Metal-Insulator Transition in Disordered Germanium-Gold Alloys

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It has been discovered that the disordered material $Ge_{1-x}Au_x$ displays an unusual type of metal-insulator transition as the composition x is varied. The onset of conductivity, as extrapolated to $T = 0$ K, is continuous, and thus the system has no "minimum metallic conductivity."

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The most fundamental classification of the electronic properties of a material is separation into metals and insulators. Many systems undergo a metal-insulator transition as a function of temperature (due to structural changes), pressure, or composition. In recent years, the problem of the metal-insulator transition in disordered systems and the understanding of the conduction process itself has become important.[1] The first step in this understanding was taken by Anderson in 1958.[2] He pointed out that noninteracting electrons which would otherwise be free could be localized in a highly disordered material. Subsequently Mott[3] was able to classify the disorder of many materials using their conductivity. He observed, in general, that the conductivity of a material, if less than approximately 300 Ω^{-1} cm^{-1}, would tend to zero with temperature. This "minimum metallic conductivity" would mark the boundary between metals and insulators at $T = 0$. A metal would thus have a conductivity greater than 300 Ω^{-1} cm^{-1} at $T = 0$. Thouless[4] developed a quantum-mechanical insight into localization which became fully developed with the work of Abrahams *et al.*[5] They used a noninteracting, one-parameter renormalization theory for localization that could be applied in all three dimensions. This model has been qualitatively successful in understanding localization measurements in one and two dimensions. However, in three dimensions, to date, this model has been poorly tested. The measurements of Thomas[6] of the resistivity of phosphorus-doped silicon have raised questions about homogeneity and the size of the critical region due to the long length scale (the distance between phosphorus impurities). The work described below does not have this limitation and does indicate the need for an interacting electron

model for localization in three dimensions. We report here the discovery of an unusual type of metal-insulator transition in both polycrystalline and amorphous films of $Ge_{1-x}Au_x$ as a function of x.

The $Ge_{1-x}Au_x$ samples are flash evaporated in a vacuum of about 5×10^{-8} Torr onto a dry-ice–cooled sapphire substrate to form a film 2000 Å thick. This method ensures spatial homogeneity, determined by α-particle Rutherford backscattering and Auger-electron spectroscopy, and minimizes clustering of the gold. The spatial variation of the concentrations is $\sim \pm 1\%$. Spatial inspection of a 500-Å film of $Ge_{0.82}Au_{0.18}$ with a scanning transmission electron microscope (its low-beam current avoids heating) revealed no gold clusters larger than the resolution of 10 Å. With the large Z for gold, such clusters are easily seen. There is clearly some migration of the gold at room temperature and samples with gold concentrations of 0.24 or more can form metastable phases. We have used x-ray scattering to establish that the samples reported here, as made, have structure factors indistinguishable from those of such an amorphous solid. The polycrystalline phase, produced by heating, produced the full powder pattern of germanium and gold. In spite of these precautions it is difficult to control the clustering of gold and thus to maintain a fixed relation between the gold concentration x and the conductivity.

We became interested in the physics of the metal-insulator transition in $Ge_{1-x}Au_x$ upon obtaining data on the temperature dependence of the conductivity such as shown in Fig. 1. For $x = 0.18$, for example, the conductivity closely follows a power law of 0.84 over the measured temperature range of 300 to 1.4 K. Although these data are
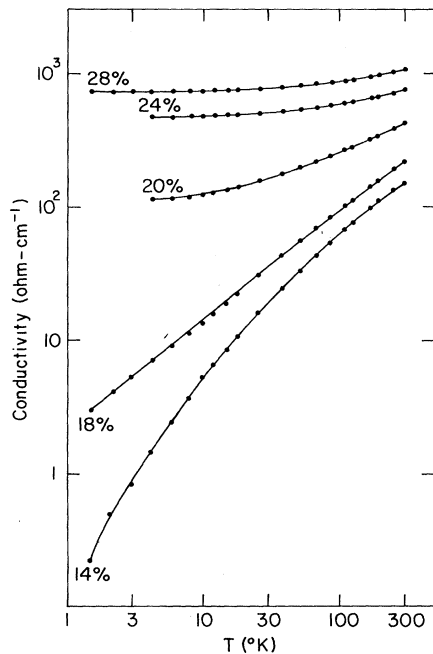
FIG. 1. Conductivity vs temperature for polycrystalline $Ge_{1-x}Au_x$ samples. With proper heat treatment at approximately 130 C the conductivity can be made to follow a $T^{+0.84}$ dependence over three decades in temperature.

FIG. 2. Conductivity vs temperature for amorphous $Ge_{1-x}Au_x$; decreasing conductivity generally corresponds to decreasing x. For curve A, $x = 0.24$ at.%; curve B, 0.20; curve C, 0.18; curve D, 0.12; curve E, 0.14; curve F, 0.14; curve G, 0.10; curve H, 0.10; curve I, 0.09; curves J_1-J_4, 0.08; and curve K, 0.06. The curves J_1-J_4 are produced by slight heating below 80 C to produce gold clustering.

from polycrystalline samples, it is qualitatively similar to the results of the amorphous system shown in Fig. 2. Two differences are the critical value of x, which is larger for the crystalline phase, and the temperature dependence at the transition, which is also larger for the crystalline phase. The major feature both phases share is that the conductivity, in the low-temperature limit, goes to a constant value on the conducting side of the transition. The magnitudes of these conductivities $\sigma(0)$ become substantially less than the minimum metallic conductivity developed by Mott.[7] Using a length scale, a, calculated from the density of unbound electrons, Mott finds

$$\sigma_{min} = 0.026 e^2 / \hbar a.$$

In our case we use the density of gold atoms, for the amorphous phase, to find an a of about 6 Å and a value of σ_{min} of 100 Ω^{-1} cm^{-1}. As can be seen in Fig. 1, Fig. 2, and the table in Fig. 3 there is no sudden change in the behavior of the data at this value. As x is varied or, with heating, the gold cluster size is varied, the zero-temperature conductivity $\sigma(0)$ goes continuously to zero. The conductivity σ_{min} had been thought to be a universal feature of metal-insulator tran-
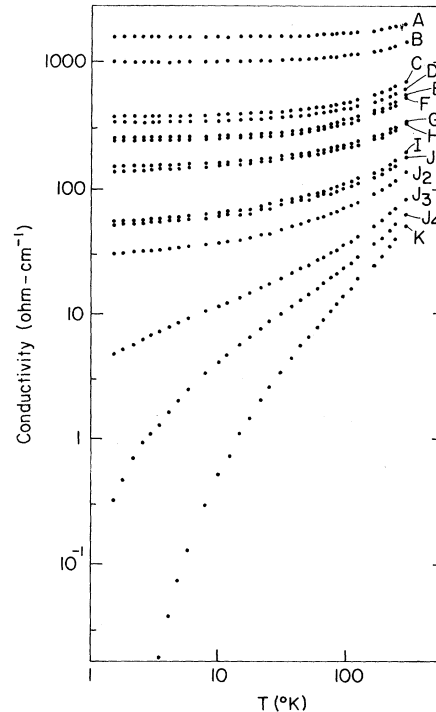
sitions with the zero-temperature conductivities falling abruptly to zero below σ_{min}. We do find that samples on the insulating side of the transition show the exponential behavior typical of random systems with localized electrons.[8]

In the interest of simplifying sample characterization, we decided to concentrate attention upon the amorphous samples whose conductivities are shown in Fig. 2 and Fig. 3. To further understand these results we subtract a $T = 0$ conductivity, $\sigma(0)$, obtained by extrapolation from each curve in the conducting regime. The result is plotted in Fig. 3 along with three curves from the insulating phase, unchanged from Fig. 2. Two features are apparent. First, with $\sigma(0)$ subtracted, all the curves in the conducting phase fall near one another with small concentration fluctuations ($\leq 1\%$) probably accounting for the variation. This means that the temperature-dependent portion of the conductivity is nearly the same for all samples in the conducting phase. Second, below 10 K, all these curves follow a power law close to $\frac{1}{3}$. A
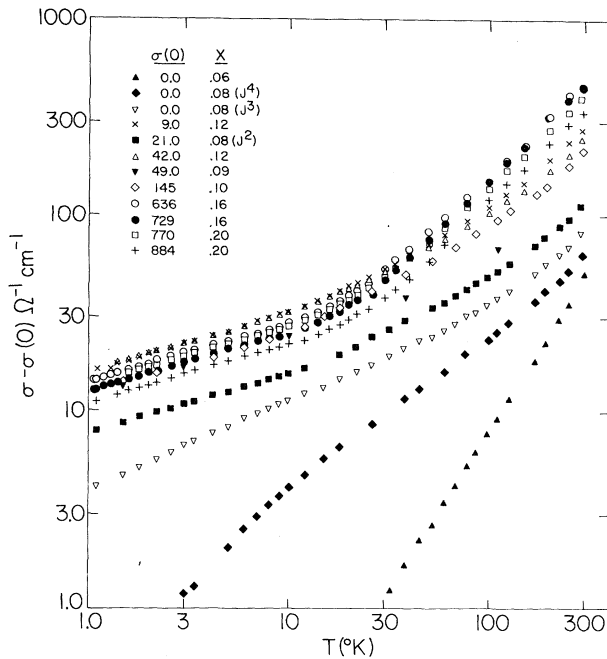
FIG. 3. The extrapolated zero-temperature conductivity $\sigma(0)$ is subtracted from the data $\sigma(T)$ and replotted vs temperature. All the curves in the conducting phase [finite $\sigma(0)$] fall near one another. There is no evidence of a minimum metallic conductivity. Below 10 K, the power-law dependence has exponent 0.30 ± 0.04.

fit by a power law produces an exponent of 0.30 with a standard deviation among samples of 0.04. The magnitude of the temperature-dependent conductivity at 1.0 K is 14 ± 2 Ω^{-1} cm^{-1}. Above 30 K, an additional temperature-dependent conductivity appears which is close to a linear function of temperature. Again, there is no change in the temperature dependence of the conductivity when σ or $\sigma(0)$ falls below Mott's conductivity of 100 Ω^{-1} cm^{-1}.

The qualitative behavior of the zero-temperature conductivity versus composition is consistent with a continuous metal-insulator transition. The modern theory of localization[5,9] predicts a zero-temperature conductivity proportional to $e^2/\hbar\xi$, with the correlation length ξ going to infinity at the transition. Altshuler and Aronov[10] find an extra conductivity contribution at finite temperatures proportional to $(kT)^{1/2}$, which is a clue to electron-electron interactions (this term is also present in the renormalization-group treatment of McMillan[9]). We tentatively interpret the temperature dependence of the conductivity as an interaction effect. Recent tunneling experi-

ments[11] on the same material have found a strong square-root anomaly in the electronic density of states, centered at the Fermi energy, due to electron-electron interactions.

At temperatures above 30 K, the temperature dependence of the conductivity becomes linear. This is most likely due to electron-phonon interactions further reducing ξ. At high temperatures and large gold concentrations where ξ is small (large conductivity), inhomogeneity due to gold clustering can become important. In fact, for gold concentrations of 0.2 or greater there is a tendency for the low-temperature behavior of the conductivity to become weaker. For gold concentrations greater than 0.24 a metastable crystalline phase forms, as seen with x-ray scattering, and we can not compare such conductivity measurements. Ideally, localization should be studied in a disordered system with no clustering where the electron density can be varied over a wide range. We are presently preparing to study these same systems quench condensed on a 4-K substrate.

In summary, we have found a system which, in both the polycrystalline and amorphous phase, shows no Mott minimum metallic conductivity. Similar behavior is being seen in the $Ge_{1-x}Cu_x$ and $Ge_{1-x}Ag_x$ system and no doubt will also appear in other metal-semiconductor systems where it is easy to pass from localized to delocalized electronic states. These results also indicate the importance of incorporating electron-electron interactions into a model of localization.

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[1]N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1979).
[2]P. W. Anderson, Phys. Rev. 109, 1492 (1958).
[3]N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1974).
[4]D. J. Thouless, Phys. Rev. Lett. 39, 1167 (1977).
[5]E. Abrahams, P. W. Anderson, D. C. Licciardello, and T. V. Ramakrishnan, Phys. Rev. Lett. 42, 673 (1979).
[6]T. F. Rosenbaum, K. Andres, G. A. Thomas, and

R. N. Bhatt, Phys. Rev. Lett. <u>45</u>, 1723 (1980).

[7]N. F. Mott, Philos. Mag. <u>26</u>, 1015 (1972).

[8]N. F. Mott, J. Non-Cryst. Solids <u>1</u>, 1 (1968).

[9]W. L. McMillan, to be published.

[10]B. L. Altshuler and A. G. Aronov, Solid State Commun. <u>36</u>, 115 (1979), and Zh. Eksp. Teor. Fiz. <u>77</u>, 2028 (1979) [Sov. Phys. JETP <u>50</u>, 968 (1979)], and Pis'ma Zh. Eksp. Teor. Fiz. <u>30</u>, 514 (1979) [JETP Lett. <u>30</u>, 482 (1979)].

[11]W. L. McMillan and J. M. Mochel, to be published.

Possible Coexisting Superconducting and Magnetic States

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The free energy is calculated for the various phases possible in a superconductor containing a periodic array of magnetic ions with ferromagnetic interactions. Suggestions are made for experimental observation of coexisting superconductivity and long-range magnetic order.

Recent discoveries[1] of superconducting compounds that contain a lattice of magnetic rare-earth ions have raised anew the questions of interaction of superconductivity and magnetism.[2]

There are two principal interactions of the magnetization M with the superconducting order parameter ψ. One is the direct interaction of M with ψ due to spin-flip scattering of conduction electrons and the magnetic moments, giving rise to leading terms in the free-energy of the form

$$F_{\vec{M},\psi} = \eta_1 |\vec{M}|^2 |\psi|^2 + \eta_2 |\nabla\vec{M}|^2 |\psi|^2. \tag{1}$$

η_1 can be shown[3] to be $\approx J^2/T_c E_f \approx T_{\text{mag}}/T_c$, and $\eta_2 \approx \xi^2 \eta_1$, where T_{mag} is the magnetic transition temperature, T_c is the superconducting transition temperature, J is the exchange energy of conduction electrons with the magnetic moments, and ξ is the superconducting coherence length. The other effect arises through the coupling of ψ to the electromagnetic field $\vec{B}$ and the coupling of $\vec{B}$ to $\vec{M}$. A dimensionless measure of the latter coupling is simply 4π. If $T_{\text{mag}}/T_c \ll 4\pi$, the first effect is much less important than the second. The second effect does not occur for antiferromagnets. Experimentally, nothing very remarkable seems to happen in antiferromagnetic superconductors below the Néel temperature.

Ignoring the effects of spin-flip scattering, the free energy of an isotropic magnetic superconductor is[4]

$$F(\psi, \vec{M}, \vec{A}) = \int d^3 r \left[\tfrac{1}{2} a |\psi|^2 + \tfrac{1}{4} b |\psi|^4 + p_0 |(\nabla - i r_0 \vec{A})\psi|^2 + \vec{B}^2/8\pi + \tfrac{1}{2}\alpha |\vec{M}|^2 + \tfrac{1}{4}\beta |\vec{M}|^4 + \tfrac{1}{2}\gamma^2 |\nabla\vec{M}|^2 - \vec{B}\cdot\vec{M} \right], \tag{2}$$

where $a = a_0(T - T_c)/T_c$, $\alpha = \alpha_0(T - T_m')/T_m'$, $p_0 = \hbar^2/2m$, and $r_0 = 2e/\hbar c$. The free-energy density of the superconducting phase, $|\psi| \neq 0$ and $B = M = 0$, is

$$F_s = -a^2/4b, \quad \text{for } T < T_c, \tag{3}$$

while the free-energy density of the ferromagnetic phase with $|\psi| = 0$ is

$$F_{\text{FM}} = -(4\pi - \alpha)^2/4\beta,$$
$$\text{for } T < T_m^0 = T_m'(1 + 4\pi/\alpha_0). \tag{4}$$

We are interested in the situation where $T_m^0 \ll T_c$. Also, for situations of experimental interest,

$$\zeta = [F_{\text{FM}}/F_s]_{T=0} \tag{5}$$

is about 5×10^2, as may be deduced from specific heat measurements[5] and/or the thermodynamic critical field[6] and considerations of spin entropy. Kuper, Revzen, and Ron[7] chose to estimate ζ from *ab initio* considerations and, in disagreement with the experimentally deduced value, found it to be about 10. This seriously affects the consideration of the relative stability of the various phases.