

Garno, Phys. Rev. Lett. **46**, 137 (1981), that the specimens in the intermediate regime are metallic, so that the metal-insulator transition is at a value of ρ_{RT} just slightly higher than that of the most resistive specimen of Fig. 2.

⁸T. Worthington, P. Lindenfeld, and G. Deutscher, Phys. Rev. Lett. **41**, 316 (1978); R. L. Filler, P. Lindenfeld, T. Worthington, and G. Deutscher, Phys. Rev. B **21**, 5031 (1980).

⁹T. Chui, G. Deutscher, P. Lindenfeld, and W. L. McLean, Phys. Rev. B **23**, 6172 (1981).

¹⁰T. Chui, P. Lindenfeld, W. L. McLean, and K. Mui, Phys. Rev. B (to be published).

¹¹G. Deutscher, O. Entin-Wohlman, and Y. Shapira, Phys. Rev. B **22**, 4264 (1980).

¹²T. Rosenbaum, K. Andres, G. A. Thomas, and P. A. Lee, Phys. Rev. Lett. **46**, 568 (1981).

¹³There is also a small temperature dependence of A . The value of A is higher by about 30% at 1.4 K for the lowest values of ρ_{RT} in Fig. 2, and lower by about the same factor at the highest values of ρ_{RT} .

¹⁴F. R. Fickett, Cryogenics **11**, 349 (1971).

¹⁵B. L. Altshuler and A. G. Aronov, Zh. Eksp. Teor. Fiz. **77**, 2028 (1979) [Sov. Phys. JETP **50**, 968 (1979)].

¹⁶Y. Imry, Proceedings of the International Conference on Magnetism, 1980 (unpublished).

Minimum Metallic Conductivity and Thermopower in Thin Palladium Films

M. J. Burns, W. C. McGinnis, R. W. Simon, G. Deutscher, and P. M. Chaikin

Department of Physics, University of California, Los Angeles, California 90024

(Received 16 April 1981)

The effects of two-dimensional electron localization have been studied by measuring thermopower and resistivity of thin (18–25 Å) films of palladium. “Metallic” samples have a small thermopower which tends to zero as $T \rightarrow 0$. Insulating samples have large thermopower which increases as $T \rightarrow 0$. The metal-insulator transition in Pd films thus involves the opening of a gap at the Fermi energy. With use of the thermopower to define the metal-insulator transition a critical resistivity of $\sim 30 \text{ k}\Omega/\square$ is found.

PACS numbers: 73.60.-n, 71.30.+h, 72.15.Jf, 72.20.Pa

There has been renewed interest in the problem of electron localization in two dimensions due to a number of recent theoretical advances¹⁻⁴ and considerable experimental work.⁵⁻⁸ Rather than a minimum metallic conductivity of $R_{2D}^{-1} \approx (30 \text{ 000 } \Omega/\square)^{-1}$, single-parameter scaling theories predict that all states are localized in two dimensions.¹ A logarithmic temperature increase in the resistivity for low- R_{\square} samples crosses over smoothly to an exponential increase (with decreasing temperature) for $R_{\square} > R_{2D}$.² Another picture suggests that the logarithmic behavior for $R_{\square} < R_{2D}$ may be understood in terms of electron-electron interactions.³ Experiments on thin metal films have been interpreted as evidence for either localization or interaction effects^{6,8} while recent experiments on electron inversion layers tend to support the interaction picture.⁷

In this Letter we present thermopower measurements which clearly indicate the opening of an energy gap as $R_{\square}(T)$ increases above R_{2D} . In terms of the thermopower there is a sharp distinction between the metallic and insulating states. We find that this metal-insulator transition occurs quite rapidly in the resistance region of

R_{2D} . Since the temperature dependence of the resistance of these films is virtually indistinguishable from that in previous studies of thin films we believe our results are quite general. While resistance (and magnetoresistance) measurements probe the density and mobility of the carriers, the thermoelectric power (S) probes their energy distribution. If the energy distribution falls to zero width about the Fermi energy as $T \rightarrow 0$ we will have $S \rightarrow 0$. Such is the usual case for metals as well as for variable-range hopping in three and two dimensions.⁹ If S increases as $T \rightarrow 0$ there is evidence for the existence of an energy gap.

We find a striking qualitative change in the thermopower as the thickness of our films is lowered so that the resistivity crosses R_{2D} . For films with $R_{\square} < R_{2D}$ the thermopower is approximately independent of R_{\square} and decreases with decreasing temperature. For films with $R_{\square} > R_{2D}$ the low-temperature thermopower increases with decreasing temperature, with higher-resistivity films showing a larger thermopower. The thermopower measurements therefore indicate that the density of states at the Fermi level vanishes

and an energy gap opens up as R_{\square} passes through R_{2D} for our samples.

The samples were prepared by electron-beam deposition of Marz-grade palladium at 0.1–1 Å/sec onto a glass substrate at room temperature. Pressure in the evaporator was 10^{-6} – 10^{-7} Torr during evaporation and thickness was measured with a quartz-crystal deposition controller. Electron micrographs taken of similar films deposited on a quartz film (in turn evaporated on a carbon film grid) show continuous palladium films of fairly uniform thickness with a great deal of non-percolating cracks (typically 20×100 Å²) for nominal 18–25-Å thicknesses. The samples were therefore highly inhomogeneous on a scale of ~ 100 Å but appeared quite homogeneous on a 1- μ m scale. Electron diffraction shows crystalline grains of ~ 25 Å thickness.

The experiments were performed in a sealed, temperature-controlled copper sample holder placed in an exchange-gas can and submerged in liquid helium. Contacts to the palladium films were made with ~ 3000 Å of evaporated silver pads. The sample was mounted so that one of the silver pads rested over a copper block heat sink to which the glass slide was attached. The remainder of the slide was cantilevered into the vacuum. A single-crystal quartz block with a heater attached was then glued on top of the other silver pad to provide the temperature gradient to the heat sink. Lead (Pb) wires were then indium soldered or silver painted to the silver pads and

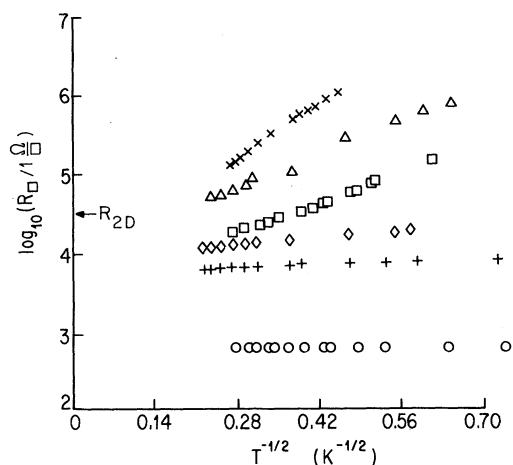


FIG. 1. Logarithm of the resistivity (in Ω/\square) as a function of reciprocal square-root temperature for the palladium films used in the thermopower study. We have used the same symbol for each film in all of the figures.

a 25- μ m Chromel-Constantan differential thermocouple was placed in close proximity to monitor the temperature gradient. The accuracy of our thermopower measurement is $\sim 20\%$, ± 0.5 μ V/K.

In Fig. 1 we have plotted the logarithm of the resistivity as a function of the square root of the reciprocal temperature for six samples of nominal thicknesses 18–25 Å. The resistive behavior of these films is virtually indistinguishable from the behavior reported for quench-condensed films of copper and gold (compare with Fig. 2 of Ref. 5). For resistivities greater than R_{2D} the temperature dependence is reasonably well fitted by an exponential with a fractional inverse power of temperature. For resistivities less than R_{2D} the exponential dependence is gone and the resistivities appear almost flat on the plot in Fig. 1.

However, as is now well known, even films with resistivities considerably below R_{2D} show an increase with decreasing temperature that varies logarithmically. In Fig. 2 we have plotted the change in resistivity divided by the square of the resistivity as a function of $\log T$. The inset in Fig. 2 shows data taken on a similarly prepared film of Pd of 2.5 k Ω/\square measured in a dilution refrigerator. There is a logarithmic behavior from 0.1 to 4 K. For ~ 20 samples with $R < 5$ k Ω and $T < 4$ K we find $\Delta R/R_{\square}^2 = [(2.0 \pm 0.2) \times 10^{-5} \Omega^{-1}] \log T$ as compared to $(2-4) \times 10^{-5} \Omega^{-1}$ found for PdAu.⁶ We note that the value of this coefficient is close to what one expects from the interaction model³ ($2.8 \times 10^{-5} \Omega^{-1}$) and about a factor of 2 smaller than what one expects from the localization picture.^{2,6,8}

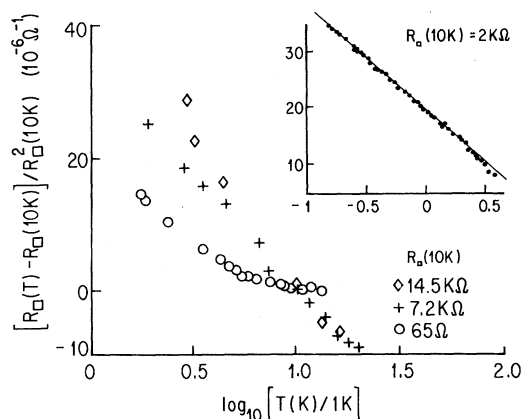


FIG. 2. Resistivity change divided by square of resistivity as a function of $\log T$ for three Pd film samples which show "metallic" thermopower. The inset is a similarly prepared sample measured to lower temperatures.

For low-resistance films the resistance increases with temperature above ~ 4 K as for conventional metals.⁸ For $R_{\square} > 5$ k Ω the low-temperature increase becomes more rapid as stronger localization and interaction effects become important as R_{2D} is approached.

The resistivity studies are primarily presented to show that the Pd films have the same behavior, at high and low R_{\square} , as thin metal films reported by other groups where only resistivity measurements were performed. We have also compared Pd and PdAu films prepared under similar conditions. They are indistinguishable in their resistance, magnetoresistance, and thermopower.

The absolute thermoelectric power (corrected for the leads) of the series of six films is shown in Fig. 3. The thermopower of even the low-resistivity samples differs significantly from the published values for bulk palladium,^{10,11} but this is to be expected. In pure metals the thermopower at ~ 10 K is dominated by phonon drag and energy-dependent scattering processes. These contributions are largely reduced by the short mean free path in thin films.

From 77 to ~ 20 K the thermopowers of all six films used in this study are the same within the accuracy of our measurement ($\sim 20\%$). Below 20 K there is a qualitative difference between the exponential and logarithmic films. The three films with $R_{\square} < R_{2D}$ follow one curve which is monotonically decreasing as temperature is lowered. The film which has a resistance of ~ 26 k Ω/\square at 10 K

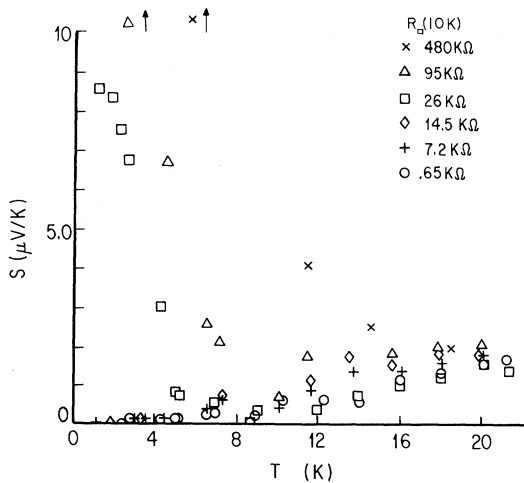


FIG. 3. Absolute thermopower as a function of temperature for Pd films. Samples with $R_{\square} < 30$ k Ω/\square show "metallic" behavior. Samples with $R_{\square} \geq 30$ k Ω/\square show the presence of an energy gap.

follows the same curve down to ~ 8 K and then shows a thermopower which increases dramatically as temperature is lowered, reaching a value at 1.2 K which is orders of magnitude larger than for the logarithmic films. Higher-resistivity films show larger low-temperature thermopowers and deviate from metallic behavior at higher temperatures.

Note in Fig. 1 that the sample with $R_{\square}(10$ K) = 14.5 k Ω has $R_{\square}(1.3$ K) ~ 20 k Ω/\square while the $R_{\square}(10$ K) = 26 k Ω/\square sample has $R_{\square}(5$ K) ~ 40 k Ω/\square . The former sample shows metallic thermopower at all temperatures studied. The latter sample shows metallic thermopower until its resistance increases above 40 k Ω/\square at ~ 5 K. We therefore suggest that the metal-insulator transition defined by the thermopower occurs close to $R_{2D} \approx 30$ k Ω/\square .

There are two prevalent pictures of the metal-insulator transition in two dimensions. In the scaling picture all states are localized. One goes gradually from a metal with weakly localized states that perturbatively give a logarithmic resistivity increase to an insulator with strongly localized states and variable-range hopping providing an exponential temperature dependence to the resistivity.² Although the thermopower has not been treated theoretically in this model, the limits are well known. In the weakly localized regime the transport will proceed via the accessible states within kT of the Fermi energy as is typical for a metal.¹⁰ The thermopower will decrease as temperature decreases and at low enough temperature we should have $S \sim (k/e)N(\epsilon_F) \times kT$.

The case of variable-range hopping is more interesting and less obvious. For conduction between localized states, the width of energies used by the carriers is determined by maximizing the contribution to the conductivity. The problem has been treated by Mott for the three-dimensional case.⁹ He finds $S \sim T^{1/2}$. A simple extension of his arguments leads to $S \sim T^{1/3}$ for the two-dimensional case. The result is that the thermopower decreases with decreasing temperature although the conductivity is "activated" or exponential with a fractional power of inverse temperature.

We therefore conclude that if the localization picture is to describe the behavior of our films we should have $S \rightarrow 0$ as $T \rightarrow 0$, independent of the resistivity and its temperature dependence. This is the natural consequence of a theory which treats the metal-insulator transition entirely as a mobility effect.

In the interaction picture the combined effects of the elastic scattering and the electron-electron interaction is to change the density of states in the vicinity of the Fermi energy as well as cause the logarithmic correction to the resistivity.³ While this change in the density of states should show up in the thermopower (in a manner similar to the way it should appear in the specific heat), the thermopower will still decrease as $T \rightarrow 0$ as long as there is a finite density of states at E_F . At present we lack the sensitivity to test this hypothesis. If Coulomb correlations are important then one might expect the metal-insulator transition to occur via the reduction of the density of states at the Fermi energy until a gap opens,¹² presumably at resistivities $\sim R_{2D}$. With the presence of a gap the thermopower takes on a characteristic semiconducting behavior with the S increasing with decreasing T [$S \sim (k/e)E_{\text{gap}}/2kT$ for $E_{\text{gap}} \gg kT$].

The increase in the thermopower in our high-resistivity samples leads us to conclude that a gap is appearing which favors the interaction model. Previous tunneling measurements have also shown an interaction gap.¹³ We are never at sufficiently low temperature in our thermopower measurements to evaluate E_{gap} from the limiting behavior of S . However, from the temperature at which the thermopower of the high- R_{\square} samples deviates from the low- R_{\square} samples we would estimate $E_{\text{gap}} \sim 2-5$ K for the $R_{\square}(10 \text{ K}) = 26 \text{ k}\Omega/\square$ film and $E_{\text{gap}} \sim 10-20$ K for the $R_{\square}(10 \text{ K}) = 480 \text{ k}\Omega/\square$.

Another possibility which must be discussed in light of the cracking observed in our films is that the metal-insulator transition may be related to the percolation between metal grains. If this is the case then the resistivity just on the insulator side is dominated by a few breaks in an otherwise metallic chain from one side of the sample to another. While these breaks may dominate the resistivity they will only affect the thermopower in proportion to the length of the breaks relative to the length of the chain. Thermopower is a zero-current measurement and one must merely add the voltages of different segments in proportion to their temperature drop in the temperature gradient. Thus for a classical percolation problem we expect a smoothly varying thermopower through the metal-insulator transition.

The thermopower is often thought of as the "entropy per carrier" for a system. This has led to some confusion as to the applicability of the third law of thermodynamics. The actual

thermodynamic condition is that the product of the thermopower and the conductivity must go to zero as temperature goes to zero ($\sigma S \rightarrow 0$ as $T \rightarrow 0$).¹⁰ From this requirement it appears that the thermopower merely reflects the behavior of the conductivity. A metal with finite conductivity at $T=0$ must have $S \rightarrow 0$ as $T \rightarrow 0$. However, for the insulating case where $\sigma \rightarrow 0$ as $T \rightarrow 0$, we may have S finite or diverging less rapidly than $1/\sigma$ (as for semiconductors) or $S \rightarrow 0$ (as for variable-range hopping).

In conclusion we have found that the thermopower reflects the change in behavior between films with resistivity greater or less than $30 \text{ k}\Omega/\square$ much more dramatically than does the temperature dependence of the resistivity. For low-resistivity films the thermopower shows metallic behavior with $S \rightarrow 0$ as $T \rightarrow 0$. High-resistivity films have semiconductinglike thermopower with S increasing as T decreases indicating the opening of an energy gap. The sharpness of the transition between these two behaviors as a function of film resistivity suggests that the gap may be opening at a well-defined value of R_{\square} and that electron-electron correlations are important.

This research was supported by the National Science Foundation under Contracts No. DMR 78-12000 and No. DMR 79-08560. One of us (P. M. C.) is an A. P. Sloan Foundation Fellow.

¹D. C. Licciardello and D. J. Thouless, *Phys. Rev. Lett.* **35**, 1475 (1975).

²E. Abrahams, P. W. Anderson, D. C. Licciardello, and T. V. Ramakrishnan, *Phys. Rev. Lett.* **42**, 673 (1979).

³Patrick A. Lee, *Phys. Rev. Lett.* **42**, 1492 (1979).

⁴B. L. Altshuler, D. Khmel'nitzkii, A. I. Larkin, and P. A. Lee, *Phys. Rev. B* **22**, 5142 (1980); B. L. Altshuler, A. G. Aronov, and P. A. Lee, *Phys. Rev. Lett.* **44**, 1288 (1980).

⁵R. C. Dynes, J. P. Garno, and J. M. Rowell, *Phys. Rev. Lett.* **40**, 479 (1978).

⁶G. J. Dolan and D. D. Osheroff, *Phys. Rev. Lett.* **43**, 721 (1979).

⁷D. J. Bishop, D. C. Tsui, and R. C. Dynes, *Phys. Rev. Lett.* **46**, 360 (1981), and **44**, 1153 (1980).

⁸L. Van den Dries, C. Van Haesendonck, Y. Bruynseraede, and G. Deutscher, *Phys. Rev. Lett.* **46**, 565 (1981).

⁹N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1979), p. 55.

¹⁰J. Tauc, *Photo and Thermoelectric Effects in Semiconductors* (Pergamon, New York, 1962); F. J. Blatt, P. A. Schroeder, C. L. Foiles, and D. Greig, *Thermo-*

electric Power of Metals (Plenum, New York, 1976).

¹¹G. Wedler and R. Chander, *Thin Solid Films* **65**, 53 (1980).

¹²A. L. Efros and B. I. Shkloriskii, *J. Phys. C* **8**, L49 (1975); A. L. Efros, *J. Phys. C* **9**, 2021 (1976); A. L. Efros, N. VanLien, and B. I. Shkloriskii, *Solid State*

Commun. **32**, 851 (1979); B. Abeles, in *Applied Solid State Science*, edited by R. Wolfe (Academic, New York, 1976), Vol. 6, p. 1.

¹³R. C. Dynes and J. P. Garno, *Phys. Rev. Lett.* **46**, 1371 (1981); W. L. McMillan and J. M. Mochel, *Phys. Rev. Lett.* **46**, 556 (1981).

Monte Carlo Simulation of a Spin-Glass Transition

R. W. Walstedt and L. R. Walker

Bell Laboratories, Murray Hill, New Jersey 07974

(Received 2 October 1981)

Monte Carlo simulations show that for a system of Ruderman-Kittel-Kasuya-Yosida-coupled classical spins there exists an energy below which the system remains trapped near a single energy minimum. Provided that a small amount of anisotropy is introduced the system then exhibits, in the neighborhood of this energy, (a) a spin-glass-like peak in the susceptibility χ , (b) a well-marked maximum at $d^2\chi/dH^2$, and (c) evidence for spin freezing at lower energies. Without anisotropy these effects are absent.

PACS numbers: 75.10.Jm, 75.30.Kz

A satisfactory understanding of the spin-glass state in disordered magnetic systems with competing interactions remains elusive.¹ In this note we confine our attention to systems of isotropic, Ruderman-Kittel-Kasuya-Yosida (RKKY) coupled classical spins. For this case there exist a number of distinct spin configurations which minimize the energy locally.² These minima, almost degenerate in energy, are separated by energy barriers. At sufficiently low temperatures the thermodynamics of the system must be "broken" and controlled by the nature of the energy surface around a particular minimum. Such regions have very small curvature in certain directions, indicating that the ground-state configuration may be substantially distorted for a small cost in energy. If the barrier heights are widely distributed the various energy wells will merge progressively as the energy increases and the system will steadily migrate over wider regions of phase space. Alternatively, if the height distribution is narrow, there should be an abrupt effect upon the thermodynamics at a temperature where the average energy equals the barrier height. It is possible that this temperature marks the spin-glass "transition."

To examine these questions we have made Monte Carlo studies of a classical spin system with RKKY coupling for which ground-state configurations are known. The Hamiltonian is $\mathcal{H} = \sum J_{ij} \vec{S}_i \cdot \vec{S}_j$, where $J_{ij} = V_0 \cos 2k_F r_{ij} / r_{ij}^3$. We find that there is a well-defined energy below

which migration between energy wells ceases on the time scale of the simulation. The susceptibility in the neighborhood of this energy (temperature) passes through a maximum *provided that a small amount of anisotropic interaction is introduced*, but not otherwise. Spin freezing, as indicated by a time-independent value of the Edwards-Anderson parameter q ,³ is found under similar conditions. The temperature associated with this critical energy is lower than the transition temperature estimated from experiment by a factor of 3. This can be explained by the severe low-temperature distortion of the true energy-temperature relation by the use of Boltzmann statistics.

To examine the barriers separating energy minima we study the microcanonical low-field shattered susceptibilities χ_{sh}^α given by

$$\chi_{sh}^\alpha / \beta = \langle (\sum_i \vec{n}_i \cdot \vec{n}_{i0}^\alpha)^2 \rangle_\mu, \quad (1)$$

where the unit vector spins \vec{n}_i are a classical representation for a system of N spins \vec{S}_i randomly sited on an fcc lattice.⁴ The vectors \vec{n}_{i0}^α , $i = 1, \dots, N$, represent the α th ground state of the system and $\langle \dots \rangle_\mu$ denotes a microcanonical average. In Fig. 1 we show a plot of χ_{sh}^α values for all seven ground states of a system of $N = 172$ spins² versus the internal energy ΔE of the system. The χ_{sh}^α values are seen to rise rapidly and quite uniformly as the energy is lowered. Below some point, however, the distribution of χ_{sh}^α values for different α 's broadens rapidly. In this