

Inhomogeneous Transport Regime in Disordered Materials*

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We propose the existence of an inhomogeneous transport regime in the disordered materials in which a gradual metal-semiconductor transition occurs. This regime is subdivided into pseudometallic and pseudosemiconducting parts by a percolation threshold. On the basis of an effective-medium theory, we propose that the pseudometallic regime falls in the density range 8.2–9.3 g/cm³ in liquid Hg and in the temperature range 1200°K to below 670°K in liquid Te.

In this Letter we distinguish five distinct regimes of electronic conduction which may exist in a disordered material:

(I) In the propagation regime electron transport is characterized by propagation of conduction electrons between scattering events,^{1,2} i.e., a value of $k_F l > 1$. Transport properties are given by the weak scattering theory¹ or its continuation to stronger scattering.³ The conductivity σ exceeds $\sigma \sim 3000 (\Omega \text{ cm})^{-1}$,² the Hall coefficient R is near the free-electron value R_{FE} , and variations in the Hall mobility μ reflect primarily variations in the conductivity.

(II) In the diffusion regime the phase-coherence length of the conduction electrons becomes comparable to or less than the internuclear spacing, and the electron undergoes a diffusion or Brownian motion.^{4,5} Friedman⁶ has shown within a specific crystalline tight-binding model that random phase implies

$$\sigma \propto (R_{FE}/R)^2, \quad \mu \propto R_{FE}/R, \quad R_{FE}/R < 1, \quad (1)$$

the proportionality constants containing parameters either weakly or explicitly dependent on the variables of state. Friedman⁶ assumed that the wave-function amplitude was constant, which is equivalent to microscopic homogeneity. We assume that Friedman's results are of general validity for disordered materials, provided that there is sufficient microscopic homogeneity.

(III) In the inhomogeneous regime microscopic inhomogeneities can arise from density fluctuations at high temperatures,⁷ cluster formation at low temperatures,⁸ or bonding modifications⁹ at intermediate temperatures. Friedman's results,⁶ with their implicit requirement of microscopic homogeneity, no longer hold. In the cases of in-

terest, these density fluctuations, clusters, or modified bonds imply a tendency towards setting up a band gap locally. Electrons at the Fermi energy become locally excluded from such inhomogeneities. As the electronic phases are usually already random on the scale of variation of the local configuration, a semiclassical theory¹⁰⁻¹⁵ can be used to treat this problem. The material may be viewed as consisting of a random submacroscopic mixture of metallic and semiconducting, electrolytic, or insulating regions. The density of states is reduced by the allowed (or metallic) volume fraction $C(E_F)$ at the Fermi energy,¹⁴

$$n(E_F) = n_0(E_F)C(E_F), \quad (2)$$

where $n_0(E_F)$ is the mean density of states within the allowed regions and is approximately equal to the density of states at the limit of the homogeneous regime, provided the density of states is negligible at E_F in the nonmetallic regions. Otherwise a term $n_1(E_F)[1 - C(E_F)]$ is added to (2).

We now divide the inhomogeneous regime into two parts. In the pseudometallic part [$1 > C(E_F) > C^*$], $C(E_F)$ is sufficiently large that continuous metallic paths extend throughout the material, that is, electrons at the Fermi energy are in extended states. When $C(E_F)$ decreases to some critical value, the percolation limit, such extended paths cease to exist.¹⁰⁻¹⁵ The site percolation problem has not been solved in the form encountered here. However, existing numerical studies for three-dimensional lattices¹⁶ suggest a value of $C^* \approx 0.2$. Within the range $1 > C(E_F) > C^*$ transport is dominated by the metallic regions. Kirkpatrick has shown¹⁵ that the resistance of a simple cubic network of resistors r_0 (bond perco-

lation) with a fraction p replaced by resistance τ_1 follows the effective-medium theory over a range of p which depends on τ_0/τ_1 . For $\tau_0/\tau_1 > 0.1$, the effective medium theory holds for all p . In the worst case, $\tau_0/\tau_1 \approx 0$, the resistance is given by the effective-medium theory for $1 > p > 0.4$, varies as $(p - p_c)^{1.6}$ for $0.4 > p > p_c$, where p_c is the percolation limit, and is ≈ 0 below p_c . In our problem, the ratio τ_0/τ_1 is replaced by σ_1/σ_0 , where σ_1 and σ_0 are the conductivities of the semiconducting and metallic regions, respectively. $C(E_F)$ and C^* replace p and p_c , respectively. The effective-medium theory can then be considered to hold over parameter ranges similar to those found by Kirkpatrick,¹⁵ within which^{15,17,18}

$$\begin{aligned} f &\equiv \sigma/\sigma_0 = a + (a^2 + \frac{1}{2}x)^{1/2}, \\ a &= \frac{1}{2} \left\{ \left[\frac{3}{2}C(E_F) - \frac{1}{2} \right] (1-x) + \frac{1}{2}x \right\}, \\ x &\equiv \sigma_1/\sigma_0. \end{aligned} \quad (3)$$

We have constructed an effective-medium theory for the Hall constant and Hall mobility¹⁹:

$$\begin{aligned} g &\equiv \mu/\mu_0 = [1 - b(1 - xy)]^{-1}, \\ h &\equiv R/R_0 = [1 - b(1 - xy)]f^{-2}, \\ b &= \frac{(2f+1)^2(1-C)}{(2f+1)^2(1-C) + (2f+x)^2C}, \\ y &\equiv \mu_1/\mu_0. \end{aligned} \quad (4)$$

The Hall constant and Hall mobility ratios, h and g , can exhibit a wide range of variations with C , depending on the particular values of x and y . Detailed numerical¹⁹ studies show that when x is in the range 10^{-2} – 10^{-1} and y in the range 1–3, g depends only weakly on C , especially in the range $C > 0.4$, while f and h vary considerably. Such values of x can be expected in high-temperature materials, and such values of y can be generally expected.

In the pseudosemiconducting part of the inhomogeneous regime [below $C(E_F) = C^*$], no extended states exist at the Fermi energy. Localized states occur within a pseudogap or mobility gap between the two energies, the mobility edges at which $C(E) = C^*$. Electron transport can occur via Mott hopping between isolated metallic regions, via electrons excited across the mobility gap in the semiconducting regions, or via Mott hopping within the semiconducting regions or between metal and semiconducting regions. The conductivity will start exhibiting strong temperature, frequency, and impurity dependences, and the thermoelectric power will start to increase.

R , σ , and μ will be intermediate between those of the pseudometallic regime and those of typical disordered semiconductors.

(IV) In the semiconducting regime the system becomes sufficiently homogeneous microscopically that the localized states within the mobility gap are unimportant for transport. The transport properties become typical of those of amorphous²⁰ or liquid² semiconductors. In particular, one expects a linear relation between $\ln \sigma$ and the thermoelectric power.²¹

What is new in the above picture is the inter-
polation of the two inhomogeneous regimes between the diffusion and the semiconducting regimes, and the elucidation of the transport properties (3) and (4). These two regimes are consequences of the fluctuations inevitably accompanying continuous changes from metallic to insulating behavior in disordered materials. Mott's^{2,22} idea of a minimum metallic conductivity applies only within the homogeneous metallic regimes. Percolation or, less extremely, inhomogeneity results in a continuous decrease in conductivity below that minimum value. Localization in disordered materials is a consequence of and implies microscopic inhomogeneity, the effects of which on electronic motion precede the formation of mobility edges, persist in energy beyond them, and are approximately describable with the aid of semiclassical percolation theory. Kirkpatrick²³ has recently arrived at similar conclusions regarding semiclassical aspects of metal-insulator transitions in inhomogeneous materials. The inhomogeneous regime was first treated by Cohen and Sak¹⁴ as a basis for the metal-insulator transition in alloy systems with clustering.

We now apply these ideas to (a) expanded liquid Hg^{21,24-26} and (b) liquid Te.^{9,27-34}

For Hg, analysis of R and σ by Even and Jortner^{25,26} shows that the propagation regime extends from 13.6 to 11 g/cm³ in density ρ , and that the diffusion regime extends from 11 to 9.3 g/cm³ in ρ . Their identification of the diffusion regime rested on Eq. (1) and in particular on the correlation of the Hall mobility with the Hall constant. They found μ to be slowly varying from 9.3 to 8.6 g/cm³ in ρ . We infer from this and Eqs. (3) and (4) that the pseudometallic range starts at 9.3 and continues at least to 8.6 g/cm³. Values of $C(E_F)$ can then be taken from σ or R via (3) or (4). These values are in agreement with a detailed thermodynamic analysis of density fluctuations in this one-component system.⁷

The detailed analysis shows that the pseudo-metallic range continues down to $\rho = 8.2 \text{ g/cm}^3$ where $C(E_F) \approx 0.2$. A linear relation between $\ln \rho$ and the thermoelectric power²¹ sets in at $\rho = 7.8 \text{ g/cm}^3$, where the energy gap begins to exceed $4kT$ and the semiconducting regime continues below 7.8 g/cm^3 . This metal-insulator transition taking place through the inhomogeneous regime over the density range 9.3 to 8.0 g/cm^3 originates from the separation of s and p bands with decreasing density in a divalent metal as proposed by Mott.³⁵

In liquid Te, μ is approximately constant^{29,31} throughout the temperature range over which data are available, 690 – 1050°K . Recent attempts by Mott² and by Warren³⁴ to assign the data to the diffusion regime are incompatible with this observation. Cabane and Friedel⁹ have proposed the simultaneous presence of local order of two kinds, twofold coordination of insulating character and threefold coordination of metallic character. The Hall mobility simply reflects the effect of the resulting microscopic inhomogeneities on the transport properties. Warren³⁴ has recently made accurate and detailed measurements of the Knight shift κ . As microscopic inhomogeneities form and reform on a time scale short compared with the Knight shift itself (picoseconds),⁹ the latter is motionally narrowed and proportional to the average and not the local density of states. κ tends to saturate at high temperature at a value κ_1 . We interpret this as implying that liquid Te becomes homogeneously metallic when $T > 1200^\circ\text{K}$. According to Eq. (2), $C(E_F)$ is given directly by

$$C(E_F) = H/H_1, \quad (5)$$

and σ and R can then be obtained by inserting (5) into (3) and (4). The resulting fit to σ and R is satisfactory, as shown in Fig. 1. The fact that the calculated values of σ are about 10% too high for $C(E_F) = 0.6$ suggests that the metallic regions are not completely within the diffusion regime. Scattering off the potential fluctuations would then reduce σ_0 with decreasing $C(E_F)$ as in metal-ammonia solutions.³⁶ This will reduce the value of y needed to fit R .

Other materials for which this approach might be promising include metal-ammonia solutions^{8,36} in the concentration region 1–9 mole percent metal (MPM), where we assign the pseudoinulator regime from 1 to 3 MPM and the pseudometallic regime from 3 to 8 MPM. Liquid In_2Te_3 , Ga_2Te_3 , and Tl_2Te behave similarly with tem-

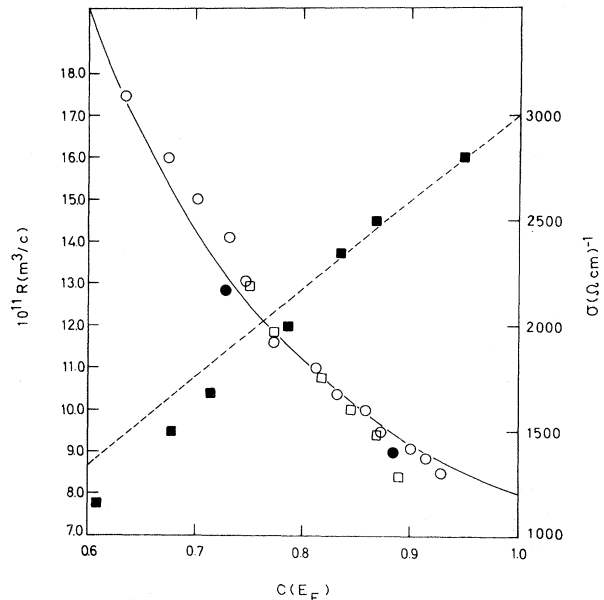


FIG. 1. Interpretation of the electrical transport properties of liquid Te in terms of effective-medium theory. Experimental conductivity data: Solid rectangles, Refs. 27–30. Experimental Hall-effect data: open circles, Ref. 31; solid circles, Ref. 29; and open rectangles, Ref. 32. $C(E_F) = \kappa/\kappa_1$ (see text) where κ is taken from Ref. 34 and $\kappa_1 = 0.575\%$. The theoretical fit according to Eqs. (3) and (4) is $x = 6 \times 10^{-2}$, $y = 0.6$. Solid line, R/R_0 ; $R_0 = 8 \times 10^{11} \text{ m}^3/\text{C}$. Dashed line, σ/σ_0 ; $\sigma_0 = 3000 \text{ } (\Omega \text{ cm})^{-1}$.

perature near their melting points,^{2,37} while $\text{Mg}_x\text{Bi}_{1-x}$ does so with varying concentration.¹⁴ $\text{Te}_x\text{Se}_{1-x}$ alloys³⁸ seem particularly interesting in this connection. In general, conductivity, Hall-effect, Knight-shift, and magnetic susceptibility data are all required for unambiguous identification of the inhomogeneous regime. In one-component systems thermodynamic considerations permit one to estimate $C(E_F)$ conveniently⁷ when chemical bonding effects do not intervene.

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Tunable Far-Infrared Radiations from Hot Electrons in *n*-Type InSb

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We report tunable far-infrared radiation from *n*-type InSb under crossed magnetic and electric fields. The emission is interpreted in terms of the transitions of hot electrons between Landau sub-bands and the radiative capture by the impurity ground state.

In the course of studying the cyclotron resonance in *n*-type InSb under a pulsed electric field,¹ we have observed, for the first time, tunable far-infrared radiation from *n*-type InSb at 4.2 K under crossed magnetic and electric fields, due to the transitions of hot electrons between Landau sub-bands or associated impurity states. The experimental results are interpreted in terms

of hot-electron effects in strong magnetic fields. There have been studies²⁻⁵ of the microwave emission from *n*-type InSb in magnetic fields at low temperatures. For example, Bekefi, Bers, and Brueck⁵ observed resonant structures (not interpreted) with varying magnetic field in the microwave emission from *n*-type InSb at 4.2 K when a sample was subjected simultaneously to