Multiphonon hopping of carriers on defect clusters in an amorphous Ge-Sb-Se system

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A series of antimony-containing ternary chalcogenide Ge$_2$Sb$_x$Se$_{80-x}$ ($5 \leq x \leq 25$) films were prepared by an electron-beam technique, and the temperature dependences of the dc and ac conductivities were studied. The dc conductivity is found to be proportional to $T^n$, with $n=4\sim 5$ below room temperature. It is shown that defect clusters cause an inhomogeneous distribution of deep localized states in the Ge-Sb-Se system and that the electronic transport is no longer dominated by Mott's variable-range-hopping (VRH) process. Quantitatively the VRH process could not be used to interpret the observed behavior; alternatively, the multiphonon process with weak electron-lattice coupling is suggested to be the dominant transport mechanism. The ac conductivity is interpreted in terms of a random-free-energy-barrier model, which strongly correlates with the dc conductivity, and this has never been explained by the current theories based on the pair approximation. This model assumes conduction by hopping, where the hopping charge carriers are subjected to spatially randomly varying energy barriers. It is shown that this model gives an excellent account of the observed behavior of the ac conductivity.

One of the characteristic properties of electrical conduction in disordered solids is a strong dispersion of the conductivity. The simplest and, indeed, the most common explanation for a conductivity that increases with frequency or temperature is the existence of one or another kind of inhomogeneity in the material. In an amorphous Ge-Sb-Se system, the temperature dependence of the dc conductivity $\sigma(0, T)$ exhibits a linear behavior when plotted as $\ln \sigma(0, T)$ versus $T^{-1/4}$, i.e., a variable-range-hopping (VRH) conduction process [nonlinear when plotted as $\ln(0, T)$ versus $T^{-1}$], suggesting that dc transport is not by band conduction. While Mott's VRH theory reproduces many experimental features, the estimated physical quantities such as $N(E_F)$, the density of localized states at the Fermi level, are not reliable because of various assumptions made. Recently, one of the authors suggested that the multiphonon hopping of localized electrons (weak-coupling system) dominates dc conduction in a-Ge. It is of interest to determine whether or not multiphonon hopping dominates the conduction process in chalcogenides. This process also predicts a $T^{-1/4}$ behavior over a limited temperature range. The number of carrier sites in the Ge-Sb-Se system is predicted to be on the order of $10^{19}$ cm$^{-3}$ (from ac conduction data). If defect clusters (with an average radius of about 30 Å) are present in the system, the mean separation of isolated dangling bonds may be comparable to the Bohr radius ($\alpha^{-1}$). An electron on such a dangling bond may lose its localized nature; the hopping of an electron can then occur between defect clusters. The dc transport cannot be explained by simple VRH theory which assumes a homogeneous distribution (in energy and space) of localized states near the Fermi level.

In this paper, the dc and ac conductivities for amorphous Ge$_2$Sb$_x$Se$_{80-x}$ ($5 \leq x \leq 25$) films are examined. The dc conductivity is found to be well described by $\sigma(0, T) = \sigma_0 (T/T_0)^n$ with $n=4\sim 5$ for the present system. The origin of this temperature dependence is discussed in terms of the continuous-time random-walk (CTRW) and effective-medium approximation (EMA). It has been shown that this analysis gives an excellent explanation for the temperature behavior of the $\sigma(\omega, T)$ in the measured frequency range.

Films of Ge$_2$Sb$_x$Se$_{80-x}$ ($5 \leq x \leq 25$) were prepared by electron-beam evaporation in a vacuum of about $1 \times 10^{-6}$ Torr at a rate of about 50 nm min$^{-1}$. The source materials were made by melt quenching. Thin-film samples of sandwich geometry were obtained on glass substrates cooled to liquid-N$_2$ temperature. Gold was chosen as a contact material. The structure and composition of the films were investigated by using a transmission electron microscope (Philips E400) and electron probe microanalyzer (Philips SEM505 plus EDAX plus Microspec WDX-2A) in the energy dispersive mode. The samples were found to be amorphous as checked by their diffraction patterns.

Figure 1 shows the temperature dependence of $\sigma(0, T)$ plotted against $T^{-1/4}$ for the Ge-Sb-Se system to examine whether Mott's VRH process dominates dc conduction. The VRH theory predicts the temperature dependence of...
\[ \sigma(0, T) = \sigma_0 \exp(-B/T^{1/4}) \]

where \( \sigma_0 \) is a prefactor \( (= 3e^2v_0[N(E_F)/\pi \alpha k]^{1/2}) \), \( B \) the constant \([=16\alpha^2/\pi N(E_F)]\), \( v \) the characteristic phonon frequency, \( \alpha^{-1} \) the effective Bohr radius of localized electrons, \( N(E_F) \) the density of states at the Fermi level, and \( k \) the Boltzmann constant. The VRH theory reproduces many experimental data but there are some difficulties. The most serious problem is the discrepancy, by many orders of magnitude, between experimental and computed values of \( N(E_F) \) (Refs. 5 and 6) and have been attributed to uncertainties involved in estimation of \( \sigma_0 \). The \( N(E_F) \) here is estimated from constant \( B \). The estimated value of \( N(E_F) \) for the Ge-Sb-Se system is about \( 10^{20} - 10^{21} \) cm\(^{-3} \) eV\(^{-1} \). The present estimation of \( N(E_F) \) might be plausible and not very high for the electron-beam-evaporated materials as these materials, such as an amorphous Ge-Sb-Se system, may have high density of neutral dangling bonds (\( D^0 \)), although melt-quenched chalcogenides have smaller density of \( D^+ \) (the principal defects are charged dangling bonds \( D^+ \) and \( D^- \)). It is also predicted that the present system has many microvoids. It is thus required to seek a more quantitatively acceptable transport mechanism, alternative to Mott’s VRH process as it is only applicable to the homogeneous systems.\(^3\)

Experimental data of Fig. 1 are replotted on a logarithmic \( T \) scale as shown in Fig. 2 for all the compositions of the Ge-Sb-Se system. It is seen from the figure that the data fit well over the entire range of temperature for all composition of the film showing that \( \sigma(0, T) \) is proportional to \( T^n \). The value of \( n \) is 4.7 to 4.1 for Ge\(_{20}\)Sb\(_x\)Se\(_{80-x}\) (5 \( \leq x \leq 25 \)) films, respectively. It has been suggested that multiphonon process with weak electron-lattice coupling may dominate hopping transport of charged carriers on defect clusters.

The distribution of deep localized states originating from defect clusters (average radius \( \approx 30 \) Å) is schematically shown in Fig. 3. The tunneling of carriers occurs between the nearest defect clusters. Although the actual tunneling occurs between cluster surfaces with distance \( S \), the effective jump distance \( R \) will be given by the center-to-center separation between the clusters. The delocalized carriers on cluster could couple to long-wavelength phonons lower than \( \omega_0 \) which is approximately given by \( (a_0/\alpha^{-1})v_D \), where \( a_0 \) is the average lattice separation, \( \alpha^{-1} \) the effective Bohr radius, which could be of the order of the cluster size \( r_c \), and \( v_D \) the Debye frequency \( [v_D = 3 \times 10^{12} \text{ s}^{-1}] \) (see Ref. 9). Such a long-wavelength phonon is allowed only in an acoustic mode. Using \( r_c \approx 30 \) Å, \( a_0 \approx 3 \) Å, and \( v_D = 3 \times 10^{12} \text{ s}^{-1} \), the small frequency \( \omega_0 \approx 3 \times 10^{11} \text{ s}^{-1} \) and \( T_0 = 10 \) K is predicted.\(^9\) The single-phonon hopping process, e.g., VRH process, which requires the condition \( h\omega_0 > \Delta \) and small \( \alpha^{-1} \), where \( \Delta \) is the site energy separation, is not expected to occur.\(^3\) Instead, multiphonon hopping between defect clusters could dominate transport mechanism similar to \( \alpha-\text{Ge} \).\(^9\) The weak electron (on clusters) -lattice coupling is assumed here since the wave functions might be delocalized across clusters.

The hopping rate due to multiphonon tunneling of localized carriers with weak electron-lattice coupling can be given by

\[ \Gamma = C \exp(-\gamma p)[1 - \exp(-h\omega_0/kT)]^{-p} \]

![FIG. 1. Temperature dependence of dc conductivity \( \sigma(0, T) \) plotted against \( T^{-1/4} \) for an amorphous Ge\(_{20}\)Sb\(_x\)Se\(_{80-x}\) system: □, Ge\(_{20}\)Sb\(_x\)Se\(_{75}\); ○, Ge\(_{20}\)Sb\(_x\)Se\(_{70}\); □, Ge\(_{20}\)Sb\(_x\)Se\(_{65}\); ▲, Ge\(_{20}\)Sb\(_x\)Se\(_{60}\); ⊙, Ge\(_{20}\)Sb\(_x\)Se\(_{55}\).](image1)

![FIG. 2. Logarithmic temperature dependence of \( \ln \sigma(0, T) \) for an amorphous Ge\(_{20}\)Sb\(_x\)Se\(_{80-x}\) system. Data originally plotted in the form of \( \ln \sigma(0, T) vs T^{-1/4} \) are the same as in Fig. 1.](image2)

![FIG. 3. Schematic energy diagram for deep localized states originating from the defect clusters.](image3)
where \( C = v_0, \gamma = \ln(\Delta/E_M) - 1, p = \Delta/hv_0, \) and \( E_M \) is the measure of electron-lattice coupling.\(^{16}\) The above equation was derived for nonradiative recombination (phonon emission) in which the electron is weakly coupled to the optical modes. It is assumed that Eq. (2) can be applicable even for acoustic modes, since the solitary distinction between optical and acoustic modes could reside in the dispersion relations. The multiphonon hopping process must involve absorption and emission of \( p \) phonons. The absorption process is proportional to the pth power as \([\exp(hv_0/kT) - 1]^{-p}\). Under the condition \( hv_0 < kT \) (high population of phonons), the hopping rate for the absorption will be the same as the emission and is proportional to \( (kT/hv_0)^p \). Thus Eq. (2) is applicable to the present hopping mechanism. This equation is similar to the multiphonon jump rate for weak coupling derived by Yoshida.\(^6\) Using \( \Gamma \), the dc hopping conductivity is given by

\[
\sigma(0, T) = N_c \langle eR \rangle^2 \Gamma/6k^2 T^p,
\]

where \( N_c \) is the number of carriers and \( R \) is the hopping distance which is taken to be the center-to-center separation of clusters. As \( N_c \) must be equal to \( N(E_F)kT \) and \( \sigma(0, T) \) is proportional to \( T^p \), the value of \( p \) should be an integral number. However, if \( \Delta \) or \( v_0 \) is distributed around a certain value, \( p \) may have a finite distribution and its mean value will be nonintegral. Experimentally obtained \( p \) values are in fact nonintegral.

Before estimating the physical parameters appearing in Eqs. (2) and (3), we turn to the ac conductivity. The ac conductivity \( \sigma(\omega, T) \) for many disordered materials can be empirically described by \( \sigma(\omega, T) = A\omega^s \), where \( A \) and \( s \) (\( s < 1.0 \)) are usually temperature-dependent parameters.\(^{18,16}\) This relation can be interpreted either by the quantum-mechanical tunneling\(^{20,21}\) (QMT) or correlated barrier hopping (CBH).\(^22\) These models are based on the pair approximation in which the motion of the carrier is contained within a pair of sites. If the dc and ac conductivities arise from the same hopping mechanism, the pair approximation cannot be applied.\(^{18,19}\) In such a situation, Dyre\(^{11,12}\) proposed a simple model based on the assumption of randomly varying free-energy barriers for jumps. This model strongly correlates the \( \sigma(\omega, T) \) with the \( \sigma(0, T) \), which has never been explained by the current theories based on the pair approximation. According to this model, the simplest possible assumption is that all free-energy barriers are equally likely. Since \( P(\Gamma) = [P(\Delta F)/(d\Delta F/d\Gamma)] \) this implies

\[
P(\Gamma) \propto \Gamma^{-1},
\]

where \( \Delta F \) is the free-energy barrier \( (= \Delta E - T\Delta S) \), \( \Delta E \) the energy barrier, and \( \Delta S \) the entropy barrier.

In the continuous-time random-walk approximation,\(^{11,12}\) ac conductivity is given as

\[
\sigma(\omega, T) = K \left[ -i\omega + \frac{1}{(\Gamma + i\omega)} \right]^{-1},
\]

where \( K \) is a constant, \( \omega \) the angular frequency of applied field, and \( 1/(\Gamma + i\omega) \) denotes the average over jump frequency distribution \( P(\Gamma) \). This equation is simplified by using Eq. (4) to yield a simple form of ac conductivity as

\[
\sigma(\omega, T) = \sigma(0, T) \frac{i\omega\tau}{\ln(1 + i\omega\tau)},
\]

where \( \tau \) is the hopping relaxation time and approximately equal to \( \Gamma^{-1} \) in Eq. (2).

In the effective-medium approximation,\(^{13-15}\) ac conductivity is given as

\[
\sigma(\omega, T) \ln \left( \frac{\sigma(\omega, T)}{\sigma(0, T)} \right) = i\omega\tau,
\]

where

\[
\tau = \frac{0.253}{3\sigma(0, T)} \ln \left( \frac{\Gamma_{\text{max}}}{2\sigma(0, T)} \right) - \frac{3}{2}.
\]

We infer from Eqs. (6) and (7) that \( \sigma(\omega, T) \) is strongly correlated with \( \sigma(0, T) \). Thus the measurement of \( \sigma(\omega, T) \) could provide knowledge of the hopping rate of localized carriers. Figure 4 shows a comparison between the CTRW and the EMA solutions of the random-free-energy-barrier model in which the conductivity ratio \( \sigma(\omega, T)/\sigma(0, T) \) is plotted versus \( \omega\tau \) (randomly selected). It is shown that CTRW and EMA solutions are almost indistinguishable, lending some credence to the simple CTRW approximation for \( \sigma(\omega, T) \).

To analyze ac conduction data for the present system, only the CTRW approximation is used for calculations. The parameter to fit the experimental data is \( \tau \) which should be equal to \( \Gamma^{-1} \) in Eq. (2). Figures 5 and 6 show the experimental ac conductivity data as a function of frequency for the Ge\(_{20}\)Sb\(_x\)Se\(_{80-x}\) \( (5 \leq x \leq 25) \) system at 87 and 300 K, respectively. The solid lines in the figures show the calculated ac conductivities (real part) using Eq. (6), where \( \sigma(0, T) \) is set to the experimental value and \( \Gamma \) is chosen to obtain the best fit. It is evident from the figures that the overall features can be interpreted in terms of the CTRW approximation. It is found that the hopping rate increases with the increasing concentration of Sb content.

The remaining physical parameters to be estimated are

![FIG. 4. Comparison between the CTRW and the EMA solution of the random-free-energy-barrier model. The solid line is the CTRW solution and the dots (●) mark the EMA solution.](image-url)
\(N_c, R, \text{ and } \gamma\). Unfortunately estimation of \(N_c\) and \(R\), independently, is difficult because of lack of \(N(E_f)\) data for the Ge-Sb-Se system. The estimations of density of states obtained by electron-spin resonance (ESR) or magnetic susceptibility are often in error due to the negative effective correlation energy, resulting from the strong electron-lattice interaction of defects in electron-beam-evaporated materials. Let us estimate \(N_c R^2\) [see Eq. (3)] from experimental data. The value of \(\gamma\) is estimated from Eq. (2). It was assumed that microvoids with an average radius of 30 Å were present in this system and \(R\) is taken as the center-to-center separation of microvoids, and therefore should be bigger than the microvoid size, i.e., \(R > 30\ \text{Å}\). The theoretical fitting of experimental data has been done at the extreme temperature limits. If we assume the minimum value of \(R \approx 30 \text{ Å}\), this yields the number of carriers \(N_c < 10^{19} \text{ cm}^{-3}\) at 87 K and \(N_c < 10^{20} \text{ cm}^{-3}\) at 300 K. The agreement is obtained for both extreme temperature data; however, we suppose that physical parameters estimated at the lower temperature limit (87 K) are more plausible, whereas parameters obtained at the upper temperature limit (300 K) may involve the contribution from band conduction. The density of states at Fermi level \(N(E_F) (= N_c/kT)\) is now estimated to be \(< 10^{21} \text{ cm}^{-3} \text{ eV}^{-1}\) for the present Ge-Sb-Se system. All the physical parameters are tabulated in Table I.

Finally, it should be checked whether the estimated parameters satisfy the weak-coupling conditions. Robertson and Friedman\(^\text{16}\) require the condition \(E_M < h \nu_0\).

Englman and Jortner,\(^\text{13}\) on the other hand, suggested that

\[\text{TABLE I. Multiphonon hopping conduction parameters for the Ge}_{20}\text{Sb}_x\text{Se}_{80-x} (5 \leq x \leq 25) \text{ system.}\]

\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Material & \(\rho\) & \(N_c R^2\) & \(\Gamma\) & \(\gamma\) & \(N_c^\text{a}\) & \(E_M/h \nu_0^\text{b}\) & \(G^\text{b}\) \\
\hline
\text{Ge}_{20}\text{Sb}_{15}\text{Se}_{75} & 4.7 & 3.4 \times 10^6 & 1.0 \times 10^{-2} & 8.5 & <3.7 \times 10^{19} & 9.5 \times 10^{-4} & 5.8 \times 10^{-3} \\
\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{80} & 4.6 & 3.6 \times 10^6 & 1.4 \times 10^{-2} & 8.6 & <4.0 \times 10^{19} & 8.5 \times 10^{-4} & 5.1 \times 10^{-3} \\
\text{Ge}_{20}\text{Sb}_{15}\text{Se}_{65} & 4.5 & 3.6 \times 10^6 & 2.1 \times 10^{-2} & 8.6 & <4.0 \times 10^{19} & 8.2 \times 10^{-4} & 5.0 \times 10^{-3} \\
\text{Ge}_{20}\text{Sb}_{20}\text{Se}_{50} & 4.0 & 3.4 \times 10^6 & 4.4 \times 10^{-2} & 9.2 & <3.8 \times 10^{19} & 4.0 \times 10^{-3} & 2.4 \times 10^{-3} \\
\text{Ge}_{20}\text{Sb}_{25}\text{Se}_{35} & 4.1 & 4.1 \times 10^6 & 4.8 \times 10^{-2} & 9.0 & <4.6 \times 10^{19} & 5.0 \times 10^{-4} & 3.0 \times 10^{-3} \\
\hline
\end{tabular}

\[\text{Temperature 300 K}\]

\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Material & \(N_c R^2\) & \(\Gamma\) & \(\gamma\) & \(N_c^\text{a}\) & \(E_M/h \nu_0^\text{b}\) & \(G^\text{b}\) \\
\hline
\text{Ge}_{20}\text{Sb}_{15}\text{Se}_{75} & 4.8 \times 10^7 & 1.0 & 8.7 & <5.3 \times 10^{20} & 7.0 \times 10^{-4} & 1.6 \times 10^{-2} \\
\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{80} & 3.5 \times 10^7 & 7.0 & 8.4 & <3.8 \times 10^{20} & 1.0 \times 10^{-3} & 2.1 \times 10^{-2} \\
\text{Ge}_{20}\text{Sb}_{15}\text{Se}_{65} & 3.0 \times 10^7 & 2.5 \times 10^4 & 8.2 & <3.4 \times 10^{20} & 1.2 \times 10^{-3} & 2.5 \times 10^{-2} \\
\text{Ge}_{20}\text{Sb}_{20}\text{Se}_{50} & 2.6 \times 10^7 & 8.3 \times 10^4 & 8.6 & <2.9 \times 10^{20} & 7.0 \times 10^{-4} & 1.5 \times 10^{-2} \\
\text{Ge}_{20}\text{Sb}_{25}\text{Se}_{35} & 2.0 \times 10^7 & 2.9 \times 10^4 & 8.1 & <2.3 \times 10^{20} & 1.2 \times 10^{-3} & 2.6 \times 10^{-2} \\
\hline
\end{tabular}

\(^\text{a}\)Computed using the minimum value of \(R \approx 30 \text{ Å}\).

\(\text{Weak electron-lattice coupling conditions: (i) } E_M < h \nu_0\) [Robertson and Friedman (Ref. 16)]; (ii) \(G = (E_M/h \nu_0)(kT/h \nu_0) < 1\) [Emin (Ref. 17)]; (iii) \(G < 1\) [Englman and Jortner (Ref. 23)].
the weak-coupling regime should satisfy the condition of \( G = \frac{(E_M / \hbar v_0)(kT / \hbar v_0)}{G_M} < 1 \). Emin\(^{17}\) required a more severe condition, \( G < 1 \), for weak-coupling states. It is noted, however, that the condition \( G < 1 \) can be valid for \( p \leq 6 \) in weak-coupling states.\(^{24}\) All these weak-coupling condition parameters are tabulated in Table I. It is observed from the table that all estimated parameters satisfy the weak-coupling conditions. Thus we conclude that electronic transport in an amorphous Ge\(_{20}\)Sb\(_{2}\)Se\(_{88}\) system can be explained by the multiphonon hopping of deep localized carriers between the defect clusters and suggested to explain the empirical relation of \( \sigma(0, T) \propto T^n \).

It is concluded that the multiphonon hopping of deep localized carriers between the defect clusters is an alternative model for interpreting transport in disordered materials. For the present data, the dc conductivity is proportional to \( T^n \) with \( n = 4-5 \) over a wide temperature range. The random-free-energy model predicts a universal frequency dependence of the ac conductivity, independent of chemical composition and temperature and it is shown that all the features of ac conductivity in the measured frequency range can be interpreted in terms of the CTRW approximation for the Ge-Sb-Se system.

\(^{11}\) J. C. Dyre, J. Appl. Phys. 64, 2456 (1988).
\(^{24}\) The multiphonon jump rate derived in Ref. 17 involves the modified Bessel function \( I_n(G) \). For a small-argument approximation, \( G \approx 0, I_n(G) \propto G^n \) is obtained. Note that the \( G^n \) expression can still be valid for \( G < 1 \) when \( p \leq 6 \).