Localized versus Itinerant Electrons at the Metal-Insulator Transition in Si:P

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The specific heat C of uncompensated phosphorus-doped silicon with P concentration N between (0.34 and 7.3)$\times 10^{18}$ cm^{-3}, i.e., in the vicinity of the metal-insulator transition, has been measured over a large range of temperatures (0.04 K$\leq T\leq$ 3 K), allowing the unambiguous detection of an anomalous contribution $\Delta C\sim T^{\alpha}$, with α becoming negative for small N. This is attributed to exchange-coupled clusters. The magnetic field dependence of C (up to 5.7 T) allows us to deduce the relative contributions of localized and delocalized electrons and gives evidence for interactions and correlations between these.

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The metal-insulator (MI) transition as driven by the combined effects of disorder and electronic correlations, the Anderson-Mott transition, is one of the major fields of research in solid-state physics. The terms metal and insulator are used to denote a finite or vanishing electrical conductivity σ for $T\rightarrow 0$, respectively. A well-defined experimental realization of such a transition is found in phosphorus-doped silicon (Si:P), where the MI transition occurs at a critical density of donors N_c,[1] or, for fixed donor density N slightly below N_c, with increasing uniaxial stress.[2] In a grossly simplified picture, the transition is due to the increasing overlap of the P-derived donor electronic wave functions until an impurity band is formed. An interesting and hitherto unexplained feature is the fact that for uncompensated Si:P the exponent ν of the electrical conductivity $\sigma\sim(N-N_c)^{\nu}$ is $\frac{1}{2}$,[1,2] while for virtually all other materials, including compensated semiconductors, it is close to 1, in agreement with scaling predictions.[3]

In a recent Letter,[4] it was suggested that the thermodynamic behavior of Si:P (in the following we refer to uncompensated Si:P, unless stated otherwise) in the vicinity of the MI transition can be modeled with a phenomenological two-component picture, where the specific heat C and the magnetic susceptibility χ contain contributions from delocalized, correlated electrons described as a Fermi liquid and from localized electrons which are coupled through a pairwise exchange interaction.

In this Letter, we present specific-heat data of high accuracy over a large range of temperatures (down to 0.04 K), magnetic fields (up to 5.7 T), and donor concentrations ($0.34\times 10^{18}\leq N\leq 7.3\times 10^{18}$ cm^{-3}). These data present an important extension of earlier work.[4-7] In brief, our main findings are the following: (i) At low T we observe a contribution to C proportional to T^{α} with α varying continuously as a function of N, becoming negative for our lowest concentrations. This might be attributed to ferromagnetic couplings and Coulomb correlations neglected in the previous[4] discussion. (ii) The magnetic field dependence of C shows a continuous transition from localized (magnetic) to delocalized (nonmag-

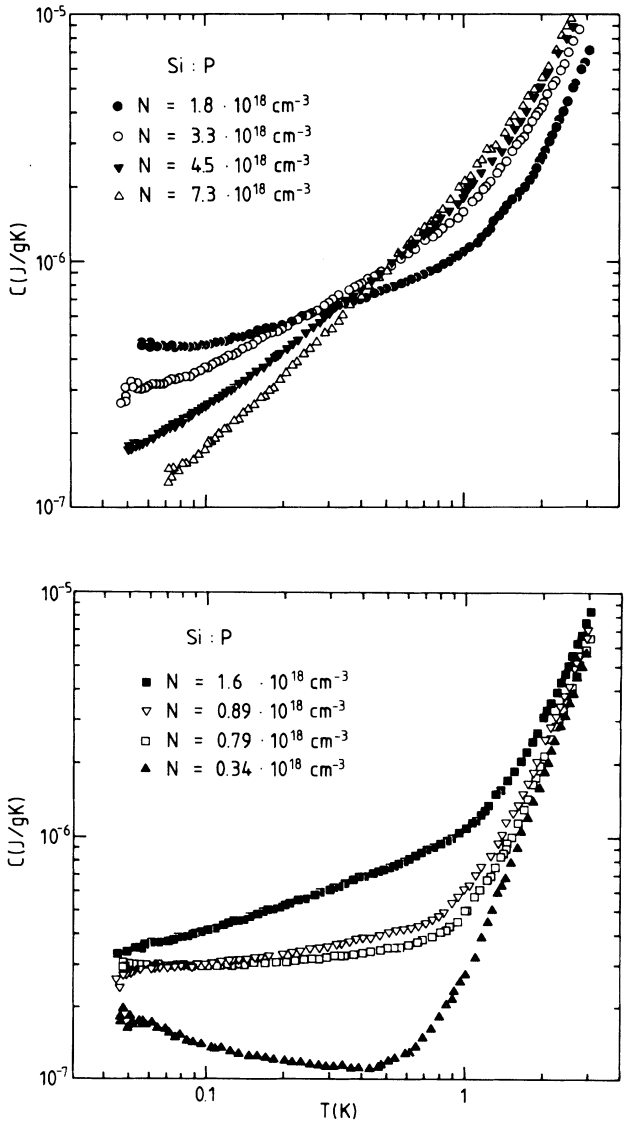

FIG. 1. Specific heat C vs temperature T of Si:P for various donor densities N.

netic) behavior, with localized contributions observable even at $N \approx 2N_c$.

The samples[8] were grown with the Czochralski method, yielding rods of 54 or 79 mm in diameter with a P concentration profile along the axes of the rods. Hence samples of roughly constant P concentration N could be conveniently cut from the rods with a diamond saw. For a given sample of dimensions $30\times20\times5$ mm^3 the variation of P concentration was less than 5%, as determined with four-point resistance measurements on several sections of the sample. The absolute P concentrations were determined using the calibration by Thurber.[9] The magnitude and temperature dependences of the electrical conductivity at low temperatures determined for several of our samples are in reasonable agreement with earlier work.[1] The specific heat was measured in a standard dilution refrigerator with the heat pulse technique. The addenda (heater, thermometer, and part of the mechanical and thermal links to the mixing chamber) contributed about 5% at 0.1 K and 20% at 1 K of the total heat capacity in zero magnetic field. Even for low-N samples and in high magnetic fields the addenda contribution was always less than 40% except for $N=0.34\times10^{18}$ cm^{-3} in 5.7 T where it rose to 60%.

Figure 1 shows the specific-heat data in zero magnetic field for all samples. Above 1.5 K, the data can be adequately described by $C=\gamma T+\beta T^3$; hence γ and β can be determined from C/T vs T plots (not shown). β yields a Debye temperature $\theta_D=660\pm20$ K for all samples, in reasonable agreement with literature data for Si. γ varies very close to the previous data of Marko, Harrison, and Quirt[5] and Kobayashi *et al.*[6] Below 1 K, strong deviations from this behavior are observed, in particular an upturn of C towards a sublinear T dependence. Some indications of such a behavior have been reported previously.[4] After subtraction of the "regular" contribution $\gamma T+\beta T^3$, the remaining "anomalous" specific-heat contribution ΔC as plotted in Fig. 2 varies as T^α between 0.04 and 0.3–0.4 K, i.e., over almost one decade in T. This allows a reliable determination of α which differs somewhat from the previous work.[4] In contradiction to earlier suggestions,[4] α is not constant, but decreases with decreasing N and passes through zero (see inset of Fig. 2). For samples with lowest P concentration, even a negative α is found. This new and unexpected result is apparently not anticipated in the phenomenological model of Bhatt and Lee[10] upon which the previous analysis is based.

The magnetic field dependence of C was investigated in detail for all samples. In brief, for the metallic samples, C depends on B only weakly. The field dependence gradually becomes stronger with decreasing N. Figure 3 gives an example for the intermediate concentration range. The following results are inferred from the present systematic investigation: (i) ΔC develops towards a Schottky anomaly with increasing B as has been

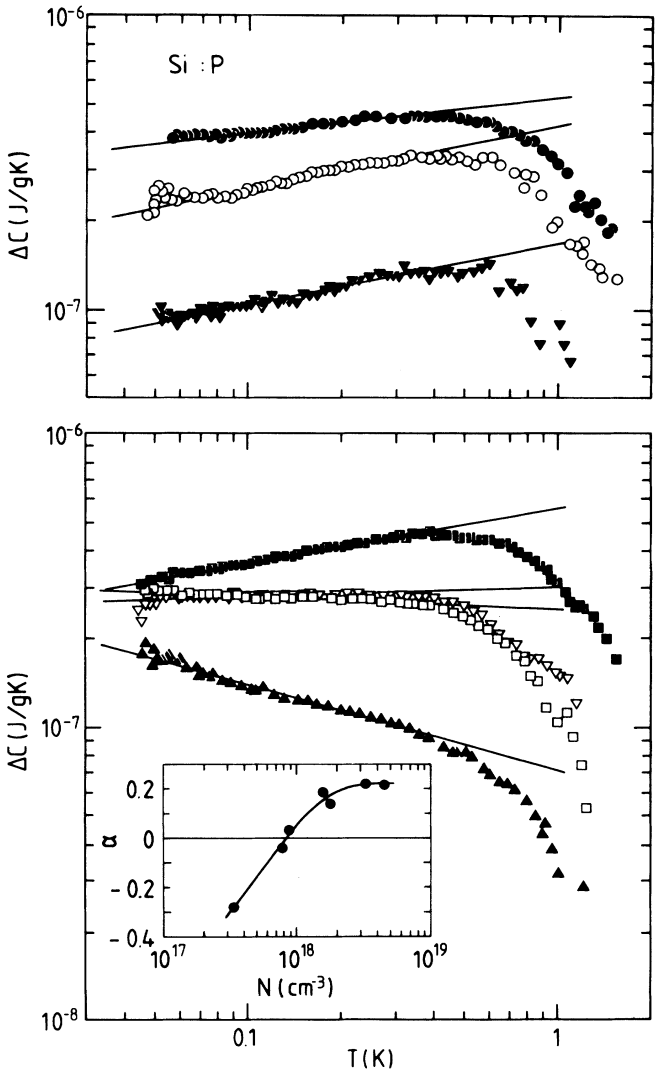

FIG. 2. Excess specific-heat contribution ΔC (after subtraction of the regular terms $\gamma T+\beta T^3$) of Si:P vs temperature T. Symbols are the same as in Fig. 1. Solid lines indicate fits of $\Delta C\sim T^\alpha$. Inset: The exponent α vs donor density N.

observed before,[7] indicating that it is mostly due to exchange-coupled clusters of localized electrons. (ii) The maximum of the anomaly increases slightly with B even in large fields. (iii) γ decreases with increasing B. This decrease is strongly concentration dependent; $[\gamma(5.7\text{ T})-\gamma(0)]/\gamma(0)$ changes continuously from -1 for $N=0.34\times10^{18}$ cm^{-3} [i.e., the small $\gamma(0)\approx0.02$ μJ/g K^2 is completely suppressed in 5.7 T] to ~-0.1 for the sample with highest P concentration [$\gamma(0)=1.78$ μJ/g K^2]. (iv) The rise in C below 0.1 K observed in 5.7 T must be attributed mostly to the Zeeman splitting of ^{31}P nuclei, as inferred from the magnitude and concentration dependences of C. It is much smaller than ex-

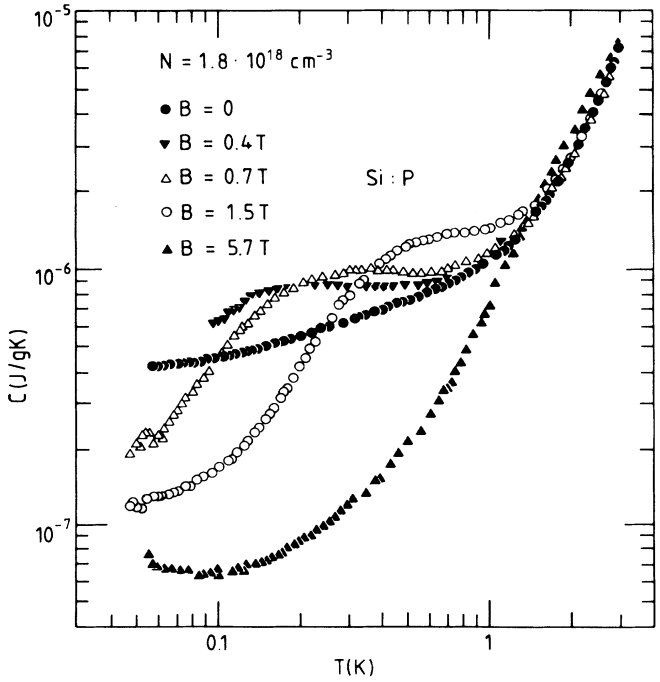

FIG. 3. Specific heat C in various magnetic fields B vs temperature T for one Si:P sample.

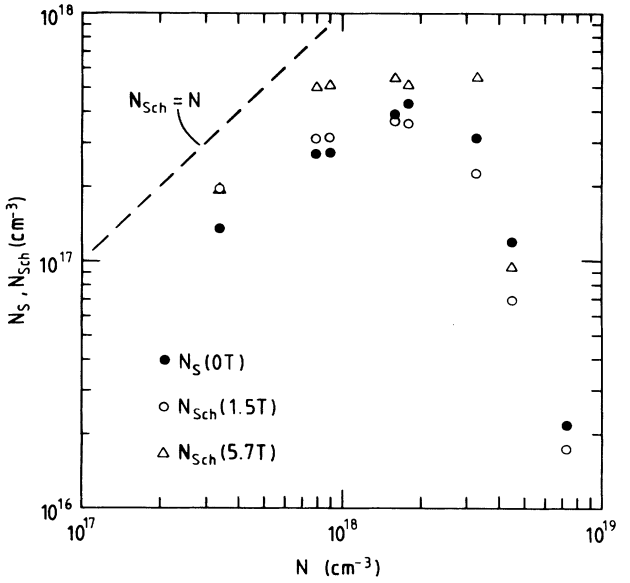

FIG. 4. Number densities of donor electrons N_S giving rise to the zero-field anomaly and N_{Sch} contributing to the Schottky anomalies in 1.5 and 5.7 T vs donor density N.

pected for ^{29}Si. This shows that even for the metallic samples the (enhanced) Korringa relaxation rate for ^{29}Si is much smaller than the inverse time scale ($t \sim 1$ s) of our specific-heat experiment while that for ^{31}P is comparable to t^{-1}. This is in agreement with recent NMR experiments on both nuclei.[11,12]

These features, in particular (ii) and (iii), illuminate the complex interplay of localized and correlated (Fermi-liquid–like) electrons, which appears to depend on magnetic field: For a given N, a large field drives the system towards the insulating side as seen here for the first time for a thermodynamic quantity. Magnetic field induced MI transitions have been observed in the electrical resistivity for a few other systems.[13]

We now discuss the zero-field anomaly ΔC in more detail which is attributed to exchange-coupled clusters. In the Bhatt-Lee model, these clusters are modeled as spin-singlet pairs with a wide range of singlet-triplet splittings,[10] leading to a rather wide specific-heat anomaly. The exponent α of this anomaly is directly related to the exponent δ appearing in the magnetic susceptibility, $\chi \sim T^{-\delta}$, $\alpha = 1 - \delta$. The positive $\alpha \approx 0.3$ observed for our most concentrated samples is thus in agreement with the slower rise of χ towards low temperatures, $\delta \approx 0.65$, than the Curie behavior expected for free spins ($\delta = 1$), as pointed out before.[4] However, the decrease of α towards negative values for our most dilute samples is much stronger than that of $1 - \delta$ in the same concentration range.[14] Although a possible influence of deep-level impurities such as oxygen, in particular for low N, cannot be excluded, there may be two other reasons for the apparent discrepancy. First, the possibility of ferromagnetic pairs is not included in the Bhatt-Lee model, and, furthermore, double occupancy of P-derived electron states should be allowed in the vicinity of the MI transition. Second, the hierarchical exchange-coupling scheme of pairs neglects the possibility of larger clusters. Indeed, a recent calculation suggests that such clusters might account for the behavior of C and χ just below the MI transition.[15] A further interesting observation which is at variance with the assumption of a wide range of exchange constants is the appearance of a "high-temperature" cutoff occurring already near 0.5 K; see Fig. 2.

The interplay between localized and delocalized electrons can be discussed with the help of Fig. 4, where the number densities N_S of electrons contributing to ΔC as determined from the associated entropy, and N_{Sch} as derived from the maximum of a fit of a two-level Schottky anomaly to the data for 1.5 and 5.7 T are compared with the donor density N. Starting from the insulating side, both quantities increase with N, pass over a broad maximum, and then decrease strongly on the metallic side, as more and more degrees of freedom are associated with the itinerant electrons. The systematic differences between N_S and N_{Sch} may be interpreted as follows. For small N, $N_S < N_{Sch}$ because isolated spins do not contribute to ΔC in zero field. For large N, $N_S > N_{Sch}$ because virtually all spins are located in clusters and contribute to ΔC, but the field anomaly is broadened compared to a Schottky anomaly because of exchange split-

tings and hence the maximum decreases with B as mentioned above, and some of these degrees of freedom reappear in N_{Sch}, which increases with B. Except for the most dilute sample, N_{Sch} as determined from the measurement in 5.7 T is higher than in 1.5 T, indicating the tendency towards localization in high magnetic fields.

Even for our highest-concentration sample with $N > 2 \times N_c$, we observe a small zero-field anomaly and a Schottky anomaly in 1.5 T (the anomaly in 5.7 T, expected around 3K, is hidden by the rapidly rising regular contributions to C). Roughly, 0.3% of the P-derived electrons still show some indication of localized behavior. This is in agreement with recent NMR measurements also giving evidence for localized electrons well above N_c.[12] The temperature of the Schottky maximum T_{max} agrees with the value expected for isolated spins only for the most dilute samples ($N < 10^{18}$ cm^{-3}), while it shifts systematically to smaller temperatures with increasing N, reflecting the increasing importance of exchange interactions between localized electrons.

It is important to point out that the density of delocalized electrons N_γ (calculated from γ with the Si conduction-band effective mass) and localized electrons obtained from N_{Sch} do not simply add up to yield the total density of donor electrons N. For example, for $N = 0.89 \times 10^{18}$ cm^{-3} the measured $\gamma = 0.24$ μJ/gK^2 translates into $N_\gamma = 2.9 \times 10^{16}$ cm^{-3} only. This shows that the two-component model of localized and itinerant electrons which appears to work successfully on a phenomenological level in a reduced concentration range[4] is incomplete. Interactions between the two components are neglected. The present discovery of a magnetic field induced shift towards localization, evidenced by the opposite field dependence of γ and N_{Sch}, and the simultaneous existence of γT and $\Delta C \sim T^\alpha$ terms over a wide concentration range sheds new light on the interaction and correlation between localized and delocalized, correlated electrons in the vicinity of the MI transitions.

It is hoped that our quantitative experimental study stimulates further theoretical investigations on a microscopic scale for this conceptually simple system in order to get more insight into the physics of the metal-insulator transition.

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