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Small-Polaron Hopping Motion in Some Chalcogenide Glasses*

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Unlike prior attempts to describe the motion of electronic charge carriers in disordered materials, we suggest that the (holelike) charge carriers may actually be self-trapped, i.e., small polarons. In support of our hypothesis, we discuss our measurements of the electrical conductivity, thermoelectric power, and Hall mobility on some chalcogenide glasses.

During the past few years a substantial experimental effort has been expended in characterizing the electrical transport properties of a wide variety of glassy chalcogenide systems. In attempting to understand and systematize the resulting observations the simple model initially proposed by Cohen, Fritzsche, and Ovshinsky, the so-called CFO model,¹ has been widely applied to such glasses. Consistent with the situation in most crystalline semiconductors, it was tacitly assumed in this model that the presence of charge carriers did not produce sufficiently large displacements of the atomic constituents so as to necessitate consideration of the possibility that the charge carriers could become self-trapped, i.e., form small polarons. It is the purpose of this Letter to first suggest reasons why one might expect the charge carriers in these glassy substances to be small polarons, and then to point out that such an *Ansatz* leads to predictions which are in agreement with our experimental observations on some chalcogenide glasses.

Let us begin our discussion by reviewing what is meant by a small polaron. Consider for the moment a charge carrier held fixed at a given position in a solid. The presence of the additional (stationary) charge would generally act as a

substantial perturbation on its immediate environment, producing a displacement of atoms in its immediate vicinity and causing a reduction in the total energy of the system. The equilibrium positions which these atoms would assume in response to the added charge will be such as to produce a potential well for the carrier. In fact if the potential well associated with the local lattice distortion is sufficiently deep the carrier will occupy a bound state, being unable to move without an alteration of the positions of the neighboring atoms. Such a situation has been referred to as "self-trapping." The unit comprised of the localized charge carrier and its concomitant atomic deformation is termed a *small polaron* when the carrier is essentially confined to a single atomic site.

Clearly a small polaron can only be expected to form if an excess charge carrier will move sufficiently slowly so as to linger at a particular atomic position for time ample to permit the surrounding atoms to adjust to its presence. Since the time characterizing the establishing of new atomic equilibrium positions is a vibrational period ν^{-1} , one readily determines that the intrinsic mobility below which small-polaron formation would appear likely is $(e/kT)\nu a^2$, (~ 0.1 to 1

$\text{cm}^2/\text{V sec}$ at 300 K), where a is a lattice constant. In that the measured values of the Hall mobility in the chalcogenide glasses are generally lower than this, consideration of the consequences of a small-polaron model for the carrier transport is certainly appropriate.

To begin our discussion of the chalcogenide glasses, let us first enunciate our picture of these materials. Specifically such glassy substances may be viewed as essentially mixtures of small regions of appropriate chemical compounds. For instance, in the case of the As-Te-I glass systems there is strong evidence² for the presence of regions of As_2Te_3 . Of course, some material which may not ordinarily form a crystal may also be trapped in the glassy matrix. Thus in such glasses we are confronted with a somewhat inhomogeneous mixture of compounds each of which retains a fair degree of its short-range crystalline integrity. In what follows we shall, for simplicity, assume that one of the constituents of the glass dominates the transport properties of the material in the sense that the mobility and conductivity of such an ingredient are very much higher than those of the other ingredients of the mixture.³ Finally, the absence of both long-ranged order and short-ranged homogeneity provides what may be thought of as a "disorder field." In agreement with prior studies of the effect of a disorder field,⁴ it is herein argued that such fields impair the coherent motion of a carrier through regions of the "dominant constituent." It is the effective slowing down of the carrier resulting from the glass's disorder which makes small-polaron formation more likely in the dominant constituent of the disordered material than in the corresponding crystalline material.

While it has been suggested that small-polaron formation will occur more readily in a disordered constituent of a glass than in its crystalline counterpart, it remains to ascertain whether the electron-lattice interaction in chalcogenide systems can be supposed to be such as to give rise to small polarons. In this regard, it should be noted that the concept of self-trapping is not restricted to ionic materials,⁵⁻⁷ although the term "polaron" reflects the initial application of the notion of self-trapping to polar materials.⁸ Indeed, the electrons in the crystalline chalcogenide materials orthorhombic sulfur⁹ and realgar¹⁰ (As_4S_4) are known to be small polarons. In these crystals the drift mobility of holes is several orders of magnitude higher than that of electrons; presum-

ably reflecting a stronger carrier-lattice interaction for electrons than for holes. Such a disparity may be expected since the atomic orbital (and hence the electron-lattice interaction) associated with a hole in these materials is different from that which involves an excess electron.¹¹ It is, therefore, with some support from our knowledge of crystalline chalcogenide materials, that it is suggested that in the *disordered* chalcogenide systems both electrons and holes interact with their atomic environment with ample strength to form small polarons. Furthermore, consistent with the studies of S_8 and As_4S_4 ,^{9,10} it will be assumed here that holelike carriers in the chalcogenide glasses interact less strongly with the atomic distortions than do excess electrons, thereby manifesting higher mobilities and hence dominating the electrical transport measurements. Thus having established the possibility that the predominant carriers are holelike small polarons, a number of experimental results which do give strong evidence that this situation does in fact prevail in some chalcogenide glass systems will now be discussed.

If the above hypothesis is correct, the electrical conductivity will essentially be thermally activated ($\sigma = \sigma_0 e^{-E/kT}$) with the activation energy E being a sum of the energy required to generate carriers E_0 and the activation energy associated with the intrinsic hopping of small polarons, W_H . The activation energy contribution W_H will vary little between glasses having the same "dominant constituent" while E_0 may change considerably from glass to glass. The value of σ_0 will generally be given by $(Ne^2 a^2 \nu / kT) p$, where N is the number of equivalent carrier sites in the dominant material ($\sim 10^{22} \text{ cm}^{-3}$), and p is a factor which for the adiabatic theory of small-polaron motion^{12,13} is unity (in the nonadiabatic regime it is less than one). Since the constants involved in σ_0 change little from material to material, σ_0 will vary little between glasses; its value, extrapolated from measurements near 300 K, will be within an order of magnitude of 10^2 mho/cm . It is important to note that this feature is in agreement with numerous experimental observations in addition to those we have made on the glasses for which we report measurements here.

By studying the thermoelectric coefficient S as a function of temperature in the intrinsic regime one can directly measure W_H . Specifically the relationships $E_0 + W_H = -kT \ln(\sigma/\sigma_0)$ and $E_0 = e \partial S / \partial(1/T)$ can be utilized to measure E_0 and thereby calculate W_H .¹⁴ We have carried out such a pro-

TABLE I. The conductivity activation energy $E_0 + W_H$, the thermoelectric-power energy E_0 , both accurate to ± 0.01 eV, and the deduced hopping energy W_H , all in eV.

Material	$E_0 + W_H$	E_0	W_H
$\text{As}_{50}\text{Te}_{50}$	0.44	0.25	0.19
$\text{As}_{50}\text{Te}_{48}\text{I}_2$	0.36	0.16	0.20
$\text{As}_{50}\text{Te}_{30}\text{I}_{20}$	0.45	0.27	0.18
$\text{As}_{50}\text{Te}_{45}\text{Ge}_5$	0.46	0.29	0.17
$\text{As}_5\text{Te}_{80}\text{Ge}_{15}$	0.43	0.24	0.19

cedure for As-Te-I and As-Te-Ge glasses of a variety of compositions. The results, presented in Table I, clearly show that for a number of our glasses W_H is essentially unaltered. This implies that there is a single "dominant constituent" in these arsenic-containing glasses—possibly (ribbonlike) As_2Te_3 . Supporting this contention is the fact that similar measurements on one sample of the nonarsenic-containing glass, $\text{Ge}_{17}\text{Te}_{83}$, yields a different value for W_H , namely $W_H = 0.12$ eV.

At this point in our discussion it is particularly useful to compare our measurements of the Hall mobility with the predictions of our model. One of the principal results of the theory of the small-polaron Hall mobility^{13, 15, 16} is that the magnitude, temperature dependence, and even the sign of the Hall mobility¹⁷ is dependent on the local (short-range) geometry of the material. From an examination of the structure of a ribbon of As_2Te_3 ,¹⁸ it is readily determined that the prevalent arrangement of nearly equivalent neighboring sites, like that of tetrahedrally bonded materials, conforms to the so-called triangular geometry studied by Friedman and Holstein¹⁵ and by Emin and Holstein.¹³ For a holelike small polaron moving in such a triangular array the sign of the Hall effect is anomalous: The sign of holelike small polarons is that of n -type carriers. Such an anomaly, p -type thermoelectric power but n -type Hall effect, is actually what is observed in our glasses. In addition, the theory predicts that the Hall mobility should be low, $\mu_{\text{Hall}} < 0.1$ to $1 \text{ cm}^2/\text{V sec}$, and characterized by a small activation energy, essentially one third of that characterizing the drift mobility. As can be seen from Fig. 1, the Hall mobility of each of the glasses measured is thermally activated: each with an activation energy roughly one third that of the drift mobility, i.e., $W_{\text{Hall}} \approx W_H/3 = 0.06$ eV. Further support for our model is found from the fact that the Hall mobilities measured by Roilos¹⁰ in As-Te-Se glasses also manifest the thermoelectric-power—

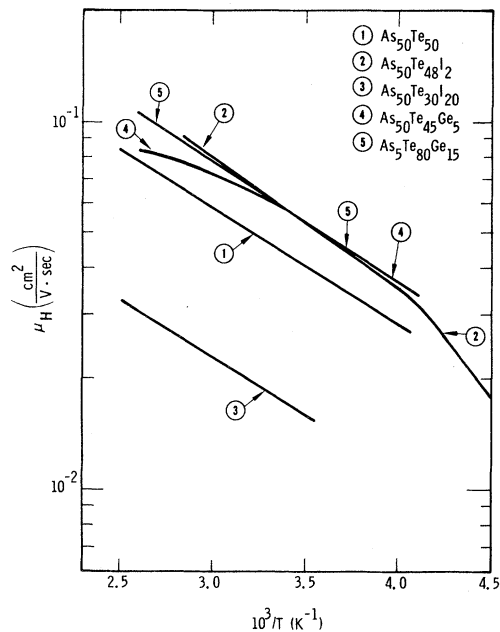


FIG. 1. The Hall mobility of several chalcogenide glasses.

Hall sign anomaly and are similar in magnitude and temperature dependence to the measurements reported here. Finally in agreement with our model is the fact that Hall-mobility measurements on our nonarsenic-containing glass, $\text{Ge}_{17}\text{Te}_{83}$, yields an activated Hall mobility with an activation energy that is roughly twice as high as that of the systems containing As and Te.

Thus measurements on the As-Te-I, As-Te-Ge, and As-Te-Se systems support the notion that, in these materials, the carriers are holelike small polarons. In particular, the magnitude of the pre-exponential factor of the thermally activated electrical conductivity, the composition-independent difference between the conductivity and thermoelectric-power activation energies, and the low thermally activated, Hall mobility of anomalous sign provide experimental arguments for the validity of our model of these glasses. Indeed, the occurrence of many of these features in other disordered systems leads us to suggest that small-polaron formation may occur in many more noncrystalline materials than just those investigated here.

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Evidence for a Jahn-Teller Effect in *p*-Ge from Magnetothermal Conductivity Measurements

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The phonon scattering by shallow acceptors in Si has been observed to decrease rapidly with magnetic field at high fields and low temperatures. This is the behavior expected for the ground-state quartet of the undistorted site. The scattering by shallow acceptors in Ge is, however, almost independent of field, indicating a quite different ground-state structure. This is believed to be the result of a dynamic Jahn-Teller distortion.

In undistorted sites, the acceptor ground states of Ge and Si are both fourfold degenerate (Γ_8). However, the states are known to be very strongly coupled to the lattice,¹⁻⁴ so that the possibility of a dynamic Jahn-Teller effect must be considered. This could lead to a complex spectrum of levels,⁵ and the problem seems to be particularly interesting because the state should couple to the lattice only at wave numbers q less than $(a^*)^{-1}$, where a^* is the Bohr radius of the state, since at higher values of q the effect of strain is averaged out over the wave function.⁶ In this Letter we report measurements of the magnetic field dependence of the thermal conductivity in Ge(Ga) and Si(B) which, together with earlier work, indicate that the structure of the acceptor state in Ge is more complex than the simple quartet structure described above, presumably because of a Jahn-Teller effect.

In the undistorted site, phonons of energy much less than that of the first excited state (80 K in

Ge, 330 K in Si) can only be scattered from transitions within the quartet—a wholly elastic process. If the degeneracy of the ground state is removed by a magnetic field, the conductivity should first fall as the level splittings become comparable to the dominant phonon energies ($\sim 4kT$) and then rise rapidly when the splittings become $\gg kT$. However, if the ground state is more complex, the behavior could be quite different.

The specimens used in this investigation were grown by the Czochralski technique⁷ and had hole concentrations of $1.0 \times 10^{16} \text{ cm}^{-3}$ for Ge(Ga) and $9 \times 10^{16} \text{ cm}^{-3}$ for Si(B). These both correspond to an average distance $d \sim (8-9)a^*$ [$a^*(\text{Ge}) \sim 37 \text{ \AA}$, $a^*(\text{Si}) \sim 15 \text{ \AA}$] which is a compromise between the desire to have a high concentration and so a potentially large effect, and the need to keep $d \gg a^*$ to avoid overlap between neighboring acceptors. The specimen dimensions were $20 \times 3 \times 3 \text{ mm}^3$ with the axis along a $\langle 110 \rangle$ direction, and the field was applied either parallel to this axis or, at