Thermodynamic Behavior near a Metal-Insulator Transition

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Measurements of the low-temperature specific heat of phosphorus-doped silicon for densities near the metal-insulator transition show an enhancement over the conduction-band itinerant-electron value. The enhancement increases toward lower temperatures but is less than that found for the spin susceptibility. The data are compared with various theoretical models; the large ratio of the spin susceptibility to specific heat indicates the presence of localized spin excitations in the metallic phase as the metal-insulator transition is approached.

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The simple and well-understood microscopic physics of shallow impurities in semiconductors, such as phosphorus-doped silicon (Si:P), makes these systems especially attractive for a study of the metal-insulator (MI) transition in disordered systems.[1] In the insulating phase at low phosphorus concentrations, n, the donor electrons are bound to the phosphorus nuclei in a hydrogenic $1s$ state. The Coulomb interactions between the electrons on different donors lead to an effective antiferromagnetic Heisenberg exchange interaction between the electron spins. The random locations of the donor nuclei lead to large variations in the magnitude of the exchange interaction. The resulting Heisenberg spin-$\frac{1}{2}$ antiferromagnet was modeled successfully by Bhatt and Lee[2] where they showed that pairs of spins gradually condense into singlets with falling temperature according to a highly correlated, hierarchical scheme. The experimental data are consistent with such a model even close to the critical density n_c, at sufficiently low temperatures.[3-6]

In the metallic phase the electrons delocalize and well above the MI transition ($n \gtrsim 2n_c$) their interactions can be adequately described in terms of a disordered Fermi liquid. However, in the critical regime just above n_c ($n_c \lesssim n < 2n_c$) we have, at the moment, only a qualitative understanding of the electronic properties. Even though temperature and magnetic field dependences of the electrical conductivity in this dirty-metal regime are in reasonable agreement with the perturbative expansion of the scaling theories,[7-11] the critical conductivity exponent 0.5 remains poorly understood. The electron spin susceptibility[12-15] and specific heat[16,17] are observed to be greatly enhanced over the expected degenerate-electron values. Such trends are predicted by the Brinkman-Rice treatment[18] for interacting electrons near the MI transition in a Hubbard model without disorder, as well as by the scaling theory of interacting electrons in disordered media.[10,11] Alternatively, an enhancement in the spin susceptibility is obtained if one assumes localized or nearly localized magnetic moments in the metallic phase just above n_c, similar to those in the $n < n_c$ insulating regime.[5,12-15,19] An experimental distinction between the various theoretical scenarios has not yet been made. This is in part due to a lack of adequate data on properly characterized samples, and also because of the many adjustable parameters in the theoretical fits.

In this paper we report specific-heat measurements in uncompensated Si:P down to 30 mK. Not only do our measurements go down to lower temperatures than previous measurements,[16,17] but they span densities closer to the MI transition with densities determined[20] from both room-temperature resistivity $\rho(293\ \mathrm{K})$ and the resistivity ratio $\rho(4.2\ \mathrm{K})/\rho(293\ \mathrm{K})$. Further, the absolute spin susceptibility χ for the *same* samples has been measured earlier by us[6,15] over the same temperature interval. Using a combination of these measurements, we are able to make detailed quantitative comparisons with various theoretical suggestions which has heretofore not been possible.

The specific heat of three single-crystal samples of $n/n_c = 0.78$, 1.09, and 1.25 were measured with a method described previously.[21] The measurements were carried out in a dilution refrigerator between 3 K and 30 mK. The addenda heat capacity was measured separately and has been subtracted out. Below 1 K, the addenda contribution was typically 1%-10% of the sample specific heat, while at the highest temperature it reached 50%.

The specific heat C for our samples is plotted in Fig. 1 as a function of temperature. The phonon contribution, AT^3, using a Debye temperature of 640 K, measured by previous investigators[16,17] in the same doping range, is shown as the dashed line. The solid lines represent the "free"-electron contribution $C_0 = \gamma_0 T$, calculated with use of the Si conduction-band mass ($m_0^* = 0.34 m_0$) which is consistent with specific-heat measurements[16,17] well above n_c. At these doping densities, however, elec-

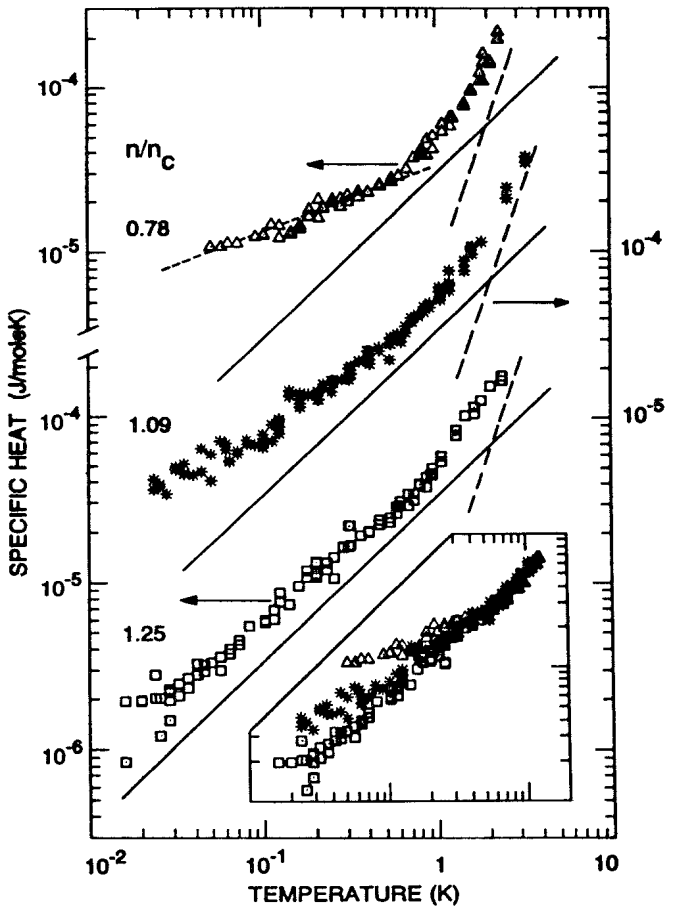

FIG. 1. Specific heat of Si:P as a function of temperature. Dashed lines represent the phonon contribution AT^3 for $\theta_D = 640$ K and the solid lines are the expected specific heat $\gamma_0 T$ for degenerate electrons with effective mass $m_0^* = 0.34 m_0$. The lighter dashed line over the $T < 0.7$ K data of the $n/n_c = 0.78$ sample represents a $T^{0.4}$ power-law fit. Inset: Different low-temperature behaviors of the three samples.

trons lie in impurity bands which may have a somewhat different mass, m^*. At our highest temperatures the ratio $\gamma/\gamma_0 \equiv (C - AT^3)/\gamma_0 T$ is close to 1.3, which agrees with earlier measurements[17] close to n_c, but is somewhat larger than the value 1.06 from Ref. 16. Our measured mass enhancement is consistent with the calculated impurity-band mass enhancement,[22] plus other Fermi-liquid corrections, and so we take the effective mass to be $m^* = 1.3 m_0^*$. The inset of Fig. 1 shows how the specific-heat data of the three samples, which are close at high temperature, deviate at low temperatures. As we go to lower temperatures, γ/γ_0 increases for all samples, though the increase is much less than the corresponding susceptibility[5] enhancement, χ/χ_0. For the insulating sample ($n/n_c = 0.78$) we find that the specific heat is consistent with a power law $\gamma/\gamma_0 \propto T^{-0.6}$ below 0.7 K. The Bhatt-Lee result for the random Heisenberg antiferromagnet predicts that for $\gamma/\gamma_0 = (T/T_0)^{-\alpha}$, $\chi/\chi_0 = \beta(T/T_0)^{-\alpha}$ where $\beta \simeq 3.1 e^{0.4\alpha}/(1-\alpha)^2$. The agreement between the exponent from the specific-heat measurement ($\alpha = 0.60 \pm 0.10$) and that from the susceptibility measurement ($\alpha = 0.63 \pm 0.03$), as well as the agreement with the theoretical value of β at low temperatures (see below), demonstrates the validity of their model in the insulating phase.

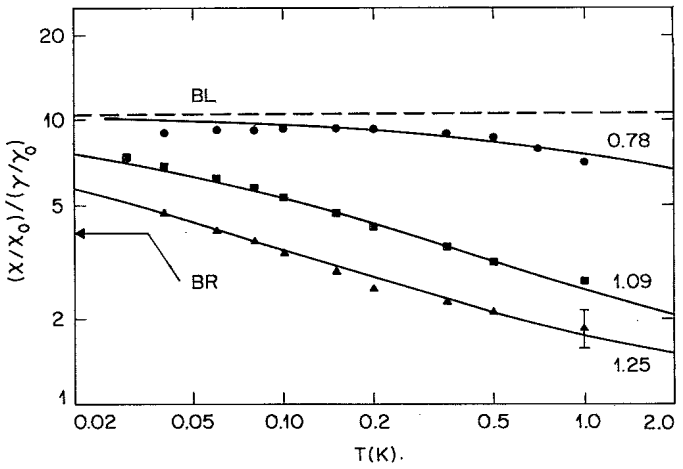

FIG. 2. The ratio of spin susceptibility to specific heat vs temperature. χ_0 and γ_0 are the degenerate-electron values. The solid lines are one-parameter fits with the localized-spin model, and the dashed line is the Bhatt and Lee prediction for insulating Si:P.

On the metallic side, because of the smaller enhancement in γ/γ_0, the asymptotic low-T behavior is not clear from Fig. 1, and a more detailed examination of the data is needed. One quantity which factors out uninteresting dependence on the electron density of states, and is therefore a natural candidate for testing various models, is the Wilson ratio, $(\chi/\chi_0)/(\gamma/\gamma_0)$. In the Brinkman-Rice picture for the Hubbard model without disorder, the Wilson ratio increases from the free-electron value of unity as $n \to n_c^+$, and saturates at the value 4. Recent scaling theories of interacting electrons in disordered systems,[8-11] on the other hand, predict in $d = 2 + \epsilon$ dimensions that as $n \to n_c^+$, $\chi \sim T^{-(\theta+x)/(d+x)}$ and $\gamma \sim T^{-x/(d+x)}$, where θ and x are ϵ and 3ϵ, respectively, to lowest order in ϵ. Thus a divergent Wilson ratio $\propto T^{-\theta/(d+x)}$ as $T \to 0$ is predicted. The Wilson ratio for our samples is shown in Fig. 2. As can be seen, all samples show an increase as T is lowered, and exceed the Brinkman-Rice limit at low temperatures. On the other hand, the values are not large enough to demonstrate the divergent form $T^{-\theta/(d+x)}$ expected for the Wilson ratio in the scaling picture. Rather, the curves show some tendency to saturate at low temperatures, and the value of the Wilson ratio for the insulating sample ($n/n_c = 0.78$) is clearly constant at $\simeq 9.3$, which is close to the value of $\beta = 10.5$ obtained in the Bhatt-Lee model for $\alpha = 0.62$. Indeed, if we were to extend their picture to the metallic

phase, by describing the susceptibility and specific heat as a sum of two contributions—one from localized spins interacting with each other as in the insulator, and another from itinerant electrons (Fermi liquid) with an effective mass m^*—we would obtain

$$\gamma/\gamma_0 = m^*/m_0^* + (T/T_0)^{-\alpha},$$
$$\chi/\chi_0 = m^*/m_0^* + \beta(T/T_0)^{-\alpha}. \quad (1)$$

This picture is similar to that used earlier,[12,13] except there the localized spins were assumed to contribute a free spin (Curie) susceptibility, whereas we believe that given the success of the Bhatt-Lee model in the insulating phase, our extension is more appropriate. In Eq. (1), we assume α to be independent of the doping level n as found by Sarachik *et al.*[5] and use the average experimental value 0.62 determined from the low-temperature specific heat and susceptibility of our insulating sample $n/n_c = 0.78$.[6] The parameter T_0 measures the fraction of electrons which can be described as localized spins and the only adjustable parameter in the Wilson ratio is $T_0' = T_0(m_0^*/m^*)^{1/\alpha}$. The solid lines in Fig. 2 are the best fits by the predictions of Eq. (1) and yield values of T_0 of 0.11 and 0.03 K for the $n/n_c = 1.09$ and 1.25 samples. With these T_0 values Eq. (1) also gives separately a good fit for the susceptibility[6,15] and the specific heat. These values of T_0 together with the upper cutoff J_0 of the exchange interactions may be used to determine the fraction f of electrons appearing in the form of localized spins. A conservative *lower* bound on f is obtained by use of $J_0 = 2$ K, the temperature below which the susceptibility data of the metallic samples show insulatinglike behavior[6]; this gives $f > 5\%$ and $> 2\%$ for $n/n_c = 1.09$ and $n/n_c = 1.25$, respectively. If, on the other hand, we use an upper cutoff which would yield $f \simeq 100\%$ for our insulating sample[6] ($J_0 \simeq 150$ K which is the order of the hydrogenic value $\simeq 300$ K), we get $f \simeq 25\%$ and 10% for the two samples, respectively. These values are consistent with the unexpectedly large fraction of localized spins observed in the NMR experiments of Alloul and Dellouve.[23]

The applicability of the above scenarios for the metallic samples can be studied in greater detail by our plotting the susceptibility enhancement χ/χ_0 directly against the specific-heat enhancement γ/γ_0 so that the temperature is an implicit parameter, as shown in Fig. 3. Such a plot has the advantage of introducing no new adjustable parameters, and is especially useful for analyzing the high-temperature behavior of spin susceptibility and specific heat within the scaling theory. The renormalization-group equations for χ and γ are expressed in terms of the disorder parameter t and the interaction constants γ_2 and z,[11] by the relations $\chi/\chi_0 = z(1+\gamma_2)$ and $\gamma/\gamma_0 = z$. To lowest order in t, the equation for $d(\ln z)/d\gamma_2$ has the remarkable feature that it is independent of t and ϵ and depends only on γ_2. This equation can easily be integrated and yields the broken lines SV and MV in Fig. 3. The curve SV corresponds to a single-valley model for the donor electrons and is appropriate if the intervalley scattering rate $\hbar/\tau_{iv} \gg k_B T$. In the opposite limit $\hbar/\tau_{iv} \ll k_B T$, a multivalley model[24] is needed; the results for such a model are shown by curve MV. The only adjustable parameters for these curves are the high-temperature starting values $\chi/\chi_0 = 2.5$ and $\gamma/\gamma_0 = 1.4$. Even though these starting values are selected to be equal to the measured high-temperature data the fits are rather poor and clearly indicate that the renormalization-group equations badly underestimate the relative enhancement of the spin susceptibility. The possibility that higher-order terms in the renormalization-group equations may cure this discrepancy is, however, not ruled out.

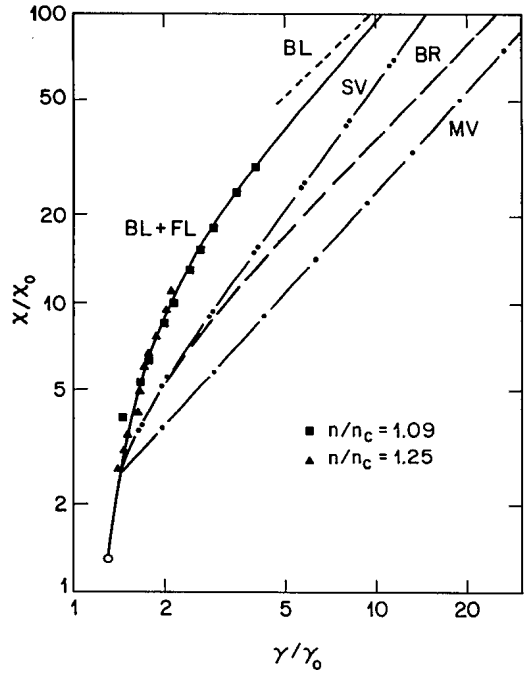

FIG. 3. Susceptibility enhancement vs specific-heat enhancement for metallic samples. The theoretical curves SV and MV are obtained with use of the scaling theory in $2+\epsilon$ dimensions with $\epsilon = 1$ for a single valley and a multivalley semiconductor. BL is the Bhatt-Lee model for insulating Si:P, BL+FL is Fermi-liquid electrons plus localized spins as described by the Bhatt-Lee model, and BR is the Brinkman-Rice model.

In Fig. 3 we also compare other models with the experimental data. The result of the Brinkman-Rice (BR) model,[18] (where the ratios χ/χ_0 and γ/γ_0 are functions of the interaction parameter U/U_c) also disagrees with the experimental data. Curve BL+FL, the phenomenological itinerant-electron plus localized-spin model as described by Eq. (1), is clearly in best agreement with the experimental points. This curve is *independent* of T_0, and the other parameters ($m^*/m_0^* = 1.3$ and $\alpha = 0.62$) have been determined before.

In conclusion, we have measured the temperature

dependence of the specific heat and the susceptibility, and hence the Wilson ratio, for Si:P near the metal-insulator transition down to 30 mK. We find that the Wilson ratio is considerably larger than can be reasonably expected in either the Brinkman-Rice or the interaction-disorder scaling-theory models of the MI transition. However, we find good agreement with a two-component model consisting of itinerant and localized electronic spins. Our model differs from a similar older model in that we have assumed that localized spins follow the Bhat and Lee[2] scenario for the random Heisenberg antiferromagnet as in the insulating phase. This agreement suggests the existence of quasilocalized spins which interact only very weakly with the itinerant electrons and give rise to extremely slow spin fluctuations in disordered metals. Further, our results, which have probed the low-energy spin excitations, appear to agree well with those obtained in recent NMR experiments[23] and inferred from static susceptibility data at higher temperatures,[25] both of which are sensitive to spin excitations at higher energies.

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