiently well connected.[32–34] Gaps between conductive islands need not preclude these islands forming a dominant constituent. In particular, if the voltage drop associated with the remaining portion of the glass is small compared with the voltage drop over the As-Te material, then the As-Te material will remain the dominant constituent despite a reduction in connectivity. These intuitive ideas have been supported by studies of various two-dimensional models of heterogeneous materials.[35-37] A more detailed analysis is not only in principle very complicated but also inappropriate in light of our ignorance of the detailed nature of both the conductive regions and the barriers.

The electrical-transport data appears to support the idea of small polarons hopping within a dominant constituent which is common to all of the As-Te based chalcogenide glasses which we have studied.[46] Specifically, the hopping energy for each of the glasses, deduced from a comparison of the conductivity activation energy with the characteristic energy associated with the thermoelectric-power's temperature dependence yields values which are very close to one another (as illustrated in Table III).[47] Furthermore these hopping energies are all very much larger than typical phonon energies. This implies that the jump processes are of a multiphonon variety. The occurrence of multiphonon processes directly implies a very substantial effective electron-lattice interaction. In other words the predominance of multiphonon jump processes at and about room temperatures requires the electronic states between which the carrier hops to be sufficiently well localized so that they interact strongly with the atomic vibrations. Indeed theoretical studies of both crystalline[7,10,11] and noncrystalline[48] systems which possess a short-range electron-lattice interaction (as that anticipated for a covalently bonded glass) demonstrate that substantial electron-lattice effects are associated with small-polaron or "sharply-localized" states. Consistent with the idea that the charge carriers form small polarons is the fact that the $\sigma_0$ values which are measured for our glasses agree with what is expected from the adiabatic theory of small-polaron hopping-motion, i.e., $\sim 10^3$ mho/cm. Furthermore, the constancy of the hopping energy from one As-Te based glass to another is supportive of the idea of there being a common dominant constituent in all of the As-Te-based chalcogenide glasses which we have investigated. The absence of evidence for a substantial disorder energy (on a scale of $kT$) between the conductive sites within the dominant constituent is also consistent with both the local nature of the small-polaron states and the notion that the glass is comprised of units which possess short-range order. The Hall-mobility measurements are also compatible with the carriers being small polarons which adiabatically hop within the dominant constituent. In particular, the theory of the adiabatic hopping motion of small polarons[49] predicts that the Hall mobility will be thermally activated with an activation energy roughly one-third of $(E_\sigma - E_S)$ and with a preexponential factor of $ea^2\nu/kT$, (usually 1.0–0.1 $\text{cm}^2/\text{V sec}$ at room temperature) where $a$ and $\nu$ are typical values of the intersite spacing and vibrational frequency, respectively. In the simplest theory the Hall effect for both electronlike and holelike small polarons will be $n$ type provided that the short-range geometry is of the three-site variety[18] such as is believed to characterize the As-Te unit. As shown in Table III the Hall-mobility activation energies are essentially one-third of $W_H$, in good agreement with the theory. The magnitude of the Hall mobility is also in general agreement with the theory. The variations in the magnitude of the preexponential by a factor ~ 2 are perhaps associated with the deviation of the samples from the ideal geometry (see Sec. II B 1 *a*) and/or polarization effects within regions of the dominant constituent.[32]

The variation of $E_S$ (the characteristic separation of energy between the conduction levels and the Fermi level) from glass to glass (see Table III) is related to the difference in the energy-level spectrum that is associated with states other than those of the dominant constituent. These levels are characteristic of defects, compositional disorder, and structural fluctuations in the remaining (non-dominant-constituent) material.

Thus the experimental data reported here is consistent with the notion of the predominant charge carriers being holelike small polarons which hop within a dominant constituent that is common to all of our As-Te-based glasses. It should be stressed that having accepted the general picture of the electrical transport in these glasses being associated with the adiabatic hopping of small polarons through a common dominant constituent in the As-Te-based chalcogenide glasses, the meaningful adjustable parameters are just $W_H$ and $E_S$. These parameters are determined by a measurement of any two of the three transport coefficients on a single glass. The remaining measurement on the particular glass and each subsequent measurement on the remaining glasses then provide still further support for the general picture.

One experimental test of the proposed importance of As-Te bonding in these glasses can be immediately suggested. This is a series of similar measurements on a glass containing no arsenic to determine if the lack of the As-Te constituent produces a marked difference in the specimen transport properties from those found in the arsenic-containing glasses. To this end we have attempted to characterize transport in several samples of the $\text{Ge}_{17}\text{Te}_{83}$ alloy. As was pointed out in Section II A, this alloy is difficult to prepare in the glassy state in quantities large enough to facilitate electrical measurements (in the apparatus used in this study). Preliminary measurements on a small sample have shown that the temperature dependence of the Hall mobility is considerably greater ($E_\mu \simeq 0.10$ eV) than that observed in the As-containing glasses. An analysis of the Seebeck coefficient and conductivity of another specimen of this alloy indicates that the difference between the conductivity and Seebeck energies, Eq. (1), is considerably less (~0.12 eV) than that found for the alloys listed in Table III. Thus, these compositions appear to differ qualitatively from our arsenic-containing glasses.

The data presented in Sec. III are not the only evidence supporting the notion of polaronic conduction in a dominant constituent present in these As-Te-containing chalcogenide alloys. A variety of transport data on similar systems appear to support this picture as well as the idea of a dominant constituent. Panus *et al.*[28] have measured the room-temperature Hall mobility of a series of six As-Te-Ge glasses in which the percentage of Ge varied from 4 to 16 at.%. The measured mobilities ($n$ type) ranged from 0.043 to 0.056 $\text{cm}^2/\text{V sec}$ and were for all practical purposes *independent* of the amount of germanium present in the alloys. Roilos[50] has measured the conductivity and Hall mobility of a series of mixtures of glassy $As_2Te_3$ and $As_2Se_3$. He found that in all cases $\mu_H$ is $n$ type, low (~0.01–0.1 $\text{cm}^2/\text{V sec}$), independent of annealing,[51] and exponentially dependent upon temperature with characteristic activation energy of about 0.05 eV. Although the conductivity of these alloys decreases by three decades as the percentage of $As_2Te_3$ decreases from 50 to 20 at.%, the magnitude of the Hall mobility decreases by little more than a factor of 2; the constancy of the activation energy of $\mu_H$ and the small compositional dependence of its magnitude appear to favor an As-Te structural unit as a possible dominant constituent in these glasses. This parallels our measurements indicating a similar decrease in magnitude of $\mu_H$ (but not in activation energy) in the case of the $As_{50}Te_{30}I_{20}$ alloy.[52]

Nagels *et al.*[53] have measured the Hall mobility of glassy $As_2Se_3$ over a fairly narrow temperature range (180–220 °C). The magnitude of the mobility (~0.08 $\text{cm}^2/\text{V sec}$) is low enough for polaronic conduction to be considered as a possibility, but the error spread (~20%) and limited range of temperature make it impossible to categorically determine whether $\mu_H$ is activated with an activation energy less than ~0.1 eV.[54]

There exists one other case in the literature where the conductivity, thermopower, and Hall effect have been measured as a function of temperature on a single chalcogenide glass. This is the work of Nagels *et al.*[55] on glassy $Tl_2Te \cdot As_2Te_3$. In this case the activation energy deduced from the $p$-type thermopower data was 0.13 eV less than that activating the conductivity. This could imply a hopping energy associated with the mobility in these materials; interestingly enough, the Hall mobility was found to be low and activated with an energy of 0.03 eV, a value of the order of $\frac{1}{3}$ of the value of $W_H$ quoted above. In this case, however, the Hall mobility was found to be *p type*, suggesting that an As-Te bonding unit does not control transport in this material if the dominant constituent picture applies to this alloy; the value of $W_H$ of 0.13 eV is at variance with the value of ~0.19 eV measured here, also suggesting a fundamental difference between this glass and the alloys reported upon in the present work.[56] For a polaron picture to yield the $p$-type Hall mobility in $Tl_2Te \cdot As_2Te_3$, the carriers would have to move in predominantly four-site arrays of equivalent positions, as in the model studied by Emin.[17]

Concomitant conductivity and Seebeck measurements have been made on a variety of chalcogenide glasses and, as Adler[57] has pointed out, it is common occurrence to find that the conductivity has an activation energy of ~0.1 to 0.3 eV greater than that deduced from the Seebeck effect. Thus, experimental indications of an activated conductivity mobility are not particularly rare.

In light of the results presented here on the As-Te-(Ge, I) glasses and those already present in the literature on similar systems, it appears that the predictions of the CFO model are quite difficult to reconcile with the observed transport properties of many of the chalcogenide alloy glasses. In particular, the activated character of both the deduced conductivity mobility and the measured Hall mobility is at variance with the CFO picture. In addition, the magnitude of $\mu_H$ is usually found to be about an order of magnitude less than the lower limit suggested by Friedman's calculation of the Hall effect in the random-phase model.[6] Thus, we feel that the polaron picture is somewhat more successful in its predictions of the transport properties of the glasses studied here, particularly in light of the possible occurrence of structural inhomogeneities in these materials.

In addition, there are other results that have been obtained from other types of experiments on alloys that may be indicative of polaron effects; a brief discussion of several of these is relevant to the issues raised in this work. We should first mention that as a consequence of the Franck-Condon principle, optical-absorption measurements in these glasses will not reflect the final relaxed (polaron) energy levels.[7] Specifically, we can only obtain information about the energy and density of polaron states in the situation where excess carriers have relaxed to a condition of thermal equilibrium with the lattice. In a luminescence experiment an appreciable fraction of the optically excited electrons and holes would be expected to have lattice displacements forming around them before recombination takes place. In this case the luminescence spectra would be expected to peak at a lower energy than the observed absorption edge. In the absence of trapping effects, the energy shift between the absorption edge and the lowest energy luminescence would be the sum of the electron and hole polaron binding energies. Since trapping effects have been shown to be important in these alloys, the true situation is undoubtedly far more complicated. This Stokes shift between absorption and luminescence has, however, been experimentally observed in the alloys $As_2Te_3 \cdot As_2Se_3$ by Fischer *et al.*[58] The explanations of these data based on the CFO picture have not been completely successful[59]; it is possible that a polaron approach to this problem would resolve some of those difficulties.

Field effect experiments have been performed by Ovshinsky *et al.*[60] on a multicomponent chalcogenide glass. These measurements entail the introduction of a large number of excess carriers into the glass while monitoring the dc conductivity in order to see any changes in the Fermi energy. The results have been interpreted within the CFO model to imply a high density of states ($> 5\times 10^{19}$ $cm^{-3}\,eV^{-1}$) at the Fermi level. An alternative explanation which does not involve large state densities in the middle of the gap is the present polaron ansatz. The large number of equilibrium carriers which are associated with narrow small-polaron bands provides a natural explanation for the insensitivity of the dc conductivity to the addition of a relatively small amount of excess charge.

In conclusion, it is worth mentioning that several binary and elemental amorphous semiconductors ($As_2Se_3$ and Se, for example) display transport properties similar to those found for many multicomponent glasses.[5,57] Unfortunately, many of the crucial transport measurements (such as the temperature dependence of the Hall mobility) have not been made as of yet; these experiments would provide a reasonable test of the possible applicability of polaron theory to these substances—particularly in light of the reduced complications regarding inhomogeneity.

## V. CONCLUSIONS

A variety of compositions of As-Te-I, As-Te-Ge, and As-Te chalcogenide glasses have been prepared and structurally characterized by several techniques. The Hall mobility, Seebeck coefficient, and dc conductivity of six representative compositions have been measured as a function of temperature; the experimental results obtained here as well as data obtained by other workers for similar glass systems have been comcompared with the familiar CFO picture for amorphous semiconductors and with a new model involving small-polaron hopping transport. Two major conclusions can be drawn:

(1) Several aspects of the transport behavior—in particular, the activated character of the deduced conductivity mobility and the magnitude and temperature dependence of the measured Hall mobility—do not appear to be consistent with the predictions of the CFO-RPM model.

(2) The transport coefficients measured here can be consistently explained by employing the notion that the prevalent charge carriers are hole-like small polarons, which primarily hop between adjacent sites in a network of As-Te units.

## ACKNOWLEDGMENTS

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