Local moments at the metal-insulator transition in Ge:Sb as probed with specific-heat measurements in magnetic fields

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Specific-heat measurements at low temperatures ($0.07 \leq T \leq 1.6$ K) are reported for Ge:Sb with donor concentrations between 0.6 and 4.0×10^{17} cm^{-3} spanning across the metal-insulator transition at $N_c = 1.44\times10^{17}$ cm^{-3}. The electronic coefficient γ of the specific heat C is roughly twice as large as expected for donor electrons with the Ge conduction-band effective mass. Below about 0.3 K an additional contribution to C is found which is attributed at least partly to exchange-coupled clusters of local moments. This is supported by measurements of C in magnetic fields where this contribution turns into a Schottky-like anomaly. Local moments persist also in the metallic region of Ge:Sb as previously inferred from magnetic susceptibility measurements. The dependence of the density of local moments on donor concentration is similar to that found previously in Si:P.

I. INTRODUCTION

The metal-insulator transition in highly doped semiconductors is a topic of considerable current interest. Much work has been devoted to the study of heavily doped Si, notably to Si:P,[1,2] where the existence of local moments also on the metallic side of the metal-insulator (MI) transition has been established by a number of measurements.[3,4] With measurements of the specific heat, in particular its magnetic-field dependence, the concentration of local magnetic moments could be determined systematically[5] as a function of donor concentration N on both sides of the MI transition occurring at $N_c = 3.6\times10^{18}$ cm^{-3}. At N_c, roughly 5–10% of the donor electrons are localized, and even at $N \approx 2N_c$ local moments could be detected at the 1% level.[5] Although their role on transport properties on the metallic side has been elusive, the scattering of conduction electrons by local moments near the MI transition was very recently demonstrated convincingly by the observation of a large magnetic-field-dependent anomaly in the thermoelectric power.[6]

Local moments were also detected in Ge:Sb on the metallic side of the MI transition by magnetic susceptibility measurements,[7] similar to Si:P. However, in Ge:Sb the critical concentration is more than an order of magnitude lower, $N_c = 1.44\times10^{17}$ cm^{-3}.[8] Also, the critical behavior of the electrical conductivity σ differs from that of (uncompensated) Si:P. In the latter, $\sigma(0)$ as extrapolated to zero temperature varies as $\sigma(0) \propto (N-N_c)^{\mu}$ with $\mu \approx 0.5$ (Ref. 9) while in Ge:Sb recent precise measurements showed $\mu = 0.9$.[8] Very recently a crossover behavior of μ was reported for Si:P with $\mu \approx 1.3$ very close to N_c (for $N_c \leq N \leq N_{cr} = 1.1N_c$) and $\mu \approx 0.64$ for $N > N_{cr}$.[10] It seemed, therefore, worthwhile to conduct a systematic specific-heat study also on Ge:Sb, although the low value of N_c and the rather large lattice contribution to the specific heat compared to Si:P make the signal-to-noise ratio very unfavorable. In the present paper we report on the results of such a study which indicates the overall similar behavior between Si:P and Ge:Sb. In particular, our results corroborate the existence of local magnetic moments on the metallic side of the MI transition.

II. RESULTS AND DISCUSSION

The Ge:Sb samples (with Sb concentrations $N = 0.6$, 1.3, and 4.0×10^{17} cm^{-3}, and nominally pure Ge) used in the present study were the same as used previously for other investigations.[7] They were of the form of small cylinders (diameter 6 mm, height 7 mm). The concentration was determined from the Hall effect measured at room temperature (without correction due to the Hall scattering factor). The specific heat was measured with the standard heat-pulse technique in the temperature range 50 mK to 3 K and in magnetic fields up to 6 T.

Figure 1 shows the temperature dependence of the specific heat C plotted as C/T vs T^2 for all samples in the temperature range up to $T = 1.6$ K. Above about 0.3 K all samples exhibit a straight line in this plot, i.e., $C/T = \gamma + \beta T^2$. From the slope β we obtain a Debye temperature $\Theta_D = 335$ K which is somewhat lower than the literature value $\Theta_D = 373$ K for pure Ge.[11] C/T for all samples exhibits a finite intersection γ with the ordinate. The finite γ even for the nominally pure Ge crystal might be due to the impurities. γ increases with N (see inset of Fig. 1) and is larger by roughly a factor of 2 than expected within the free-electron model when taking the effective mass m^* of the Ge conduction band and the valley degeneracy ($v = 4$) into account, $\gamma = \frac{1}{3}(k_B/\hbar)^2 k_F m^*$, where $k_F = (3\pi^2 N/v)^{1/3}$ (cf. the solid line in the inset of Fig. 1). Below about 0.3 K, C/T increases strongly towards low T as has been observed before for Si:P.[2,12]

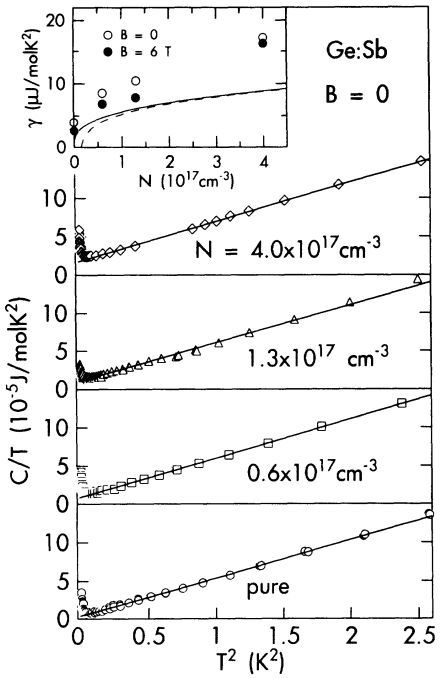

FIG. 1. Specific heat C of Ge:Sb for different Sb concentrations N plotted as C/T vs T^2. Here and throughout this paper 1 mol refers to the amount of Ge. Inset shows linear specific-heat coefficient γ vs N for $B=0$ and 6 T together with the free-electron values using the Ge conduction-band effective mass and valley degeneracy (solid line indicates γ for $B=0$ and dashed line for $B=6$ T).

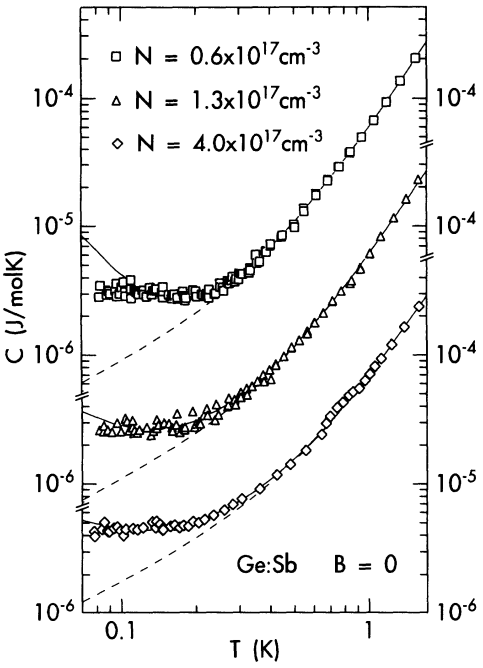

FIG. 2. Specific heat C of Ge:Sb vs temperature T (log-log). Dashed lines indicate the extrapolation of $C=\gamma T+\beta T^3$ towards low T. Solid lines are fits of $C=\gamma T+\beta T^3+\Delta C$ and include the additional low-T contribution ΔC (see text).

This upturn in the doped samples is attributed to local magnetic moments; for the pure Ge sample its possible origin will be discussed below.

Measurements in a magnetic field $B=6$ T were performed in order to check for a possible magnetic-field dependence of γ. (β is, of course, expected to be independent of magnetic field which was indeed verified.) γ was determined for $B=6$ T from a C/T vs T^2 plot (not shown). The result is included in the inset of Fig. 1. A slight decrease of γ in 6 T is observed which can be mainly attributed to the decrease of γ in the nominally pure Ge. The expected decrease of γ due to the spin splitting of the density of states (assuming a free-electron density of states) is also indicated in the inset of Fig. 1 (cf. dashed line) and is much smaller than the measured decrease for the doped samples. It is known from the study of neutron-irradiated compensated Si:P in the insulating region well below N_c that irradiation-induced defects lead to a sizable γ which is strongly reduced in a magnetic field.[13] We therefore speculate that such defects, and possibly also impurities, both giving rise to states in the gap, lead to the finite γ, and also to the low-T upturn in pure Ge. The problem is aggravated because of the very low-doping level in our samples which could also lead to some unintentional compensation.

Figure 2 shows specific heat vs T for $B=0$ on a log-log plot. The upturn away from the extrapolated high-T behavior (dashed lines) towards low T is clearly visible. The solid lines represent fits of $C=\gamma T+\beta T^3+\Delta C$ to the data with $\Delta C\sim T^{\alpha}$. Figure 3 displays $\Delta C=C-\gamma T-\beta T^3$ vs T on a log-log plot showing that α varies between -2.4 and -1.1, as indicated by the straight lines in Fig. 3. Indeed, a similar contribution ΔC was found in Si:P with $\alpha\approx 0.2$ on the metallic side. With dilution α

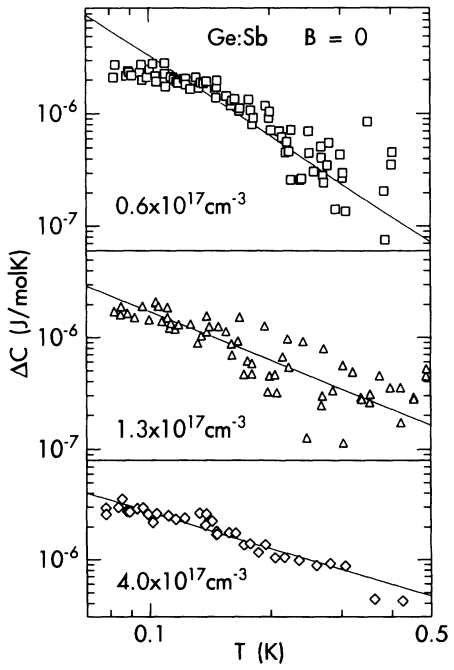

FIG. 3. Anomalous specific-heat contributions $\Delta C=C-\gamma T-\beta T^3$ as a function of temperature T. Solid lines indicate $\Delta C\sim T^{\alpha}$.

decreased and became negative, reaching $\alpha \approx -0.3$ at the lowest concentration ($\approx 0.1 N_c$). The excess contribution was attributed to exchange-coupled clusters of local moments in the spirit of the Bhatt-Lee model[14] of a hierarchy of antiferromagnetic pairs of local moments.

We interpret the anomalous contribution ΔC found in the present work along the same lines as previously found for Si:P. A recent extension of the Bhatt-Lee model taking into account the distribution of exchange couplings J yielded a satisfactory explanation also of the negative values of α.[15] In brief, the negative values of α result from the shift of the maximum of the distribution at J_0 to lower exchange energies with increasing dilution, when the thermal energy becomes larger than J_0. The overall negative values of α found for Ge:Sb with the same trend of an increase of $|\alpha|$ with decreasing N would indicate a correspondingly lower scale of the distribution of J with respect to Si:P. This might correspond to the overall lower scale of energies in Ge:Sb as compared to Si:P (cf. 9.6 meV vs 45 meV for the distance of the donor level from the conduction-band minimum). On the other hand, the magnetic susceptibility of Ge:Sb showed an overall similar behavior to that of Si:P for the same reduced concentration.[7] This point deserves further investigations.

In order to clarify the origin of the low-T upturn and the assignment in terms of exchange-coupled clusters, we measured C in several magnetic fields. As an example, Fig. 4 shows C vs T for the sample with $N = 1.3 \times 10^{17}$ cm^{-3} on a log-log scale for different fields $B = 0$, 0.8, 1.5, and 6 T. C is strongly influenced by the magnetic field. However, most of the low-T increase of C with B must be attributed to a contribution $b_N T^{-2}$ of ^{73}Ge nuclei (the contribution of ^{121}Sb and ^{123}Sb is negligible). In fact, the

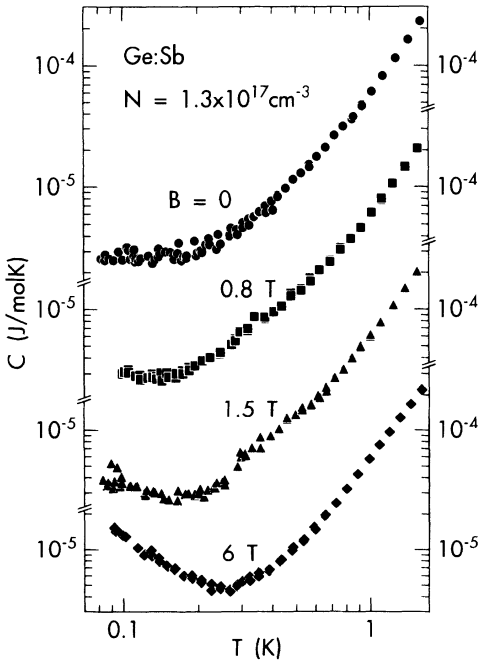

FIG. 4. Specific heat C of a Ge:Sb sample vs temperature T in several magnetic fields B.

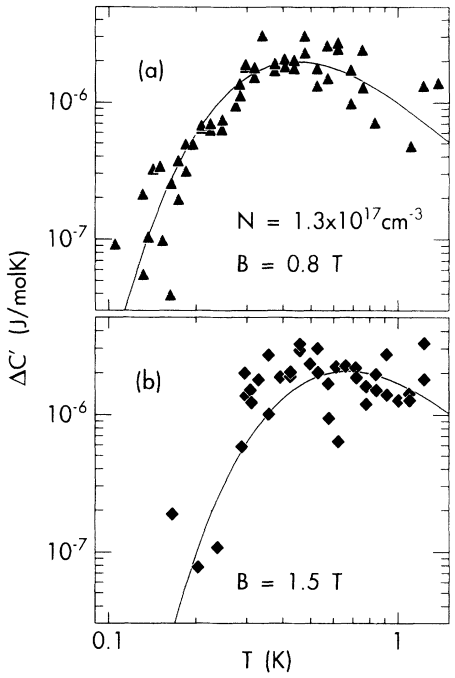

FIG. 5. Anomalous specific-heat contribution $\Delta C' = C(B) - \gamma(B)T^3 - \beta T^3 - b_N(B)T^{-2}$ for $N = 1.3 \times 10^{17}$ cm^{-3} as a function of temperature T for (a) $B = 0.8$ T and (b) $B = 1.5$ T.

expected coefficient of this contribution is $b_N = 2.72 \times 10^{-8}\ B^2$ J K/mol T^2. Experimentally b_N is between 1 and 1.5×10^{-7} J K/mol in $B = 6$ T for the insulating samples and increases to 5.5×10^{-7} for the metallic sample. These values are smaller than expected in-

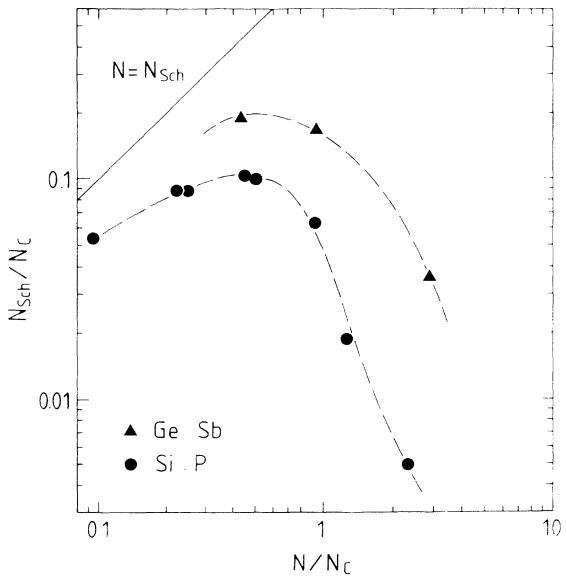

FIG. 6. Density of local moments N_{Sch} as determined from the Schottky anomaly in $B = 1.5$ T as a function of donor concentration N for Ge:Sb and Si:P, normalized to the respective critical concentration N_c. Data for Si:P after Ref. 5.

dicating that the spin-lattice relaxation time for ^{73}Ge nuclei is very long even in the metallic samples and most of the nuclear specific heat is not observable in the time window of our experiment (1–10 s). This agrees with NMR measurements in Ge:As where at the MI transition the spin-lattice relaxation time T_1 measured at 4.2 K is 100–200 min.[16] The increase of b_N in the metallic sample with respect to the insulating ones might indicate the onset of the Korringa relaxation.

Figure 5(a) shows the specific-heat anomaly $\Delta C'$ for $N=1.3\times10^{17}$ cm^{-3} in $B=0.8$ T. Here $\Delta C'=C-\gamma(B)-\beta T^3-b_N(B)T^{-2}$. γ and β are obtained from high-temperature fits of C/T vs T^2 such as shown in Fig. 1, and $b_N(B)$ was determined assuming a T^{-2} behavior below 0.15 K. $\gamma(B)$ was obtained assuming a linear field dependence between 0 and 6 T. $\Delta C'$ amounts to roughly 10% of C at low T and decreases to 1% near 1 K. $\Delta C'$ can be very well represented by a Schottky anomaly suggesting the existence of spin-$\frac{1}{2}$ two-level systems with a density of $N_{\rm Sch}=2.7\times10^{16}$ cm^{-3} and an effective field $B_{\rm eff}=0.9$ T. Figure 5(b) shows $\Delta C'$ for the same sample in $B=1.5$ T. We obtain $N_{\rm Sch}=2.5\times10^{16}$ cm^{-3} and $B_{\rm eff}=1.2$ T. As in Si:P, $N_{\rm Sch}$ is independent of B up to 1.5 T. The scaling of $B_{\rm eff}$ with field is only fair.

Finally, Fig. 6 shows the density of local moments $N_{\rm Sch}$ plotted versus the total number N of donor electrons in Ge:Sb. Both quantities are normalized to $N_c=1.44\times10^{17}$ cm^{-3}, in order to facilitate a comparison with Si:P studied earlier.[5] The Si:P data are plotted with $N_c=3.6\times10^{18}$ cm^{-3}. The behavior of both metal-insulator systems is strikingly similar, despite the difference of a factor of 25 in N_c. Here the Si:P data[5] were also taken in 1.5 T. This is important because of the dependence of the height of the Schottky anomaly on magnetic field at larger fields.[5,17] This point could not be investigated in the present system due the low concentration of local moments and the corresponding lack of accuracy. The relative concentration of local moments right at the MI transition corresponds to roughly 15% of the donor electrons in Ge:Sb and 5% in Si:P.

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