Thermoelectric Power of a Disordered Metal near the Metal-Insulator Transition

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The thermoelectric power S of uncompensated Si:P with P concentration N near the metal-insulator transition occurring at N_c has been measured at very low temperatures ($0.04 \leq T \leq 3$ K). For $N \gg N_c$, S is negative and shows the linear T dependence of a metal, whereas close to N_c an anomalous behavior with a sign change of S at low T is observed. The strong dependence of S on magnetic fields up to 6 T relates the anomaly to magnetic scattering, thus giving the first experimental evidence for localized moments near the metal-insulator transition in a transport property.

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The metal-insulator (MI) transition in disordered systems is one of the central themes in condensed matter physics. Besides disorder, electron-electron interactions are thought to play a major role in this transition. Recent theoretical work emphasizes the role of local moments near the MI transition, possibly even leading to a non-Fermi-liquid behavior with the magnetic susceptibility χ and the linear specific-heat coefficient γ diverging for $T \rightarrow 0$ [1–3]. Doped semiconductors like Si:P where the disorder stems from the random distribution of donors constitute a convenient system for studying the MI transition, which occurs as a function of the donor concentration N at a critical concentration N_c. In this material, the existence of local moments in the metallic state has been observed in magnetic resonance [4] and static χ measurements [5]. Their density as a function of N has been mapped out in detail with specific-heat measurements [6]. The possible influence of local moments on the electrical conductivity σ [2,7] is difficult to estimate because of the large T and B dependence of σ due to localization effects and electron-electron interactions [8]. In this situation, more specific information on transport in disordered materials close to the MI transition is highly desirable.

A particularly sensitive transport property is the thermoelectric power S. In view of the giant thermopower observed in Kondo systems, S should be susceptible to local moments near the MI transition. However, generally an accurate analysis of S is difficult, because (in a Fermi-liquid description) the explicit dependence of the scattering time τ and density of states at the Fermi level $D(E_F)$ on energy has to be taken into account. Furthermore, at moderate and high temperatures ($T \lesssim \Theta_D$, the Debye temperature) S is often dominated by the phonon-drag contribution due to the electron-phonon interaction. Therefore one has to work below 1 K to circumvent this difficultly. Approaching the transition from the metallic side a divergent coefficient S/T is predicted for $T \rightarrow 0$ [9,10], $S/T \sim (N - N_c)^{-\mu}$, where the exponent μ should depend on the significance of the electron-electron interactions or whether symmetry-breaking fields such as an external magnetic field, magnetic impurities, or spin-orbit coupling are present. On the insulating side where σ is due to variable-range hopping [11], S will also be influenced by correlations. In the noninteracting case, S should be proportional to $T^{1/2}$, whereas interactions which lead to a Coulomb gap in the density of states yield a constant thermopower [12,13]. As Si:P represents a well-defined and rather simple system that is available in the form of crystals with high quality and purity, there is reasonable hope that S of this material at very low T might provide valuable information about the nature of the MI transition.

In this Letter, we present measurements of the thermopower of Si:P at very low T in the vicinity of the MI transition. The data cover a large range of temperatures low enough to suppress phonon-drag effects (down to 40 mK) and of magnetic fields (up to 6 T). The donor concentrations N range from 2.7×10^{18} cm^{-3} in the insulating regime up to 73.7×10^{18} cm^{-3} far above the transition. While far above N_c S can be described quantitatively within the nearly-free-electron model, the anomalies observed around N_c show the importance of magnetic moments on transport properties.

The samples were P-doped single crystals grown with the Czochralski method, yielding rods of 54 mm in diameter. Taking advantage of a P concentration gradient along the axis of the rods, several samples with different N could be conveniently cut from a single rod using a diamond saw. N was determined from the room temperature resistivity using the calibration of Thurber [14]. A more accurate (relative) determination of N near N_c was obtained from the ratio of the resistance at 4.2 and 296 K [15] where the uncertainties of the sample geometry could be eliminated. We thus determined $N_c = 3.52 \times 10^{18}$ cm^{-3}. From the variation of the resistance ratio across the samples we estimate the macroscopic inhomogeneities in N to be less than 0.1%. The samples with typical dimensions of $18 \times 1 \times 0.8$ mm^3 were etched to remove surface contaminations. Spot welding of gold wires to the samples yielded Ohmic contacts with a resistance of less than 0.1 Ω.

The thermopower S was measured in a standard dilution refrigerator with a conventional dc technique. One end of the sample was firmly attached to a copper heat sink, connected to the mixing chamber of the dilution re-

frigerator. To establish a T gradient of 3%–10% across the sample a small Pt-W heater was glued to the other end. Small copper clamps, connected to the voltmeter through superconducting leads, were screwed directly onto the contacts of the sample. These clamps, 8 mm apart, carried also the carbon thermometers. As the value of S of metals vanishes for $T \rightarrow 0$ the measurement at very low T requires a very sensitive voltmeter. Hence a superconducting quantum interference device picovoltmeter system was used to measure the thermoelectric voltages, with a resolution of 5 pV for sample resistances of 1 Ω.

Figure 1 shows S for a heavily doped sample ($N = 73.7 \times 10^{18}$ cm^{-3}) deep in the metallic regime. S is negative and below 1 K varies linearly with T. Such a behavior is expected for the diffusion thermopower S_d of a metal. Not only the T dependence, but also the magnitude of S can be quantitatively understood within the framework of a "nearly-free-electron" (NFE) gas with $T \ll T_F$ where $S_d = -(\pi^2 k_B^2/3e) T [\partial \ln \sigma(E)/\partial E]_{E_F}$. The solid line in Fig. 1 represents $S_d^{(f)} = -(\pi^2 k_B^2/3e) T/T_F$, i.e., the thermopower of nearly free electrons in the case of a constant mean free path. This is just what one would expect for an impure system far away from the MI transition, since impurity scattering, i.e., scattering by the donor ions, should dominate at low T. For this sample $E_F = \hbar^2 k_F^2/2m^*$ corresponds to $T_F = 682$ K, obtained with the conduction-band effective mass $m^* = 0.33 m_0$ and $k_F = (3\pi^2 N/\nu)^{1/3}$ where $\nu = 6$ is the valley degeneracy of Si. Above 1 K, S shows a stronger T dependence arising from the phonon-drag contribution S_{ph}. For $T \ll \Theta_D$, $S_{ph} = -C_L/3Ne$, where C_L is the lattice specific heat (per unit volume). The dashed line in Fig. 1 represents a fit to the data with $\Theta_D = 660$ K in excellent agreement with specific-heat measurements [6].

Figure 2(a) shows on a linear plot how S changes when N is reduced by a factor of 10 to $N \approx 7 \times 10^{18}$ cm^{-3}. For comparison the data and fit of the previously discussed sample are also shown. Roughly, S still exhibits a linear behavior at low T. $|S/T|$ increases with decreasing N, i.e., decreasing T_F, as expected for NFE, although S falls short of the prediction of the NFE model, i.e., $S \approx 0.65 S_d^{(f)}$. In fact, deviations from the linear T dependence, visible in a slight curvature of the data, indicate that the NFE model is no longer applicable. $S \sim T^{1.17}$ describes the T dependence for both $N = 7.29 \times 10^{18}$ and 7.0×10^{18} cm^{-3} [cf. the dashed lines in Fig. 2(a)]. These deviations are the precursor of the completely different behavior of S close to N_c.

Figures 2(b) and 2(c) display the thermopower of samples in the vicinity of the MI transition. Qualitatively all metallic samples in this plot show the same unusual T dependence. S changes sign, passes over a maximum around 100 mK, and decreases towards $T = 0$. S of the metallic samples with finite σ must vanish for $T \rightarrow 0$, since the product $S\sigma$ vanishes according to the third law of thermodynamics as $T \rightarrow 0$. For $N < N_c$, S also displays a sign change, although it no longer displays a

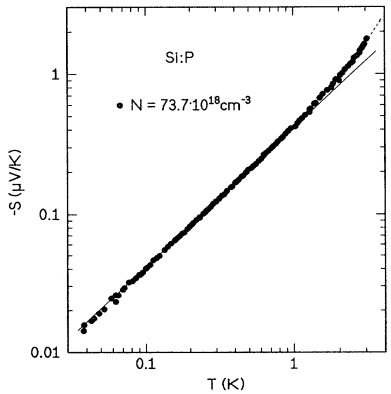

FIG. 1. Negative thermopower $-S$ vs temperature T for a heavily doped Si:P sample far above N_c. The solid line indicates behavior of nearly free electrons; the dashed line includes phonon drag.

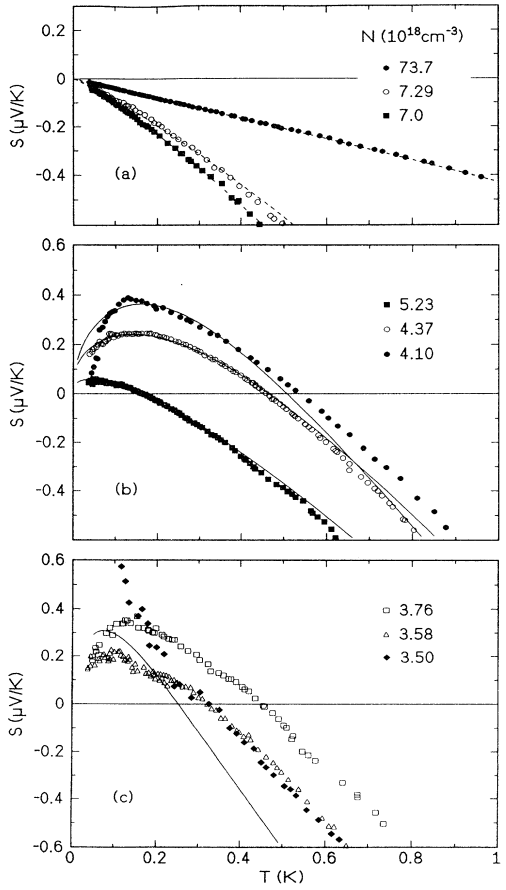

FIG. 2. Temperature dependence of thermopower S in a linear plot for various Si:P samples with different P concentration N. The dashed lines represent power-law fits [(a)] and solid lines fits according to a single-ion Kondo model [(b) and (c)]. The solid line in (c) is calculated for $N = 3.76 \times 10^{18}$ cm^{-3} and illustrates the breakdown of this model near N_c.

maximum. Instead S increases with decreasing T in the whole investigated T range. Above 300 mK, S of the two neighboring samples below and above the MI transition ($N=3.50\times10^{18}$ and 3.58×10^{18} cm^{-3}, respectively) nearly coincide. This illustrates that the MI transition shows up only for $T\rightarrow 0$. The increasing S of the insulating sample below 300 mK probably arises from activation of the electrons from E_F to the mobility edge E_c, with $S\sim 1/T+\text{const}$ [13]. The variable-range hopping regime (with or without Coulomb gap) expected at even lower T for this sample is not accessible in this experiment. A further reduction in N shifts the steep increase of S towards higher T. For $N=2.7\times10^{18}$ cm^{-3} (not shown), S changes sign at 3.5 K. This feature is compatible with the above interpretation because an increase in the relevant energy scale, i.e., of the distance between E_F and E_c, changes the temperature where the activation processes can occur. The steep increase of S of the insulating samples for $T\rightarrow 0$ reflects the strong T dependence of σ.

To obtain more information about the origin of the anomalous thermopower behavior of the metallic samples near N_c we investigated the dependence of S on magnetic field B. As an example S of a sample which exhibits a very marked anomaly in zero field is shown in Fig. 3. The anomaly in S is gradually suppressed with increasing B. For $B\gtrsim 1.5$ T the sign change no longer occurs and in $B=6$ T S varies roughly linearly with T at low T with $S=0.68S_d^{(f)}$. This is close to the deviations from the NFE model for $N\approx 7\times10^{18}$ cm^{-3}. (However, contrary to samples in the direct vicinity of N_c, S for the latter samples is almost field independent.) Apparently B drives S towards a more "metallic" behavior, in contrast to the tendency of localization generally observed in transport properties of heavily doped semiconductors. This rules out an explanation of the magnetic field effect in terms of wave-function shrinkage. A weak-localization

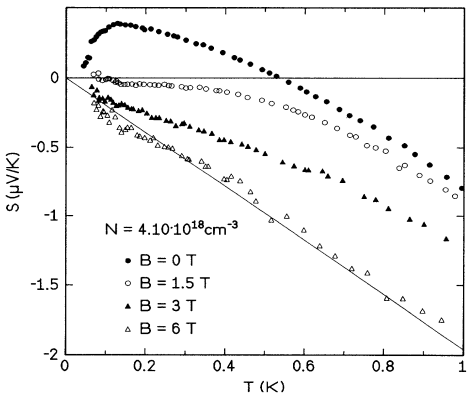

FIG. 3. Thermopower S in various magnetic fields B vs temperature T for a metallic Si:P sample near N_c. In $B=6$ T, S shows roughly linear behavior (indicated by the solid line). Here, the value of $|S/T|$ is reduced by a factor 0.68 compared to the nearly-free-electron model.

effect can equally be ruled out (see below). Therefore a contribution to S arising from magnetic scattering which is suppressed in a large field must be inferred, thus showing evidence of local moments. Their density was previously estimated from specific-heat data [6]. Near N_c roughly 5%–10% of the electrons are localized and even at $N=7.3\times10^{18}$ cm^{-3} a small contribution from a few localized electrons was detected [6]. This corresponds to the observation that the first deviations from a linear T dependence of S occur at $N=7.29\times10^{18}$ cm^{-3} [see Fig. 2(a)].

The assignment of the low-T anomaly of S to localized moments suggests an interpretation in terms of the Kondo effect. We will first analyze our results in terms of the Kondo model and discuss its limitations in particular due to disorder, and a possible breakdown of this simple model close to the MI transition below. Obviously in Si:P at least two scattering mechanisms are relevant for P concentrations just above N_c: a magnetic contribution S_m and a part we denote by S_d due to both scattering in a disordered potential and electron-electron correlations. Possible changes of $D(E)$ with N will also be absorbed in S_d. If we assume independent scattering processes (Matthiessen's rule) the Nordheim-Gorter (NG) rule can be applied stating that the different contributions to S have to be weighed with their respective resistivities:

$$S=(S_m\rho_m+S_d\rho_d)/(\rho_m+\rho_d)\,. \tag{1}$$

Sufficiently above N_c the electrical resistivity ρ can be well explained in terms of current theories of weak localization and electron-electron interactions [16] and there is no evidence for a large magnetic contribution to ρ. In this concentration range an analysis of S in terms of independent magnetic moments undergoing the Kondo effect works quite well. The solid lines in Fig. 2(b) show fits of S by Eq. (1) using the measured $\rho=\rho_m+\rho_d$ and $S_d=0.68S_d^{(f)}$ (see above). ρ_m and S_m were calculated directly from the expressions given by Maki [17] with the Kondo temperature T_K and the phase shift δ due to scattering from the Coulomb potential V of the P ions as fit parameters. The concentration of local moments N_s was taken from [6]. Note that in the NFE model $m^*\sim D(E_F)$, hence $D(E_F)$ does not enter the expression for ρ_m [17].

For $N=5.23\times10^{18}$ cm^{-3} the single-ion Kondo model works well with $T_K=1.4$ K and $\delta=-24.7°$ as fit parameters. With these parameters and $D(E_F)=8.7$ eV^{-1}atom^{-1} (i.e., 0.68 of the NFE model) we obtain for $V=-\tan\delta/\pi D(E_F)=16.7$ meV atom and the exchange energy between conduction electrons and localized moments $J=-[D(E_F)\cos^2\delta\ln(T_K/1.13T_F)]^{-1}=30.6$ meV atom. For these parameters the calculated total ρ_m increase for $T\rightarrow 0$ would be $\Delta\rho_m\approx 1.2\times10^{-4}$ Ω cm, hence $\rho_m\ll\rho\approx 6\times10^{-3}$ Ω cm which explains why a magnetic contribution to ρ is not observed. The fit for $N=4.37$ and 4.10×10^{18} cm^{-3} yields $T_K=1.3$ and 0.8 K, respectively. This tendency to a lowered T_K might be ex-

pected as $D(E_F)$ decreases with N, but agreement with the data systematically deteriorates as N approaches N_c as illustrated by the solid line in Fig. 2(c) (a fit by $N=3.76\times10^{18}$ cm^{-3}). Also, for classical Kondo systems the susceptibility χ shows a saturation below T_K which is not observed in Si:P for N just above N_c [5].

Despite these shortcomings in our simple analysis, Fig. 3 illustrates nicely how the Kondo thermopower is gradually suppressed as B increases. For $g\mu_B B \lesssim k_B T_K$ the Kondo anomaly is simply shifted to higher T (cf. data for $B=1.5$ T) while for higher fields it is suppressed altogether, as expected for this simple model. Of course, S may also be influenced by weak localization effects. However, as the transport coefficient $L^{12}=S\sigma$ is not changed by weak localization [10], $S(B)$ should be affected by the suppression of weak localization on a much smaller field scale than used in our experiments.

We now discuss possible reasons for the deficiency of our simple model close to N_c. The first point to consider is the assumption of independent Kondo ions. For the insulating phase of Si:P it is well known [18] that the magnetic moments are coupled pairwise through a direct exchange interaction. The specific heat shows that interactions between the localized moments are important below 1 K also in the metallic regime [6,19]. Thus one is dealing not with independent moments in the vicinity of N_c but interactions by either direct or—on the metallic side—indirect RKKY exchange also have to be considered. The influence of a pairwise RKKY interaction between statistically distributed local moments on S of a Kondo alloy was calculated by Matho and Béal-Monod [20]. However, under the same assumptions as above the calculated maximum of S falls well short of the observed magnitude for all N.

Two possibilities for the breakdown of our analysis close to N_c remain: (i) S_d deviates strongly from NFE behavior. In particular, a fine-structured $D(E)$ with E_F shifting to energies where $\partial \ln D(E)/\partial E < 0$ could lead to a sign change in S. However, the smooth evolution of the maximum of S for $N \to N_c$, together with the pronounced B dependence, makes this unlikely. (ii) The system becomes intrinsically inhomogeneous near N_c on a mesoscopic—and ultimately on a macroscopic—scale because of fluctuations associated with any second-order phase transition. Hence, a distribution of T_K's must be invoked. This might ultimately lead to a "breakdown" of Fermi-liquid behavior due to the presence of moments with extremely low T_K's and a concomitant divergence of χ and γ for $T \to 0$ [2,3]. Also the analysis in terms of the NG rule close to N_c which is based on Boltzmann transport theory might be questioned.

As far as a possible critical behavior of S_d near N_c is concerned, no definite conclusion as to whether S_d diverges or not can be drawn as long as there is no theory available which describes S_m in the vicinity of N_c.

In conclusion, we have shown the first firm experimental evidence in a transport property for local moments at the MI transition of a disordered metal. The appearance of a large magnetic contribution to S supports the idea that a more comprehensive description of the MI transition has to take into account the presence of magnetic moments on an equal footing with the effects due to disorder and electronic correlations. For instance, this calls into question the usual interpretation in terms of the leading correction of σ for $T \to 0$ ($\Delta\sigma = mT^{1/2}$) arising from electronic correlations, in particular close to N_c. We recall that even the sign change of m occurring in doped semiconductors for $N \gtrsim N_c$ (i.e., at $N \approx 1.13 N_c$ for Si:P) is not understood. The breakdown of a description in terms of a single-ion Kondo effect close to N_c suggests a wide distribution of T_K's in disordered systems. Our results should provoke theoretical work beyond the simple models employed here.

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