Specific heat of Si:(P,B) at low temperatures

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The specific heat C of Si:(P,B) with carrier concentration N between 0.8 and 17.8×10^{18} cm^{-3} and compensation ratio varying from 0.25 to 1 was measured in the temperature range between 0.06 and 3 K and in magnetic fields up to 6 T. Above the critical carrier concentration N_c of the metal-insulator transition (MIT), the linear coefficient of C varies as expected for a nearly-free-electron metal and drops rapidly for $N<N_c$ as found previously for uncompensated Si:P. Below 1.5 K an additional contribution ΔC is found that is attributed to localized magnetic moments. These persist even on the metallic side of the MIT. In larger magnetic fields ΔC develops into a Schottky anomaly. Although the overall behavior of ΔC in Si:(P,B) is again similar to that in Si:P, some quantitative differences, e.g., in the temperature dependence of ΔC and the concentration of localized magnetic moments just below N_c, are observed. [S0163-1829(97)08307-0]

I. INTRODUCTION

The metal-insulator transition (MIT) in doped semiconductors such as Si:P has been investigated for many years. Two main mechanisms drive this transition, disorder because of the statistical distribution of donors or acceptors, and electron correlations. Compensation of doped semiconductors leads to changes in the properties close to the MIT but it is not clear to which extent this is due to enhanced disorder or to changes in the effective electron-electron interaction. Two compensation methods are available. One is irradiation with fast neutrons introducing lattice defects which act as acceptors. These can be progressively annealed out by consecutive annealing steps. The other is to dope additionally with an element of the third main group, e.g., boron. The influence of compensation has been studied in several comparative investigations of uncompensated Si:P and neutron-compensated (nc) Si:P as well as Si:(P,B). From here on, Si:P is always meant to stand for uncompensated material unless noted otherwise. The electrical resistivity $\sigma(N,T)$ of Si:(P,B) depends strongly on the compensation ratio K.[1] Assuming a critical behavior $\sigma(N,T\rightarrow0)\sim(N-N_c)^{\mu}$ for carrier concentrations N close to the critical concentration N_c, a critical exponent $\mu\approx0.5$ has been suggested for uncompensated Si:P, based primarily on stress-tuning experiments very close to N_c.[2] Data for Si:(P,B) with $K\approx0.2$ are compatible with $\mu\approx0.5$ while $\mu\approx1$ was found for larger K.[1] Likewise, for nc-Si:P $\mu\approx1$ was suggested.[3] This ''exponent puzzle'' has not been fully resolved. One possibility is that the apparent differences in the critical behavior might be due to a difference in the width of the critical region, given by the concentration range just above N_c where $d\sigma/dT>0$.[4] This range is larger for compensated than for uncompensated samples.[5]

Another issue of interest is the existence of localized magnetic moments on the metallic side of the MIT. ESR measurements[6] suggest that a larger fraction of localized magnetic moments (for given N/N_c) exists in metallic Si:(P,B) compared to metallic Si:P. Specific-heat measurements in zero magnetic field and in fields up to 6 T mapped out in detail the concentration of localized magnetic moments $N_S(B=0)$ or $N_{\mathrm{Sch}}(B>0)$ as a function of dopant concentration.[8,9] Previously, specific-heat results had already qualitatively pointed to the existence of localized magnetic moments on the metallic side in Si:P.[10,11] In addition, the dc susceptibility χ of metallic Si:P shows a weak divergence for $T\rightarrow0$, directly indicating localized magnetic moments.[12] Furthermore, the maximum in the thermoelectric power $S(T)$ at very low temperatures, which is of similar magnitude in Si:P (Ref. 13) and Si:(P,B) (Ref. 14) has been attributed to scattering by localized magnetic moments. This interpretation is backed by the suppression of the maximum in large magnetic fields.

Neutron-compensated Si:P samples have also been investigated with the specific heat C. While one study was confined to zero-field measurements[3] and thus was not able to address the question of localized magnetic moments, the latter were detected in nc-Si:P, again through the magnetic-field dependence of C.[15] However, a straightforward interpretation is hampered by the fact that neutron irradiation induces paramagnetic defects, in addition to the doping-induced localized magnetic moments, whose concentration might depend on the compensation ratio.

For a quantitative determination of the localized moments on the metallic side of compensated Si:P it therefore is necessary to study Si:(P,B). This is done in the present work. In addition, we report on an investigation of two float-zone-refined (fz) uncompensated Si:P samples (with very low oxygen impurity level compared to the usually investigated Czochralski-grown crystals) in order to check for possible impurity contributions to the specific heat.

II. EXPERIMENT

The specific heat was measured in a ^{3}He/^{4}He dilution refrigerator in the temperature range $0.06\ \mathrm{K}\leqslant T\leqslant 3\ \mathrm{K}$ in magnetic fields B up to 6 T. The standard heat-pulse technique was employed. The temperature on the samples was measured with a Matsushita carbon resistor (ground down to a thin slab, to minimize its heat capacity), which was calibrated in $B=0$, 1.5, 3, 4.5, and 6 T against a precalibrated Ge thermometer located in the field-compensated region of the cryostat. The maximum magnetoresistance (at the lowest

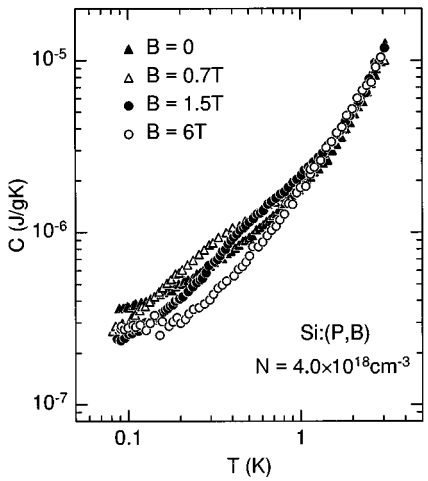

FIG. 1. Log-log plot of the specific heat C vs temperature T in magnetic fields B for $N=4.0\times10^{18}$ cm^{-3}.

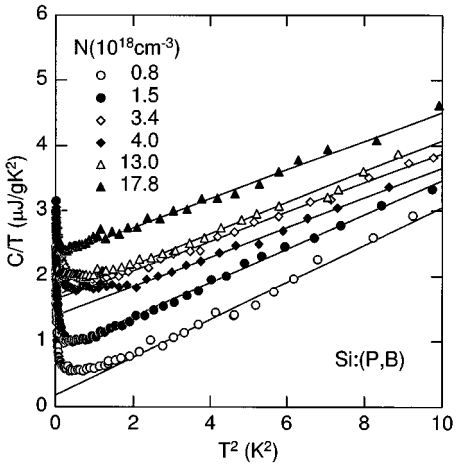

FIG. 3. Specific heat C divided by temperature T vs T^2 for some Si:(P,B) samples.

temperature) was 2% in 6 T. The carrier concentration $N=N_P-N_B$ of the Czochralski-grown single crystals was determined with the Hall effect at room temperature using the Hall scattering factor of uncompensated Si:P,[5] and the compensation ratio $K=N_B/N_P$ and N_c were taken from (Ref. 5). Samples with $N=0.8$, 1.5, 3.4, 4.0, 13.0, and 17.8×10^{18} cm^{-3}, with $K\sim0.65-1$, 0.65, 0.25, 0.25, 0.45, and 0.37, and $N_c=4.94$, 4.94, 3.54, 3.54, 3.78, and 3.78, respectively, were investigated.

In order to check the possible influence of deep-level impurities such as oxygen we additionally measured the specific heat of two samples of uncompensated Si:P, which were purified by float-zone melting, with $N=0.45\times10^{18}$ cm^{-3} and $N=6\times10^{18}$ cm^{-3}. This treatment leads to a reduction of the oxygen content from $\sim(5-9)\times10^{17}$ to $\sim(0.1-2)\times10^{16}$ cm^{-3}.[16]

III. RESULTS AND DISCUSSION

Figures 1 and 2 show the specific heat C for two Si:(P,B) samples with $N=4.0\times10^{18}$ cm^{-3} and $N=1.5\times10^{18}$ cm^{-3}, i.e., just above and below N_c, versus temperature T on a log-log scale. In the absence of a magnetic field the specific heat for $T>1.5$ K consists of the electronic contribution linear in T and the T^3 lattice contribution, $C=\gamma T+\beta T^3$. Figure 3 shows zero-field data for some samples plotted as C/T versus T^2. The Debye temperature $\theta_D=(660\pm20\text{K})$ determined from β is in good agreement with the literature data for pure Si. $\gamma(N)$ is shown in Fig. 4. For noninteracting electrons $\gamma=(\pi^2/3)k_B^2N(E_F)=(\nu\pi/3)^{2/3}(k_B/\hbar)^2m^*N^{1/3}$ where $N(E_F)$ is the single-particle density of states at the Fermi level. The solid line in Fig. 4 shows the nearly-free-electron behavior taking the effective mass m^* of the Si conduction-band minima and the valley degeneracy $\nu=6$ into account. For comparison, $\gamma(N)$ of uncompensated Si:P (Refs. 9 and 10) and nc-Si:P (Refs. 3 and 15) versus N is also shown in Fig. 4. In all cases the linear term of specific heat for samples above the MIT behaves roughly like that of nearly free electrons. On the other hand, the Knight shift of compensated Si:(P,B) in the metallic region decreases more rapidly with decreasing N than for Si:P when normalized to the value at 10 N_c.[7] This suggests a lower density of states of itinerant electrons in the compensated system than in uncompensated Si:P.

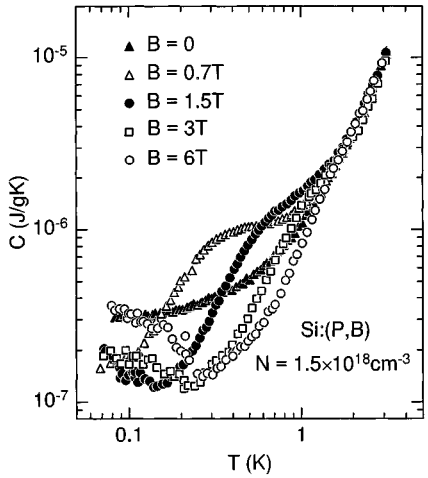

FIG. 2. Log-log plot of the specific heat C vs temperature T in magnetic fields B for $N=1.5\times10^{18}$ cm^{-3}.

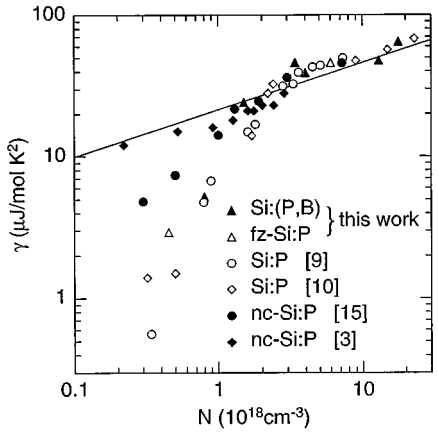

FIG. 4. Linear coefficient γ of the specific heat vs carrier concentration N.

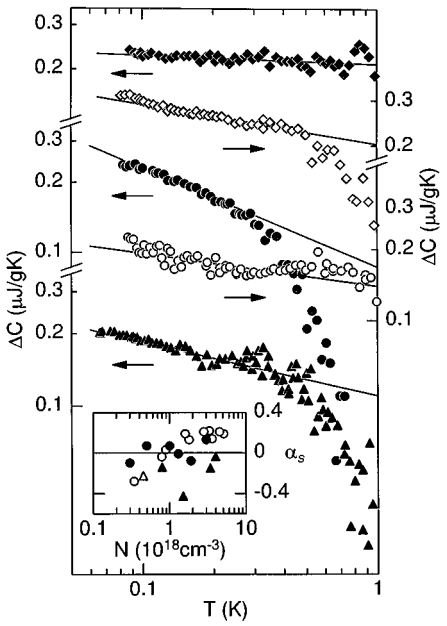

FIG. 5. Excess specific heat ΔC vs temperature for several concentrations. The concentrations are (from top to bottom in units of 10^{18} cm^{-3}) for Si:(P,B): 4.0, 3.4, 1.5, and 0.8 and for fz-Si:P : 0.45. Solid lines indicate power laws. The inset shows the exponent α_S vs concentration for Si:(P,B) (full triangles), fz-Si:P (open triangle), uncompensated Si:P (open circles, after Ref. 9), and nc-Si:P (full circles, after Ref. 15).

As expected for the insulating regime, γ deviates from the behavior of nearly free electrons below $N \simeq 2\times 10^{18}$ cm^{-3}, although in all types of material a finite γ is still observed for low N. A possible explanation is that upon dilution for $N<N_c$ the sample separates into smaller and smaller metallic regions, containing on the average N_R electrons, which still may exhibit a finite γ as long as their typical size is such that the average spacing of one-electron levels $\delta \approx E_F/N_R$ is smaller than the thermal energy.[9] Furthermore, γ of the two fz-Si:P samples of the present investigation fits well in the $\gamma(N)$ dependence of the Czochralski-grown Si:P samples. γ of Si:(P,B) is in good agreement with the values of uncompensated Si:P.[9,10] While important differences are observed among the different types of compensated Si:P, γ of nc-Si:P (Refs. 3 and 15) is noticeably higher than of Si:(P,B). Hence this large γ is probably not directly related to compensation, but arises from defects induced by irradiation. This is supported by the fact that in neutron-irradiated overcompensated Si:P ($K>1$) also a strongly magnetic-field-dependent linear contribution has been found.[15] With decreasing density of acceptors (upon annealing of the samples) γ passes through a minimum just where $K<1$.

Below 1.5 K an excess specific heat is observed in addition to the linear and cubic contributions. Figure 5 shows this excess specific heat $\Delta C = C-\gamma T-\beta T^3$ versus temperature for several concentrations. ΔC follows a power law, $\Delta C \sim T^{\alpha_S}$, between 0.06–0.08 and 0.3–0.6 K. As in uncompensated Si:P this power law is observed in both insulating and in just metallic samples. In nc samples such a power law has also been seen,[15] albeit in a smaller temperature range. The occurrence of a power law in ΔC on the insulating side arising from localized magnetic moments was explained by Bhatt and Lee.[17] Their phenomenological model starts from statistically distributed spin-1/2 moments with a broad distribution of exchange interactions J between spin pairs. In this pair approximation the couplings are treated in a hierarchical renormalization scheme, excluding iteratively the highest triplet levels and assuming the rest of the spins as free. This model in its original form yields only positive values for α_S. May[18] modified this model of hierarchically coupled spin pairs in order to account for the observation that both positive and negative values for α_S have been found.[8] As opposed to Bhatt and Lee, May[18] considers an upper limit of the distribution of J and obtains a maximum of the specific heat as a function of temperature at $T_{\max}$. $T_{\max}$ decreases with decreasing concentration. For a fixed temperature window this yields a change from $\alpha_S>0$ to $\alpha_S<0$ as experimentally observed for Si:P (Ref. 8) and, with larger scatter, also for nc-Si:P.[15] Figure 5 (inset) shows the exponent α_S as a function of carrier concentration N for the Si:(P,B) samples of the present study together with the other data just mentioned. The insulating fz-Si:P sample shows $\alpha_S<0$, which fits very well to the $\alpha_S(N)$ dependence of uncompensated Si:P, corroborating that $\alpha_S<0$ is not due to other impurities. $\alpha_S(N)$ of Si:(P,B) is negative over the whole concentration range measured and approaches barely zero for the metallic sample with $N=4.0\times 10^{18}$ cm^{-3}. For the higher concentrations, $N=13.0$ and 17.8×10^{18} cm^{-3}, an excess specific heat, which is expected to vanish rapidly well in the metallic region, could just be resolved against the γT and βT^3 contributions. However, a power-law fit is not reliable in this case due to the scatter in the very small ΔC. Taking the above models at face value, the more negative α_S's would imply an overall weakening of the pair exchange interaction in compensated samples compared to uncompensated ones.

On the metallic side of the MIT the Bhatt-Lee model is questionable because it is not clear if the RKKY interaction between localized magnetic moments via the itinerant electrons could be modeled into a similar pairwise coupling scheme. First of all, however, the coexistence of localized magnetic moments and itinerant electrons has to be considered. Several models have been put forward to explain the existence of localized magnetic moments in a strongly disordered metal.[19,20,9] They are all based on a disordered Anderson-Hubbard model with off-diagonal disorder, i.e., randomly distributed hopping energies t_{ij}, and weak on-site Coulomb repulsion U. Different types of mean-field approaches have been employed to establish a criterion for the existence of magnetic moments. The Anderson-Hubbard model is projected to a Kondo model in the parameter field where localized magnetic moments exist, with randomly distributed exchange constants J_{ij} between itinerant and localized electrons. This leads to a broad distribution $P(T_K)$ of Kondo temperatures $T_K \sim \exp[-1/N(E_F)J_{ij}]$, which can be modeled as $P(T_K) \sim T_K^{-\alpha_K}$ leading to a specific heat varying as $\Delta C \sim T^{1-\alpha_K}$ with an exponent $\alpha_K \sim 0.9$.[9] This compares favorably with $\alpha_S = 0.2$ for Si:P above the MIT,[9] while the present study yields $\alpha_S \simeq 0$ for Si:(P,B). This indicates that α_K varies between 0.8 and 1. An alternative interpretation would be to consider the electronic specific heat altogether, i.e., $C_e = C-\beta T^3$, rather than dividing the electronic specific heat into itinerant and localized-moments contributions. An

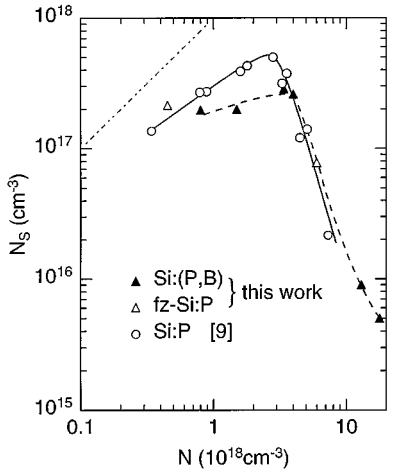

FIG. 6. Concentration of localized magnetic moments N_S vs carrier concentration as derived from the zero-field specific heat. Dashed-dotted line indicates $N_S=N$, solid and dashed lines are guides to the eye.

effective Landau theory for disorderd interacting electron systems was developed by Castellani and Di Castro[21] some time ago. They predict that $C_e\sim T^{0.4}$ for the general case (no symmetry-breaking fields) and $C_e\sim T^{1.2}$ for the case of magnetic impurities. Our data do not support these temperature dependencies, since we do not observe well-defined power laws in C_e (cf. Fig. 1). In addition, C in a magnetic field (to be discussed below) cannot be described at all with this model.

We now compare our zero-field specific-heat data on Si:(P,B) with the ESR-derived magnetic susceptibility χ of Hirsch *et al.*[6] as measured in 0.3 T. On the insulating side, $N\approx 2.6\times 10^{18}$ cm^{-3}, the smaller exponent of $\alpha_S\approx -0.3$ corresponds to a larger susceptibility exponent $\alpha_\chi\approx 0.75$ (Ref. 6) when compared to Si:P where $\alpha_S\approx 0.1$ and $\alpha_\chi\approx 0.6$. This relationship is very roughly in line with the prediction of the Bhatt-Lee model $\alpha_S=1-\alpha_\chi$. Recent measurements of the dc susceptibility of Si:P in very low fields[22] on the *same* samples as employed previously for the specific heat[8,9] have shown that the apparent contradiction $\alpha_S\neq 1-\alpha_\chi$ arises from the *assumption* of an algebraic distribution $P(J)\sim J^{\alpha_S-1}$. As a matter of fact, one can calculate ΔC from the measured χ with the Bhatt-Lee model and finds good agreement with the measured ΔC for insulating samples. Measurements of the low-field static susceptibility of Si:(P,B) are necessary to determine whether the same type of discrepancy between α_S and $1-\alpha_\chi$ noted above can be resolved in the same way. In the just metallic range, too, the same systematic difference of α_S and α_χ between Si:(P,B) and Si:P is observed: again one finds a smaller $\alpha_S\approx 0$ and larger $\alpha_\chi\approx 0.74$ in the former material.

The number of spins contributing to ΔC can be estimated from the entropy of the excess specific heat: $N_S=S/k_B\ln(2)$. Since $\Delta C/T$ increases for $T\to 0$ the entropy below our lowest measuring temperature cannot be estimated reliably. As a rough guess we have extrapolated C/T linearly to a finite value for $T=0$. Figure 6 shows N_S versus total carrier concentration N. The concentration of magnetic moments is similar to that in uncompensated Si:P with a strong decrease of N_S for $N>N_c$. However, even for $N\sim 3-4N_c$ magnetic moments are still observed. ESR measurements[6] on Si:(P,B) on the metallic side of the transition show for $N/N_c\sim 1.1$ a local-moment concentration for $T<0.1$ K that is larger by a factor 3–5. This coincides qualitatively with our finding of a larger ΔC at 0.1 K for Si:(P,B) than for Si:P (cf. Fig. 5 and Ref. 8). However, the *integrated* localized-moment concentration N_S is not larger in Si:(P,B) than in Si:P for $N>N_c$, as can be seen from Fig. 6. If anything, the Si:(P,B) data are a factor of 2 lower on the insulating side. As an aside, we note that the N_S for the two fz-Si:P samples falls nicely on the curve for Czochralski-grown Si:P samples.

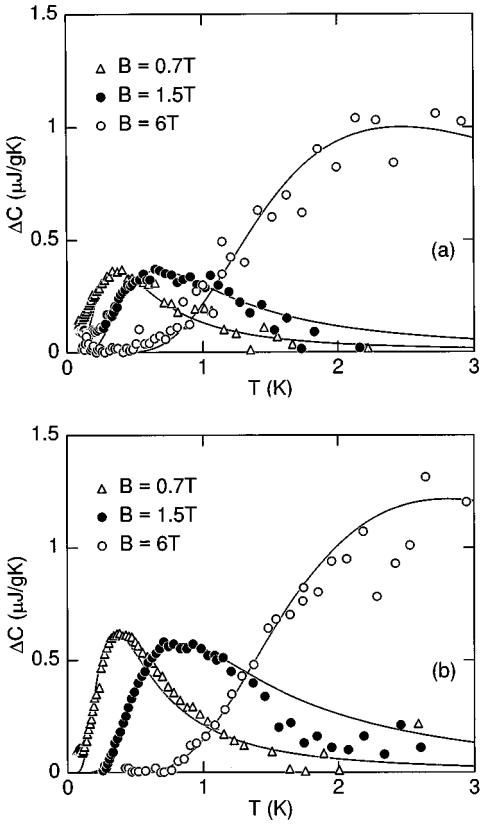

FIG. 7. Excess specific heat ΔC vs temperature in magnetic fields for (a) $N=4.0\times 10^{18}$ cm^{-3} and (b) $N=1.5\times 10^{18}$ cm^{-3}.

We now turn to the magnetic-field dependence of the specific heat. Figure 7 shows the excess specific heat ΔC in several magnetic fields for the metallic and an insulating sample of Figs. 1 and 2, respectively. Here ΔC was obtained for high fields ($B\geqslant 3$ T) by subtracting the zero-field βT^3 term because the phonon contribution is not expected to be field dependent. The remaining specific heat $C-\beta T^3$ can at lowest T be well described by a (field-dependent) γT term and a nuclear Zeeman term $b_N T^{-2}$, the latter being visible as an upturn in high fields. For lower fields, $B=0.7$ and 1.5 T, the zero-field γT term was used because ΔC is sizable at the lowest temperatures. ΔC can be well represented by Schottky anomalies. For large fields the height of the Schottky maximum increases, indicating a shift from itinerant to localized moments as has been discussed before.[8] Another possibility is that a large distribution of exchange interactions leads to an enhancement of the Schottky anomaly in high magnetic fields. It is interesting to note that the enhancement in 6 T compared to 0.7 and 1.5 T is roughly a

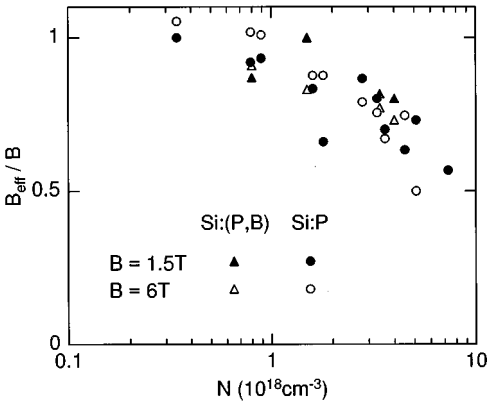

FIG. 8. Effective magnetic field B_{eff} (normalized to the applied field B) vs carrier concentration N for 1.5 and 6 T. Data for Si:P (Ref. 9) were actually taken in 5.7 T.

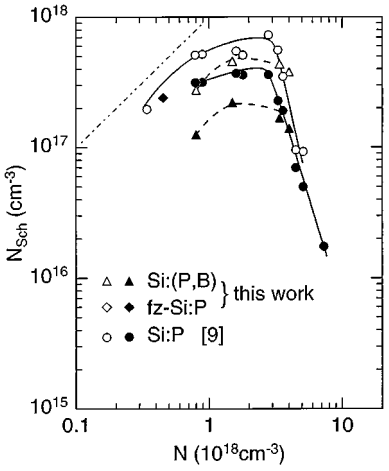

FIG. 9. Concentration of magnetic moments N_{Sch} vs carrier concentration as derived from Schottky-anomaly fits (open symbols $B\sim 6$ T, full symbols $B=1.5$ T). Dashed-dotted line indicates $N_{\mathrm{Sch}}=N$, solid and dashed lines are guides to the eye.

factor of 2, for both metallic and insulating sample, cf. Fig. 7. From the temperature of the Schottky maximum we obtain the effective field B_{eff}. Figure 8 shows B_{eff}/B for Si:(P,B), together with data for uncompensated Si:P, as a function of N. It is seen that B_{eff}/B decreases slowly from unity for small N below N_c and then decreases slightly more rapidly, although the large scatter in the data precludes a definite statement. The fact $B_{\mathrm{eff}}/B<1$ is readily explained by the predominantly antiferromagnetic interactions in the Bhatt-Lee model. There is good agreement between uncompensated and compensated samples.

The concentration of localized magnetic moments N_{Sch} as obtained from ΔC in 1.5 and $\sim$ 6 T is displayed in Fig. 9 where it is plotted versus N. Again, the data for Si:(P,B) are a factor of 2 lower than for Si:P in the just insulating region for a given B. Moreover, there is an average factor-of-2 difference for the data between 1.5 and $\sim$ 6 T in each material except for the most insulating sample, which was already discussed above. Note that here too the float-zone Si:P samples fit very well into the behavior of the Czochralski-grown uncompensated samples.

The existence of a comparable density of localized magnetic moments on the metallic side of Si:P and Si:(P,B) is proven by measurements of thermoelectric power $S(T)$. The maximum in $S(T)$ for $B=0$, which can be well described with the Kondo model, has roughly the same height and position for both Si:P (Ref. 13) and Si:(P,B),[14] implying a similar N_S.

In conclusion, we have shown that the linear term of the specific heat in Si:(P,B), nc-Si:P, and uncompensated Si:P on the metallic side of the MIT behaves as expected for a nearly-free-electron gas. On the insulating side the strong decrease of γ of uncompensated Si:P and Si:(P,B) is comparable and in contrast to nc-Si:P with a higher value of γ, which probably is related to irradiation-induced defects. The excess specific heat of Si:(P,B) arising from localized magnetic moments is overall similar to that of uncompensated Si:P, with a large contribution to C even on the metallic side of the MIT, but the exponent α_S remains negative in the metallic region. This might account for the discrepancy to the ESR-derived susceptibility where a larger concentration of local moments was inferred in Si:(P,B) than in Si:P. On the just insulating side of the MIT, the total concentration is actually a little smaller. These rather small differences, which need to be explored theoretically in more detail, cannot, however, account for the apparently different critical behavior in the electrical conductivity of Si:P and Si:(P,B).

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