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Transport properties of amorphous antimony telluride

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The electrical conductivity, Seebeck coefficient, and Hall coefficient of micron thick films of amorphous Sb_2Te_3 have been measured as functions of temperature from room temperature down to as low as 200 K. The electrical conductivity manifests an Arrhenius behavior with a pre-exponential factor that is larger than that of a conventional semiconductor. The Seebeck coefficient is *p* type. Unlike a conventional semiconductor, the energy characterizing the Seebeck coefficient's temperature dependence, about 0.10 eV, is considerably smaller than the activation energy of the electrical conductivity, about 0.28 eV. In addition, the heat-of-transport constant of the Seebeck coefficient is much larger than that of conventional semiconductors. The Hall mobility is low (near 0.1 $cm^2/V\,s$ at room temperature), anomalously signed (*n*-type), and increases with rising temperature with an activation energy of about 0.05 eV. These results are consistent with the charge carriers being holelike small polarons that move by thermally assisted hopping.

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I. INTRODUCTION

Chalcogenide glasses have attracted considerable attention because of their utility in switching devices.[1] For example, threshold switching occurs when passage of a sufficiently high current through a chalcogenide-glass semiconductor induces at least a significant portion of the glass to switch its electrical behavior to be that of an electrical conductor. The conducting behavior persists if the current is held above some minimum level. The mechanism of such threshold switching is yet to be established.[2]

Indeed, the fundamental nature of the steady-state electronic transport of these covalent glasses remains controversial. In particular, there are two fundamentally different starting points in addressing the electronic transport in covalent materials.[3,4] In one picture, a charge carrier moves rapidly between atomic sites without the surrounding atoms relaxing about the carrier's transitory atomic position. Alternatively, the positions of atoms relax about a carrier at an atomic site thereby greatly slowing the carrier's interatomic motion. In other words, the charge carriers that dominate the charge transport of these chalcogenide glasses either remain quasifree or they self-trap to form small polarons.

The disorder inherent in a glass, by impeding charge transport, can induce a carrier's collapse from being quasifree to being self-trapped.[5–8] Such collapses have been identified in materials upon the introduction of magnetic disorder,[9] structural disorder,[10] and compositional disorder.[11] Does the disorder associated with forming these chalcogenide glasses induce such a collapse?

The nature of a charge carrier is indicated by its charge transport. A quasifree charge carrier moves with a moderately high mobility, $\geqslant 1\ cm^2/V\,s$ at 300 K, which tends to decrease with rising temperature. By contrast, a self-trapped charge carrier typically moves with a very low mobility, $\ll 1\ cm^2/V\,s$ at 300 K, which increases with rising temperature. Is the charge transport in these chalcogenide glasses governed by a modest density of high-mobility carriers associated with a relatively wide band of extended states or by a relatively high-density of low-mobility carriers associated with a narrow band of localized states?

This question can be addressed through combined measurements of several steady-state transport coefficients: the electrical conductivity, the Seebeck coefficient, and the Hall mobility.[12,13] Arsenic-based glasses (e.g., As_2Te_3, As_2Se_3, and As_2S_3) have been studied intensively.[14–17] However, many devices are best served by Sb-containing compounds. Although crystalline Sb_2Te_3 has been extensively studied,[18–21] there are few reports of transport measurements of noncrystalline Sb_2Te_3.[22–24]

The preference for utilizing Sb rather than As in chalcogenide-glass switches is based on the relative instability of Sb-based noncrystalline materials. In particular, the crystallization temperatures of Sb-based noncrystalline solids are below those of their As-containing counterparts. Indeed, noncrystalline Sb_2Te_3 has only been grown as films, whereas bulk samples of the As-containing binary chalcogenide glasses have been readily produced. As a result, steady-state electronic transport measurements of noncrystalline Sb_2Te_3 are more limited than those of As-based binary chalcogenide glasses.[14–17] Measurement temperatures must remain safely below the crystallization temperature. In addition, the high resistances of semiconducting film samples, relative to bulk samples, produce a lower limit on measurement temperatures.

Here measurements of the steady-state electrical transport of noncrystalline Sb_2Te_3 from room temperature down to about 200 K are reported. The electrical conductivity, Seebeck coefficient, and the Hall mobility are qualitatively similar to those found for As_2Te_3. Specifically, the electrical conductivity is found to be thermally activated with a pre-exponential factor of about 10^3 S/cm. The characteristic energy of the *p*-type Seebeck coefficient is significantly smaller than the activation energy of the electrical conduc-

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tivity and the "heat-of-transport" constant is considerably larger than that of conventional semiconductors. The Hall mobility is n-type, low (about 0.1 $\text{cm}^2/\text{V s}$ at room temperature), and falls with decreasing temperature.

In Sec. II, we describe the growth of noncrystalline films of Sb_2Te_3. Section III outlines the measurement techniques employed in the transport measurements. The results of our measurements of the electrical conductivity, Seebeck coefficient, and Hall mobility are presented in Sec. IV. The paper concludes in Sec. V with an interpretation of these results as being indicative of the charge carriers being holelike small polarons. Alternative interpretations of our findings are also discussed.

II. SAMPLE PREPARATION

Films of Sb_2Te_3 were grown at Sandia National Laboratories by Overmyer in the laboratory of Siegal. Radio frequency sputtering was used to deposit micron thick noncrystalline films of Sb_2Te_3 on thin (150 μm thick) glass substrates. Since Sb and Te have comparable atomic weights and electro-negativities, the sputtering target was chosen to have the same stoichiometry as that desired in the deposited film. It was noted that the crystallization temperature of Sb_2Te_3 is only slightly above room temperature.[23] Therefore, to avoid heating-induced crystallization, the substrates were cooled by placing them on a relatively large (20 cm) water-cooled copper disk. Noncrystallinity was established by the absence of crystalline peaks in x-ray diffraction measurements of the deposited films. All films deposited upon cooled substrates with sputtering powers between 25 and 50 W were noncrystalline. However, crystalline peaks were observed in x-ray diffraction when the substrate was not cooled. The two noncrystalline films used in our transport measurements were grown on a cooled substrate with a sputtering power of 40 W with argon partial pressure of 100 mTorr.

We encountered no indication that our noncrystalline semiconducting films, deposited on cooled substrates, evolved with time. In particular, we observed no changes in the low electrical conductivity of our films during the months of transport measurements following film growth. Our films did not transform to crystalline Sb_2Te_3, an electrical conductor. By contrast, relatively thin films deposited at room temperature are reported to initially be about an order of magnitude more electrically conducting than our films.[22] Over the ensuing days and weeks the electrical conductances of these films increased by about two orders of magnitude as their crystalline region grew. In addition, surface oxidation of films deposited on heated (110 °C) substrates slightly lowered these films' conductances.[22]

III. TRANSPORT MEASUREMENTS

A. Conductivity measurements

For these measurements, deposited films were each trimmed to a rectangular shape whose typical dimensions are 5 by 20 mm. Four gold wires were attached along the length of the sample with silver paint. The electrical conductance is determined by measuring the voltage drop between the two inner contacts as current flows between the two outermost contacts. Currents in the range of 0.1 to 10 nA were obtained from a Keithley 220 current source. Voltage drops of 10^{-4} to 1 V were measured with a Keithley 617 electrometer. Measurements of the voltage drops as a function of current were used to verify Ohmic flow.

To measure the temperature dependence of the conductance, the samples were cooled with a closed-cycle refrigerator. The temperature of the sample was monitored with a Cernox™ temperature sensor clamped to the copper block to which the sample was attached with varnish. The conductivity was also measured in conjunction with our measurements of the Seebeck coefficient.

B. Seebeck coefficient measurements

The samples used for Seebeck measurements were varnished to pieces of electrically insulating glass that were in turn varnished onto a copper block. The copper block was heated with resistors. The temperature of the copper block was monitored with a Cernox™ resistance thermometer. To keep the temperature of the sample near the temperature of the copper block, a plate maintained near the temperature of the copper block was placed above the sample in order to minimize its radiative heating or cooling. The copper block assembly was kept in a vacuum surrounded by liquid nitrogen.

Thermocouples were connected to the inner pair of electrical contacts to the sample. Chip resistors, which serve as heaters, were attached with varnish to both ends of the sample. A temperature gradient along the sample was established by energizing one of the two chip heaters. After their values stabilized, the voltage drop and temperature difference between the two inner contacts were measured to obtain the Seebeck coefficient, the ratio of these two quantities. The "seesaw method"[25] was employed in that the temperature differential was then reversed by changing the energized chip heater. The entire process was repeated with twice the power to the chip heater to insure that the temperature differences were small enough for the Seebeck coefficient to be independent of temperature differential. The temperature differences that were utilized were never more than 5 K.

The sample's temperature was taken to be that of the copper block plus half of the relatively small temperature difference between the sample's ends. These temperatures agreed within a few K with those recorded earlier by a thermocouple placed between the center of the sample and the copper block. Measurement of the sample resistance after each Seebeck measurement (when the chip heaters were turned off) also indicated sample temperatures close to that of the copper block. Voltage measurements were made using a Keithley 2010 multimeter to differentially read the preamp outputs of two Keithley 617 electrometers. Since both voltage contacts were connected to high impedance equipment, the sample could be grounded at either one of the current contacts without introducing a grounding loop.

C. Hall mobility measurements

The Hall mobility measures the deflection of an electrical current under the influence of an applied magnetic field. The

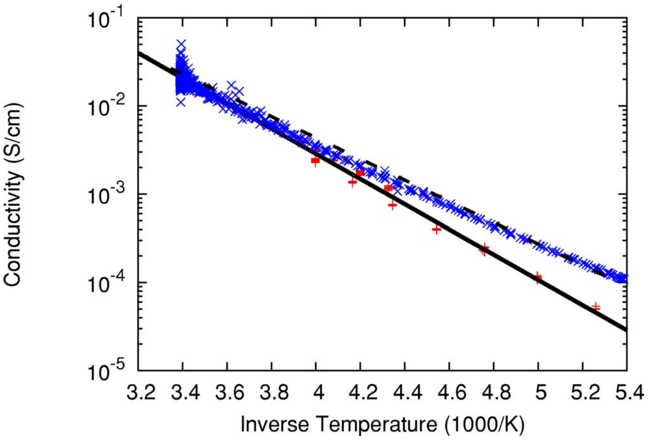

FIG. 1. (Color online) The electrical conductivity is plotted versus inverse temperature for two noncrystalline films of Sb_2Te_3. A least-squares fit of the data above 250 K to an Arrhenius plot yields values of E_σ=0.284 eV, σ_0=1490 S/cm and E_σ=0.24 eV, σ_0 =280 S/cm for the two films.

Hall mobility can be obtained by measuring three quantities: (1) the sample's resistance, (2) the Hall resistance (the potential drop a magnetic field induces perpendicular to a current divided by that current), and (3) the strength of the magnetic field. A true Hall resistance is simply proportional to the magnetic field. The proportionality of the magnetic field strength to the measured Hall resistance was used as assurance of its validity.

The van der Pauw[26] technique was utilized to measure a sample's resistance and Hall resistance. For this purpose, a film sample was first cut into a near square. Four gold wires were attached with silver paint at the corners of the square. The square was then partially subdivided by inserting cuts perpendicular to the midpoints of each of the square's four sides. These cuts extend from the square's perimeter halfway to its center. This scheme has been utilized to minimize effects of asymmetry associated with the positioning of the four contacts.[27,28]

The Hall mobility was measured at different temperatures in fields up to 7 T. The applied current was chosen to be as large as possible (3–25 μA), subject to the limitation that the applied voltage across any pair of contacts always be less than 100 V. The temperature of the sample was controlled by that of the copper block upon which it was mounted. The sample and its electrical contacts were insulated from the copper block by a piece of electrically insulating glass. This assembly was placed in the cryostat that cooled our superconducting magnet. Heat was radiated from the copper block to the cryostat's liquid helium bath. A copper radiation shield covered the sample to minimize its radiative cooling.

IV. RESULTS

A. Electrical conductivity

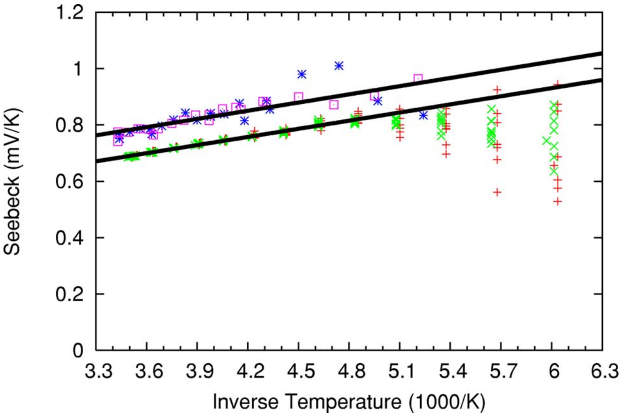

FIG. 2. (Color online) The Seebeck coefficient is plotted versus inverse temperature for two noncrystalline films of Sb_2Te_3. Solid lines show fits of the data above 200 K to Eq. (1) for the two films. The parameters for the two solid lines are E_S=0.096 eV, A=4.1 and E_S=0.10 eV, A=5. Data depicted with × are taken at twice the heater power as those depicted with +. Similarly, data depicted with □ are taken at twice the heater power as those at depicted with *.

Figure 1 depicts representative measurements of the electrical conductivities of two noncrystalline films of Sb_2Te_3. The electrical conductivities of noncrystalline films of Sb_2Te_3 are thermally activated between room temperature and 200 K. The activation energies E_σ determined by fitting the data above 250 K to Arrhenius plots $\sigma=\sigma_0\exp(-E_\sigma/k_BT)$, range between 0.24 and 0.30 eV. The pre-exponential factors σ_0 assume values from several hundred S/cm to over 1000 S/cm. These values of the pre-exponential factors are comparable to those found for other chalcogenide glasses.

The values for the pre-exponential factors that we and others generally find are significantly larger than are typically encountered with conventional semiconductor transport. In particular, the pre-exponential factor for conventional semiconductor transport is the product of the density of thermally accessible conducting states $N(T)$, the carrier charge q, and the carrier mobility $\mu(T)$: $\sigma_0=N(T)q\mu(T)$. With a room-temperature value of $N(T)\sim 10^{19}$ cm^{-3}, $q=1.6\times10^{-19}$ C, and $\mu(T)\sim 1-10$ cm^2/V s for a conventional semiconductor with a moderate carrier mobility; the pre-exponential factor is in the range of 1–10 S/cm. The large pre-exponential factor indicates either a much larger mobility (comparable to that for the best high-mobility crystals) or a considerably larger density of states (as occurs for small polarons).

B. Seebeck coefficient

The Seebeck coefficients of two films of noncrystalline Sb_2Te_3 are plotted against reciprocal temperature in Fig. 2. At sufficiently high temperatures the data can be fit with the standard formula for the high-temperature behavior of the Seebeck coefficient of a semiconductor

$$S=\frac{k_B}{q}\left(\frac{E_S}{k_BT}+A\right), \tag{1}$$

where k_B is the Boltzmann constant and q is the charge on a carrier.

Most generally, the Seebeck coefficient is the entropy transport associated with a charge carrier divided by the carriers' charge. For independent noninteracting charge carriers the Seebeck coefficient is

$$S = \frac{1}{qT}\langle E - \mu \rangle_{\sigma}, \tag{2}$$

where T is the temperature, E is the energy of a carrier, μ is the chemical potential, and the average is carried out over conducting states. When evaluated for a semiconductor, Eq. (2) assumes the form of Eq. (1), where E_S is the difference between the near edge of the energy band associated with carrier motion E_c and the chemical potential $E_S = E_c - \mu$. The *heat-of-transport* constant A is the average kinetic energy (energy beyond the band edge) transported with the charge carriers measured in units of $k_B T$. Equation (2) also applies with phonon-assisted transitions of charge carriers between localized states and extended states (trap-limited transport). In these instances, E_c represents the energy characterizing the edge of the band of extended states. By contrast, for phonon-assisted hopping between localized states E_c represents the relevant edge of the energy band of relaxed states between which carriers jump.

For conventional semiconductors E_S equals the activation energy of the electrical conductivity and A is 1–2. However, we find that (1) the characteristic Seebeck-coefficient energy E_S is significantly smaller than the activation energy of the electrical conductivity and that the heat-of-transport constant is significantly larger than that found for conventional semiconductors. Indeed, our findings are similar to reports for many other chalcogenide glasses.[14,15,24] Specifically, a least-squares fit to the Seebeck coefficient data above 200 K yields $E_S = 0.10 \pm 0.01$ eV and $A = 5.1 \pm 0.6$ for the sample whose conductivity activation energy is about 0.28 eV. Similarly, we find $E_S = 0.096 \pm 0.001$ eV and $A = 4.10 \pm 0.06$ for the sample whose conductivity activation energy is about 0.24 eV.

The mobility for small-polaron hopping is Arrhenius at temperatures above a fraction of the temperature that characterizes the phonons with which the carriers interact. The activation energy of the small-polaron mobility typically exceeds the characteristic phonon energy. This activation energy contributes to E_σ but not to E_S. Thus, the observed differences between E_σ and E_S of about 0.15 eV are consistent with small-polaron hopping.

The widths of electronic bands in conventional semiconductors and of bands of extended electronic states in noncrystalline solids are primarily associated with interatomic electronic transfer. The associated heat-of-transport constants in common crystalline semiconductors are comparable to unity. By contrast, the band widths and densities-of-states for localized states, such as small-polaron states, are primarily associated with disorder. The associated heat-of-transport constants are indicative of the steepness of the rise of an energy band's density of states upon moving from an edge toward its center. For example, as shown in the Appendix, $A = 1 + s$, when the bandwidth exceeds $k_B T$ and the density of states for a band of localized states rises in proportion to ϵ^s away from its edge. Thus, the heat-of-transport constants for hopping within narrow bands of localized small-polaron states can significantly exceed unity.

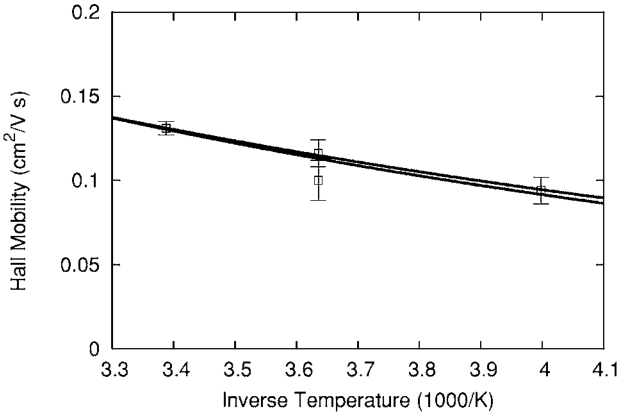

FIG. 3. The Hall mobility is plotted versus inverse temperature for a noncrystalline film of Sb_2Te_3. As described in the text, different treatments of the data yield the two points shown at 275 K. The two solid lines depict least-squares fits of the Hall mobility data to $\mu_{\mathrm{Hall}} = C \exp[-E_{\mathrm{Hall}}/(k_B T)]$ utilizing each of the two points at 275 K.

C. Hall mobility

The Hall mobility of a noncrystalline film of Sb_2Te_3 is found to be n type, opposite to the sign of the Seebeck coefficient. The magnitude of the Hall mobility is plotted against temperature in Fig. 3. The uncritical inclusion of all data yields the 275 K data point with larger error bars in the plot of Fig. 3. As discussed below, the higher mobility 275 K data point with smaller error bars in Fig. 3 is obtained when several questionable measurements taken at 275 K are discarded. The Hall mobility is very low (0.13 cm^2/V s at 295 K) and falls slowly with decreasing temperature. The Hall mobility can be described as thermally activated with an Arrhenius behavior whose activation energy is 0.05 eV, about 1/3 of the hopping activation energy deduced from our conductivity and Seebeck effect measurements. The Hall mobility's anomalous sign, very low value, and weakly activated temperature dependence are all incompatible with conventional semiconductor transport. However, these three features, also observed in other chalcogenide glasses, are consistent with the phonon-assisted hopping of small polarons.[15,16]

The plotted values of the Hall mobility were obtained from a least-squares fit to the Hall resistance plotted against the strength of the applied magnetic field. Figures 4 and 5 show these plots at three temperatures 295, 275, and 250 K. The error bars given for the slope represent only the statistical error obtained from the least-squares fit.

The Hall measurements at 275 K were made nearly two months later than those performed at 295 and 250 K. Two point conductance measurements indicated that the silver-paint contacts degraded somewhat during this hiatus. The scattering of the data also increased following this interruption. Even though repeating the measurements with longer settling times reduced the noise somewhat, some signifi-

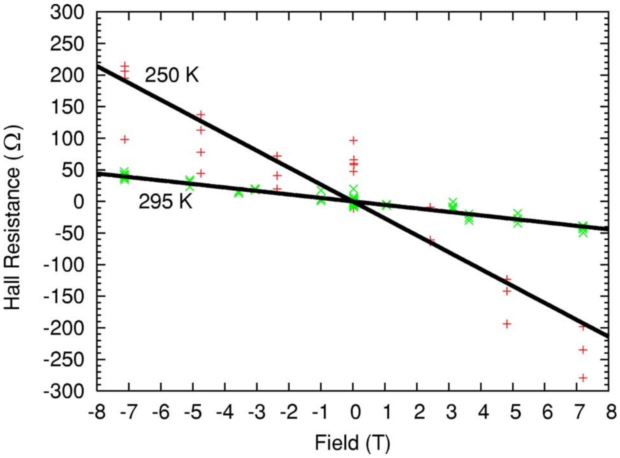

FIG. 4. (Color online) The Hall resistance is plotted versus applied magnetic field at 250 and at 295 K. The solid lines indicate the linear least-squares fits that are used to determine the Hall mobility.

cantly disparate points remained. If we employ the criterion developed by Chauvenet[29] to justify discarding highly disparate points and we ignore the exceptionally dispersive data at 2.5 T, we obtain a plot of Hall resistance versus field, Fig. 5, that is comparable with the plots obtained at 295 and 250 K. Figure 3 indicates that use of these modified data rather than the raw data slightly improves the fit of the Hall mobility-versus-temperature data to an Arrhenius plot.

V. DISCUSSION

The addition of a static severely localized electronic charge will generally induce significant displacements (~0.01 nm) of the equilibrium positions of the adjacent atoms. If the electronic charge carrier becomes bound within the potential well produced by these atomic displacements it is said to be "self-trapped." That is, the electronic charge is confined by atomic displacements that its very presence induces. The unit comprising a severely localized self-trapped electronic charge and the associated atomic displacements is termed a "small polaron."

Self-trapping is a nonlinear process. That is, localization or slowing of a charge carrier fosters the displacements of surrounding atoms. These atomic displacements in turn produce a potential well that fosters further localization. As a result of this feedback effect, charge carriers in covalent systems, in which the electron-lattice interaction is short ranged, either remain free (inducing minor atomic relaxation) or self-trap to form small polarons.[3,30] Disorder, by slowing and confining charge carriers, can trigger their collapse into small polarons.

Small polarons are generally associated with narrow energy bands whose widths are produced primarily by disorder.[31] By contrast, the energy bands of free carriers in disordered materials are typically relatively wide (>1 eV) as they are primarily determined by the electron-transfer energies. Thus, small polarons are associated with much higher densities of states than are free carriers.

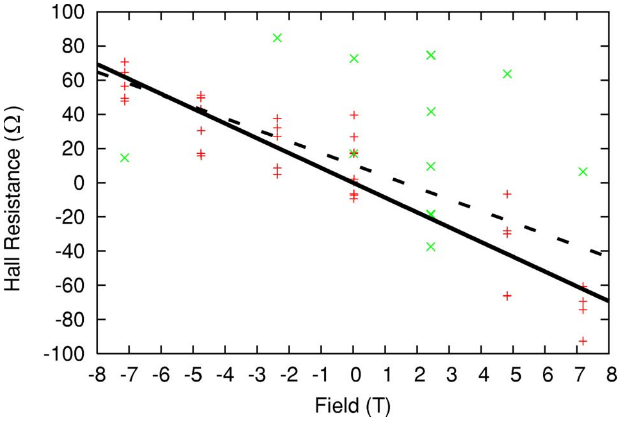

FIG. 5. (Color online) The Hall resistance is plotted versus applied magnetic field at 275 K. The dashed line is a linear least-squares fit to the data. Data depicted with × would be excluded as unreliable using Chauvenet's criterion. The solid line indicates a linear least-squares fit upon removal of the unreliable points.

Small polarons are often identified through their distinctive steady-state transport. In particular, small polarons typically move with very low mobilities ($\ll 1\ \mathrm{cm}^2/\mathrm{V\,s}$) by thermally assisted multiphonon hopping. At sufficiently high temperatures, above a fraction of the characteristic phonon temperature, the small-polaron mobility becomes Arrhenius:[32]

$$\mu = \frac{qa^2\nu}{k_BT} P e^{-E_\mu/k_BT}, \tag{3}$$

where a is the jump distance, ν is the frequency characterizing the phonons with which carriers interact, E_μ is the activation energy for small-polaron hopping, and P is the probability $(0<P<1)$ that the electronic-transfer energy is sufficiently large that a charge carrier will avail itself of the opportunity to jump that appropriate atomic displacements offer. For very small electronic transfer energies, electronic transfer limits electronic hopping and P is concomitantly proportional to the square of the appropriate electronic transfer energy. However, when the electronic transfer energy is sufficiently large compared with the characteristic phonon energy, the charge carrier readily adjusts to the atomic vibrations. In these instances, hopping is said to be "adiabatic" and $P \approx 1$. The pre-exponential factor of the Arrhenius small-polaron mobility is then $\mu_0 \sim q\nu a^2/(k_BT)$, typically $<1\ \mathrm{cm}^2/\mathrm{V\,s}$ at room temperature. Thus, the small-polaron mobility is $\ll 1\ \mathrm{cm}^2/\mathrm{V\,s}$. By contrast, extended state mobility is $>1\ \mathrm{cm}^2/\mathrm{V\,s}$.

Small polarons' self-trapped carriers are severely localized. As such, small-polaron hopping typically involves a significant fraction f of chemically equivalent sites (e.g., Te sites). As a result, the electrical conductivity (the product of the carrier density, the carrier charge, and the carrier mobility) for small-polaron hopping in the high-temperature regime, in which the thermally activated mobility is Arrhenius, has the form

$$\sigma \approx \frac{q^2 \nu}{a k_B T}(Pf) e^{-(E_S+E_\mu)/(k_B T)}, \tag{4}$$

where it has been noted that the carrier density for hopping within a narrow small-polaron band is $\sim 1/a^3$. Thus, the pre-exponential factor of the electrical conductivity for adiabatic small-polaron hopping is $\sigma_0 \approx 10^3$ S/cm, where P and f are both ~ 1. The activation energy of the electrical conductivity is the sum of the energy characterizing thermally produced charge carriers E_S and the energy characterizing carriers' hopping mobility E_μ.[12]

For small-polaron hopping the characteristic energy of the Seebeck coefficient is just E_S. Thus, the activation energy of the electrical conductivity for small-polaron hopping exceeds the characteristic energy of the Seebeck coefficient E_S, by the activation energy of the mobility E_μ. Furthermore, as demonstrated in the Appendix, the heat-of-transport contribution to the Seebeck coefficient A can be exceptionally large for the narrow sharply peaked energy bands expected of small polarons in some disordered materials.

The Hall mobility for small-polaron hopping provides a direct measure of the carrier mobility. In particular, the small-polaron Hall mobility is generally quite small, $\ll 1$ cm^2/V s. Distinctively, the small-polaron Hall mobility is thermally activated albeit with a smaller activation energy than that which enters into the electrical conductivity. Calculations and measurements both indicate that the activation energy of the Hall mobility is often about 1/3 that of the conductivity mobility: $E_{\text{Hall}} \approx E_\mu/3$.[12,15,16,33–38] Finally, as a result of small-polarons' severe localization the sign of their Hall effect can be anomalous.[13,39]

To appreciate the significance of the sign anomalies for small-polarons' Hall effect, we address their origin. The Hall-effect sign is normal for conventional transport when carriers predominantly occupy states in the vicinity of energy-bands' extrema. In particular, motion of electrons restricted to positively massed states gives a negatively signed (n-type) Hall effect. Conversely, motion of vacant states restricted to negatively massed states (holes) gives a positively signed (p-type) Hall effect. By contrast, the Hall-effect sign can be anomalous when the bands are so narrow that carriers occupy states throughout their energy bands.[39,40]

An analogous situation occurs for charge carriers that hop between localized states. Weakly localized states, such as shallow donors or acceptors, can be described as a superposition of long-wavelength electronic states associated with band extrema. In these cases, the Hall-effect sign for hopping between donor states is n type and that for hopping between shallow acceptor states is p type. By contrast, severely localized states are associated with a superposition of states throughout the entire energy band. As a result, the sign of the Hall effect for hopping between severely localized states can be anomalous.[13]

The Hall-effect sign for hopping between severely localized states depends upon the local atomic coordination of these sites and the symmetries of their electronic states. In particular, the Hall-effect sign should be n-type for small-polaron "holes" hopping amongst the lone-pair orbitals of Te atoms surrounding threefold coordinated Sb-atoms expected in noncrystalline Sb_2Te_3.[41]

Thus, distinctive features of our observations of the steady-state transport in noncrystalline Sb_2Te_3 are consistent with the charge carriers being small-polaronic holes. In particular, the pre-exponential factor of the electrical conductivity is very large, $\sigma_0 \sim 10^3$ S/cm. The activation energy of the thermally activated conductivity exceeds the characteristic energy of the p-type Seebeck coefficient by a significant amount $E_\sigma - E_S \approx 0.15$ eV. The heat-of-transport constant of the Seebeck coefficient we measure, A about 4 and 5, is much larger than that for conventional transport $A \approx 1$. The Hall mobility is very low, about 0.1 cm^2/V s at 295 K, n-type, and thermally activated with an activation energy of about 0.05 eV. Indeed, very similar features have been observed in many As-Te based glasses, As_2Se_3, and As_2S_3 where they have been taken as evidence of small-polaron hopping.[14–16]

It is useful to explore whether these results can be explained within a conventional transport model. The Mott–Cohen-Fritzsche-Ovshinsky model views noncrystalline semiconductors as analogous to conventional doped semiconductors.[42,43] Hole transport is viewed as occurring through two parallel conduction paths: (1) high-mobility coherent transport within extended states beyond a mobility edge and (2) low-mobility phonon-assisted hopping transport within localized states within a mobility edge. The electrical conductivity is thus viewed as the sum of these two contributions:

$$\sigma_T = \sigma_{\text{ext}} + \sigma_{\text{loc}}. \tag{5}$$

The observed low Hall mobility is envisioned as arising from carriers with high mobility μ_{ext}, whose contribution to the observed mobility is suppressed by the conductivity being dominated by carriers with low mobility μ_{loc}:

$$\mu_H = \frac{\mu_{\text{ext}}\sigma_{\text{ext}} + \mu_{\text{loc}}\sigma_{\text{loc}}}{\sigma_{\text{ext}} + \sigma_{\text{loc}}} \approx \mu_{\text{ext}} \frac{\sigma_{\text{ext}}}{\sigma_{\text{ext}} + \sigma_{\text{loc}}} \approx \mu_{\text{ext}} \frac{\sigma_{\text{ext}}}{\sigma_{\text{loc}}}, \tag{6}$$

where $\sigma_{\text{loc}} \gg \sigma_{\text{ext}}$.[2,44–46] The thermally activated behavior is presumed to arise because the activation energy of the extended-state conductivity exceeds that of the localized-state conductivity:

$$\frac{\sigma_{\text{ext}}}{\sigma_{\text{loc}}} = \frac{N_{\text{ext}}\mu_{\text{ext}}}{N_{\text{loc}}\mu_{\text{loc}}} \exp[-(E_{\text{ext}} - E_{\text{loc}})/(k_B T)], \tag{7}$$

where N_{ext} and N_{loc} are the densities of thermally accessible extended and localized states that participate in transport, respectively. Since the Hall mobility activation energy is quite modest, about 0.05 eV near room temperature in our measurements, and $\mu_{\text{loc}} \ll \mu_{\text{ext}}$, the condition that $\sigma_{\text{loc}} \gg \sigma_{\text{ext}}$ demands that $N_{\text{loc}} >>> N_{\text{ext}}$. Thus, as in the small-polaron model, the electrical current is predominately carried by the thermally activated hopping of a high density of localized carriers. Indeed, the observed pre-exponential factor of the electric conductivity is close to that for the adiabatic ($P=1$) hopping of small polarons between atomic sites $\sigma_0 \sim 10^3$ S/cm.

The random-phase model (RPM) has been employed to explain Hall-effect sign anomalies for extended states. This model makes the extreme assumption that the phase of an extended state is randomized between adjacent atomic sites.[47] Thus, the RPM presumes the same complete loss of phase coherence as in small-polaron hopping between severely localized states. With this assumption (equivalent to arbitrarily small electronic transfer energies) the RPM treatment of the Hall effect parallels that for nonadiabatic small-polaron hopping (but with a vanishing electron-lattice interaction) and yields the same sign anomalies. The underlying question is whether the RPM is a meaningful treatment of transport among states that retain considerable coherence amidst disorder.

Finally, it should be noted that electronic transport studies of a number of noncrystalline solids indicate conduction by both electrons and holes.[48] For example, the Seebeck coefficient of Ge_xTe_{1-x} changes sign with x and fits of its Seebeck data to the semiconductor formula (1) yield negative values of A.[24] Our preliminary measurements of $Sb_2Ge_2Te_5$ also yield a negative value of A. An analysis of the transport data in such circumstances becomes problematic due to the necessity of introducing significant adjustable parameters.

The hypothesis that equilibrated carriers in noncrystalline Sb_2Te_3 collapse into small polarons provides a ready explanation of our experimental findings. In particular, the difference between the activation energy of the electrical conductivity and the characteristic Seebeck energy, the low Hall mobility with its small activation energy, and the anomalous sign of the Hall coefficient are all direct manifestations of the hopping transport of small-polaron holes. Indeed, the small-polaron-hopping model has been used to explain the analogous results of transport experiments obtained for similar chalcogenide glasses (As_2Te_3, As_2Se_3, As_2S_3).[14–16] In our opinion this simple model provides the cleanest explanation for the transport properties of amorphous antimony telluride.

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APPENDIX: HEAT-OF-TRANSPORT COEFFICIENT

The Seebeck coefficient for phonon-assisted hopping between equivalent localized states is given by

$$S = \frac{\langle E-\mu\rangle}{qT}, \tag{A1}$$

where q represents the carrier's charge, T indicates the absolute temperature, E denotes the carrier's energy, and μ represents the chemical potential. The indicated average is performed over the thermally accessible states within which the carrier can move.

For a semiconductor the average may be rewritten as

$$\langle E-\mu\rangle = E_c - \mu + \langle\epsilon\rangle, \tag{A2}$$

where ϵ is the electronic energy measured from the appropriate edge of the relevant band of electronic states E_c. In particular,

$$\langle\epsilon\rangle = \frac{\int_0^\Delta \rho(\epsilon)e^{-\beta\epsilon}\epsilon d\epsilon}{\int_0^\Delta \rho(\epsilon)e^{-\beta\epsilon}d\epsilon} = -\frac{\frac{\partial}{\partial\beta}\int_0^\Delta \rho(\epsilon)e^{-\beta\epsilon}d\epsilon}{\int_0^\Delta \rho(\epsilon)e^{-\beta\epsilon}d\epsilon}$$

$$= -\frac{\partial}{\partial\beta}\ln\int_0^\Delta \rho(\epsilon)e^{-\beta\epsilon}d\epsilon, \tag{A3}$$

where Δ is the width of the band of localized states, $\rho(\epsilon)$ represents the density-of-states of the band, and $\beta \equiv 1/k_BT$ with k_B denoting the Boltzmann constant. The heat-of-transport constant of the formula for a semiconductor's Seebeck coefficient is then simply $A = \langle\epsilon\rangle/(k_BT)$.

For illustration, consider a particular density of states for a band of width Δ:

$$\rho(\epsilon) \equiv \frac{NC_s}{\Delta}\sin^s\left(\frac{\epsilon}{\Delta}\pi\right), \tag{A4}$$

with $0 \leq \epsilon \leq \Delta$. The density-of-states is normalized with the constant C_s so that the integral of the density-of-states over the band equals N. The parameter s characterizes the steepness of the rise of the density-of-states with energy ϵ.

Using this density-of-states, the integration with respect to energy[49] and subsequent differentiation with respect to β described in Eq. (A3) can be performed analytically. The heat-of-transport constant for even and odd values of s then becomes

$$A(p) = 1 - \frac{\pi p}{e^{p\pi}-1} + 2\sum_{i=1}^{s/2}\frac{p^2}{[p^2+(2i)^2]} \tag{A5}$$

and

$$A(p) = \frac{\pi p}{e^{p\pi}+1} + 2\sum_{i=0}^{(s-1)/2}\frac{p^2}{[p^2+(2i+1)^2]}, \tag{A6}$$

where $p \equiv \beta\Delta/\pi$.

In the extreme limit of a vanishingly narrow band relative to k_BT, $p \to 0$, A vanishes for both even and odd values of s. However, as p approaches the realistic regime where $p \gg 1$, the heat-of-transport constants for even and odd values of s both asymptotically approach, $A = 1+s$. This limit may also be obtained directly from Eq. (A3) since $\langle\epsilon\rangle \to (s+1)k_BT$ upon replacing $\rho(\epsilon)$ with ϵ^s and Δ with ∞ in the upper limit of the ϵ integration.

Heat-of-transport coefficients well in excess of unity can arise for hopping within bands of severely localized (small-polaron) states. Since these energy bands are associated with localized states, their widths primarily arise from disorder. Small-polarons in amorphous semiconductors are anticipated to produce especially narrow energy bands.[31] In particular, such severely localized states are insensitive to the bond-angle disorder characteristic of covalent glasses. Such narrow energy bands, associated with $s \gg 1$, produce large values of A. Experimentally determined values for A in chalcogenide glasses are often 4–5.

A different situation prevails for extended electronic states. The width of a band of extended electronic states depends primarily on electronic transfer. For common crystalline semiconductors, the heat-of-transport constants are comparable to unity. Since disorder only slightly broadens energy bands associated with extended-state (high-mobility) motion, it is generally assumed that $A=1$ for extended-state motion in amorphous semiconductors.[2]

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