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Current issues in the physics of heavily doped semiconductors at the metal –insulator transition

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Current issues in the physics of heavily doped semiconductors at the metal–insulator transition

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Heavily doped semiconductors, in particular Si:P and Si:B, have been prototype materials for the study of the metal–insulator (MI) transition at low temperature, T. Because of the statistical distribution of donors or acceptors in the (usually single-crystalline) host, disorder plays a crucial role for the MI transition. In addition, electron–electron interactions are important as evidenced by the rather large corrections to the Boltzmann conductivity already far above the MI transition. Usually, the MI transition is investigated by studying samples of varying dopant concentrations, N, although stress tuning and magnetic-field tuning have also been employed. An issue of considerable importance which we will discuss in this review is the critical behaviour of the electrical conductivity, $\sigma(T \to 0) \sim (N - N_c)^{\mu}$, close to the critical dopant concentration N_c, i.e. the exponent puzzle of $\mu \approx 0.5$ versus $\mu \approx 1$. The question of critical behaviour of the Hall constant will also be addressed. We further discuss the role of magnetic moments on thermodynamic and transport properties close to the MI transition. It has been known for some time that localized moments which of course are present on the insulating side of the MI transition, exist also on the metallic side. Only recently, however, was their influence detected on a transport property, namely the thermoelectric power. We review some of the salient features of local magnetic moments at the MI transition and report on measurements of the specific heat and magnetization *on the same samples*. The direct comparison of thermodynamic quantities allows a test of models for local moments at the MI transition. Finally, thermoelectric-power measurements together with electrical resistivity reveal strong differences between uncompensated Si:P and compensated Si:(P,B) on the insulating side of the MI transition, with evidence of opening of a Hubbard gap in Si:P only considerably below N_c.

Keywords: doped semiconductors; critical behaviour; Hall constant; electronic transport properties; localized magnetic moments

1. Introduction

Heavily doped semiconductors have long been among the favourite research subjects concerning metal–insulator transitions. They are prime candidates for a quantum phase transition occurring strictly only at $T = 0$. In this strict sense, we denote a solid as metallic when the DC conductivity $\sigma(T)$ remains finite for $T \to 0$ and as insulating when $\sigma(0) = 0$. Here we focus on metal–insulator (MI) transitions which involve a transition from delocalized to localized states, as opposed to band-like transitions such as Bloch transitions due to energetic separation of initially overlapping

bands or Peierls transitions due to a lattice distortion. The two generic mechanisms driving the delocalization–localization MI transition are disorder in a single-electron picture (Anderson transition) or electron–electron interactions (Mott–Hubbard transition). Of course, in real systems both disorder and electron–electron interactions are present which render this field interesting and difficult to treat at the same time. For instance, the progressively slower electron diffusion in a disordered metal as the MI transition is approached leads to a progressive loss of screening and hence to an enhancement of the electron–electron interactions (for reviews see Lee & Ramakrishnan 1985; Belitz & Kirkpatrick 1994). Early suggestions considered the MI transition to be discontinuous (Mott 1990) while scaling approaches suggested a continuous second-order transition (Abrahams *et al.* 1979) for three-dimensional systems. Since then, a lot of theoretical (Lee & Ramakrishnan 1985; Belitz & Kirkpatrick 1994) and experimental (for a review on Si:P, see Rosenbaum *et al.* 1983; for Si:B, see Sarachik 1995) effort has been invested in delineating the critical properties of the MI transition. In particular, the critical behaviour of the electrical conductivity $\sigma(0) \sim (N - N_c)^{\mu}$ has received close experimental scrutiny. Here N is the doping concentration and N_c is the critical concentration.

Several investigations, notably on uncompensated semiconductors, have reported $\mu \approx 0.5$ (for reviews see Rosenbaum *et al.* 1983; Sarachik 1995) while $\mu = 1$ for uncompensated semiconductors and most amorphous alloys. This apparent classification into $\mu \approx 0.5$ and $\mu \approx 1$ without a clear physical distinction with respect to universality classes constitutes the 'exponent puzzle' (Thomas 1985; von Löhneysen 1990). We have recently offered a possible solution to this puzzle (Stupp *et al.* 1993) which stirred a lot of interest and debate. The key point of the argument is to limit the critical region to the small concentration range above N_c where $\sigma(T)$ actually decreases with decreasing T, i.e. becomes more 'insulating like'. For instance, above $N \approx 1.1N_c$ in Si:P $m = \mathrm{d}\sigma/\mathrm{d}\sqrt{T}$ becomes negative up to rather large N due to the multi-valley nature of the conduction band. In the first part of this review, we will present a summary of the recent discussion of this issue including the question of the critical behaviour of the Hall constant close to N_c.

Another very interesting problem is the role of magnetic moments. It has been known for a long time that a small fraction of the localized moments derived from the spin-degenerate groundstate of the hydrogenic-like donor (or acceptor) wave function on the insulating side, survives on the metallic side of the MI transition. On the insulating side, the magnetic moments have been modelled by Bhatt & Lee (1982) with a hierarchy of exchange-coupled antiferromagnetic pairs. A stringent test of this model is possible by directly measuring the susceptibility and specific heat systematically on the same samples. This has been done only recently (Schlager & von Löhneysen 1998). We will also discuss briefly the origin of the localized moments on the metallic side of the MI transition. Although they have been observed in a number of magnetic (Paalanen *et al.* 1986; Alloul & Dellouve 1978; Roy & Sarachik 1988) and specific-heat (Marko *et al.* 1974; Kobayashi *et al.* 1977; Lakner & von Löhneysen 1989) measurements, their role on the electrical resistivity has been elusive. However, as has been shown recently, they lead to a pronounced Kondo-like anomaly in the thermoelectric power both in uncompensated Si:P (Lakner & von Löhneysen 1993) and compensated Si:(P,B) (Ziegler *et al.* 1996). Furthermore, although the localized moments do not lead to spin-flip scattering processes that directly affect the electrical conductivity, these spin-flip processes influence the electron–electron interaction leading to a shallow maximum in $\sigma(T)$ of Si:P in the crossover region $N \approx N_c$ where the overall T dependence changes from $m > 0$ to $m < 0$ (Blaschette *et al.* 1996).

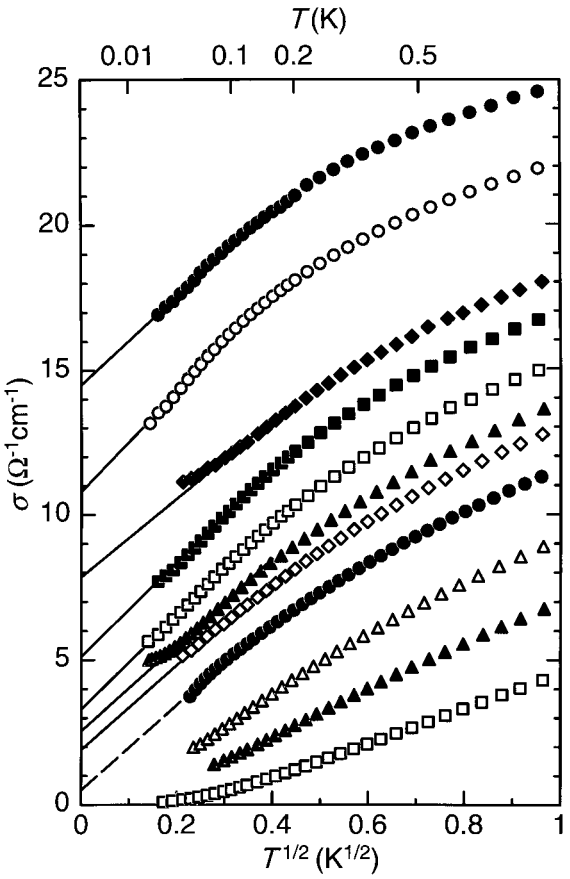

Figure 1. Electrical conductivity σ versus $\sqrt{T}$ of Si:P close to the MIT. P concentrations (in 10^{18} cm^{-3}) are from top to bottom: 3.69, 3.67, 3.63, 3.60, 3.58, 3.56, 3.55, 3.52, 3.50, 3.45, 3.38 (after Stupp *et al.* 1993).

Distinct differences appear between Si:P and Si:(P,B) in the transport properties on the insulating side of the MI transition (Liu *et al.* 1996). These are a direct manifestation of the Hubbard interaction. For uncompensated Si:P the non-interacting-electron picture always leads to a half-filled band due to the spin degeneracy of the lowest valley-orbit split 1s (A_1) hydrogenic level. Hence the on-site electron–electron interaction which is certainly present in the dilute limit because the negatively charged doubly occupied donor is barely stable in the single-impurity limit, leads to a completely occupied lower and empty upper Hubbard band. The splitting into lower and upper Hubbard bands then causes concentration-dependent anomalies in the thermoelectric power which are absent in compensated Si:(P,B) because there the lower Hubbard band always contains unoccupied, albeit localized levels.

2. Critical behaviour of the electrical conductivity and Hall constant

As mentioned in the introduction, the question of the critical behaviour of the conductivity has been a subject of considerable controversy. In a pioneering and very elegant experiment, Paalanen *et al.* (1982) tuned a single just insulating Si:P sample through the MI transition by applying uniaxial stress at very low T. These

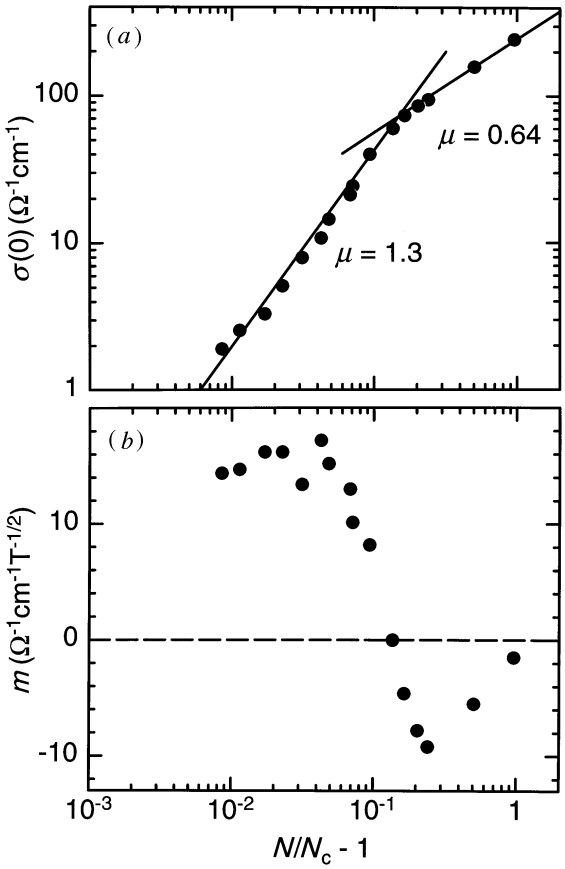

Figure 2. (*a*) $\sigma(0) = \sigma(T \to 0)$ and (*b*) $m = \mathrm{d}\sigma/\mathrm{d}\sqrt{T}$ versus reduced concentration $N/N_\mathrm{c} - 1$, with $N_\mathrm{c} = 3.52 \times 10^{18}\mathrm{cm}^{-3}$ (after Stupp *et al.* 1993).

experiments clearly indicated an exponent $\mu \approx 0.5$ (Paalanen *et al.* 1982; Thomas *et al.* 1983). We show in figure 1 our more recent data of $\sigma(T)$ on Si:P for P concentrations close to the MI transition (Stupp *et al.* 1993). The data are plotted versus $\sqrt{T}$, this dependence is approximately obeyed between 35 mK and 150 mK. The slight upturn at the lowest T can be attributed to thermal decoupling from the cold source. Although our data do not extend as low as previous data (Paalanen *et al.* 1982; Thomas *et al.* 1983; Rosenbaum *et al.* 1980), the overall similar T dependence for our samples makes the extrapolation to $T = 0$ (solid lines in figure 1) rather unambiguous except for samples with $N \leqslant 3.52 \times 10^{18}\ \mathrm{cm}^{-3}$. Note that these data comprise the largest set of samples with $m > 0$ for uncompensated semiconductors. As mentioned in the introduction, it is peculiar to Si:P and Ge:Sb (due to the multivalley nature) that the effective Hartree term in the conductivity correction due to electron–electron interactions (Lee & Ramakrishnan 1985; Belitz & Kirkpatrick 1994) is larger than the exchange term, leading to $m < 0$ for $N > 1.1N_\mathrm{c}$ above the MI transition (see figure 2*b*). Spin-orbit effects may perhaps similarly lead to this behaviour because it is observed also for Si:B (Rosenbaum *et al.* 1983; Sarachik 1995).

Figure 2*a* shows $\sigma(0)$ versus reduced concentration $(N - N_\mathrm{c})/N_\mathrm{c}$ with $N_\mathrm{c} = 3.52 \times 10^{18}\mathrm{cm}^{-3}$, as inferred from figure 1. A crossover of the critical exponent μ from

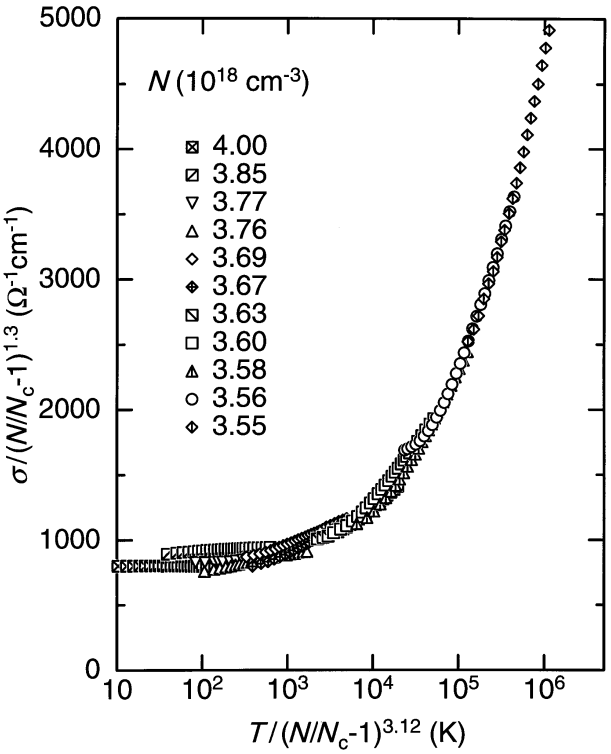

Figure 3. Scaling plot of the electrical conductivity $\sigma(T, N)$ of Si:P with $N_c = 3.52 \times 10^{18}$ cm^{-3} (after Stupp *et al.* 1994*a*).

$\mu = 0.5$ to 1.3 with decreasing N is observed upon approaching N_c. The crossover coincides with the concentration where m changes sign. Hence the main objections to $\mu = 0.5$ are: (i) the fit is actually best in the non-critical region where $m < 0$; (ii) samples with $\sigma < 20\,\Omega^{-1}$ cm^{-1} i.e. most of the samples with $m > 0$, are not at all described by the $\mu = 0.5$. On the other hand, the main objection to $\mu = 1.3$ is that samples close to N_c exhibit rounding due to an inhomogeneous P distinction (Rosenbaum *et al.* 1994). In fact, it was shown that stress-tuning data close to the MI transition exhibited a considerable sample dependence (Rosenbaum *et al.* 1994) as opposed to the data of figure 1 which show a steady change of σ as the MI transition is approached (except for the thermal decoupling mentioned above).

It is noteworthy that dynamic scaling for the $\sigma(T, N)$ data of figure 1 is fulfilled (Stupp *et al.* 1994*a*). In a three-dimensional system, the appropriate scaling function is

$$\frac{\sigma(N,T)}{[(N-N_c)/N_c]^{\nu}} = \mathcal{F}\left(\frac{T}{[(N-N_c)/N_c]^{z\nu}}\right), \tag{2.1}$$

with ν being the localization-length exponent and z the dynamical exponent (Lee & Ramakrishnan 1985; Belitz & Kirkpatrick 1994). Wegner scaling predicts $\mu = \nu$ in three dimensions. The scaling plot of figure 3 for data $N_c \leqslant N \leqslant 1.1N_c$ and $T < 0.44$ K suggests $\nu = 1.3$ and $z = 2.4$, in agreement with $\mu = 1.3$. Conversely, it has been shown by Belitz & Kirkpatrick (1994) that dynamical scaling is not obeyed well for the stress-tuning data.

Another objection concerns just this dynamic scaling function. Castner (1994)

suggested that data above 100 mK for samples close to the MI transition which we classify as metallic, can be described by Mott variable-range hopping (VRH) which is characteristic of insulating behaviour, i.e. $\sigma(T) = \sigma_0 \exp(-(T_0/T)^p)$ with $p = \frac{1}{4}$. However, the temperatures, T_0, obtained are actually smaller than the measuring temperatures while the Mott VRH law is derived assuming $T < T_0$. In addition, *all* low-T data ($T < 100$ mK) of figure 1 were discarded by Castner because they do not follow the Mott VRH fit. Furthermore, noting that in a large magnetic field $\sigma(T)$ follows a $\sqrt{T}$ dependence much closer (Stupp *et al.* 1993, 1994*b*; Hornung *et al.* 1994), it is not conceivable how a postulated zero-field VRH behaviour could possibly turn into a quasimetallic $\sqrt{T}$ behaviour in a large field, given that the magnetoconductance in Si:P is always negative in the N, T, B range under consideration. Therefore, the above arguments (Castner 1994) have to be met with some reservation.

A suggestion by Shlimak *et al.* (1996) to take the $\sigma(T, N)$ at finite (easily accessible) temperatures $T > T_1$ begs the question because it presupposes that $\sigma(T, N)$ for $T < T_1$ can be described by $\sigma = \sigma(0, N) + \delta\sigma(T)$ with the second term independent of N. Hence more experiments are needed. In particular, it would be nice to stress tune a sample right through the MI transition by monitoring the divergence of the dielectric constant on the insulating side and the emergence of a finite $\sigma(0)$ on the metallic side at the same critical concentration.

The question of critical behaviour of the Hall constant R_{H} has been an issue of considerable controversy. Theoretically, R_{H} is predicted to be non-critical for an Anderson transition without electron–electron interactions, while the latter lead to a divergence of R_{H}^{-1} at the MI transition. On the other hand, critical behaviour of R_{H}^{-1} has recently been suggested for a transition driven purely by disorder (Wang *et al.* 1992). Experimentally, earlier reports suggested non-critical behaviour of R_{H}^{-1} (Koon & Castner 1988) with the possible exception of Ge:Sb (Field & Rosenbaum 1985). More recently, a divergence of R_{H}^{-1} with an exponent $\mu_{\mathrm{H}} \approx 0.4$ has been found for Si:B (Dai *et al.* 1993) and Si:P (Dai *et al.* 1994; Madel *et al.* 1997) by extending the measurements to temperatures down to $\lesssim 0.05$ K. However, there has been considerable dispute over the data interpretation (Castner 1995; Dai *et al.* 1995). Part of the discussion is aimed at the determination of 'correct' critical concentration N_{c}. It is important to realize that the absolute dopant concentration for Si:P, for example, is not known accurately, in fact, two different scales that differ by several percent are used. This causes considerable confusion. However, as long as a single consistent scale is used in an experiment or in a set of different experiments, the exact absolute concentration is not relevant for the critical behaviour if the concentration range around the critical point is much smaller than N_{c}.

3. Localized magnetic moments

Localized magnetic moments in heavily doped semiconductors have been mostly detected with magnetization, magnetic resonance and specific heat. The dependence of the concentration of localized moments on the P concentration N has been mapped out systematically from specific-heat measurements for Si:P (Lakner & von Löhneysen 1989; Lakner *et al.* 1994) and more recently also for Si:(P,B) (Wagner *et al.* 1997). The data for Si:P are shown in figure 4 with the behaviour of Si:(P,B) being quite similar. The concentration of local moments has been determined (i) from the zero-field excess specific heat $\Delta C = C - \gamma T - \beta T^3$, i.e. conduction electron and phonon contributions substracted from the measured specific heat C, via the

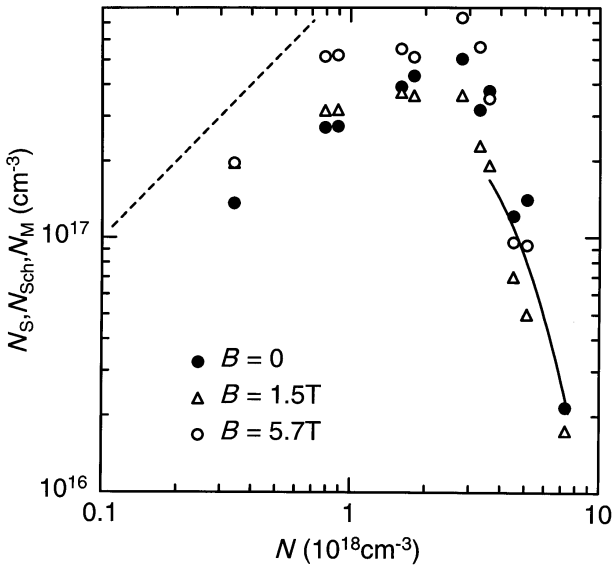

Figure 4. Concentration of magnetic moments N_S determined experimentally in zero field, and N_{Sch} in finite magnetic fields 1.5 and 5.7 T versus doping concentration. Dashed line indicates $N_{Sch} = N$ expected in the dilute insulating limit. Solid line gives the concentration of local moments N_M in the metallic phase as calculated theoretically (after Lakner *et al.* 1994).

entropy $S = \int(\Delta C/T)\,\mathrm{d}T = N_S \ln 2$; and (ii) from the Schottky anomaly observed in applied magnetic fields $B = 1.5$ and 5.7 T, yielding N_{Sch}. In both cases, $S = \frac{1}{2}$ is assumed for the spin. The dependence of N_S and N_{Sch} on N is not critical at N_c. Due to the disorder some localized moments survive in the metallic state (see below). The fact that $N_S < N_{Sch}$ on the insulating side can be readily explained because truly isolated spins do not contribute to N_S but, of course, undergo a Zeeman splitting and therefore contribute to C in a magnetic field. On the other hand, due to interactions between moments the Schottky anomalies become broadened and hence N_{Sch} obtained from the height of the Schottky anomaly underestimates the number of local moments for heavily doped Si:P. Likewise the (predominantly antiferromagnetic) interactions can be overcome by large applied magnetic fields B and this leads to $N_{Sch}(5.7\ \mathrm{T}) > N_{Sch}(1.5\ \mathrm{T})$, as seen in figure 4. The increasing importance of antiferromagnetic interactions can also be inferred from the concentration dependence of the effective field B_{eff} as determined from the temperature of the Schottky maximum: while $B_{eff}/B \approx 1$ for $N < 10^{18}\ \mathrm{cm}^{-3}$, this ratio is approximately 0.7 at N_c and decreases to 0.5 at $2N_c$ (Lakner *et al.* 1994).

The random distribution of dopant atoms leads to a wide distribution of nearest-neighbour distances and, hence, nearest neighbour exchange couplings. (A random distribution of P in heavily doped Si:P was indeed proven recently by the direct imaging of P atoms by scanning tunneling microscopy and spectroscopy (Trappmann *et al.* 1997).) This wide distribution of exchange couplings led Bhatt & Lee (1982) to a description of the magnetic properties of doped semiconductors in terms of a hierarchical coupling of antiferromagnetic pairs of localized moments. In this model, only free spins which are not coupled to pairs at a given T (with density $N_{free}(T)$) contribute to the specific heat at that temperature with

$$C_{loc} = k_B T \ln 2\, \mathrm{d}N_{free}(T)/\mathrm{d}T, \tag{3.1}$$

while the magnetic susceptibility is given by

$$\chi_{\rm loc} = \mu_0 \mu_{\rm B}^2 N_{\rm free}(T)/k_{\rm B}T. \tag{3.2}$$

Hence if $C_{\rm loc}$ follows an algebraic T dependence, $C_{\rm loc} \sim T^{\alpha_{\rm c}}$, then $\chi_{\rm loc} \sim T^{-\alpha_{\rm m}}$ with $\alpha_{\rm m} = 1 - \alpha_{\rm c}$. It was found some years ago (Lakner & von Löhneysen 1989; Lakner *et al.* 1994) that the excess specific heat ΔC of Si:P varies roughly algebraically, $\Delta C \sim T^{\alpha}$, with $\alpha \approx 0.2$ in the metallic region and $\alpha \leqslant 0$ for the most insulating samples, the latter implying that if a strict algebraic T dependence were the case then $\alpha_{\rm m} > 1$ in the Bhatt–Lee model, which is not observed. The magnetic susceptibility $\chi_{\rm loc}(T)$ due to localized moments always varies with an exponent $\alpha_{\rm m} < 1$ if algebraic behaviour is assumed.

Figure 5 shows $\chi_{\rm loc}$ (with the Pauli paramagnetism and core and Landau diamagnetism subtracted, normalized to the Curie susceptibility of N independent $S = \frac{1}{2}$ moments at 1 K) versus T on a log–log plot (Schlager & von Löhneysen 1998). Similar data have been reported before (Ootuka & Matsunaga 1990). The clear curvature of the data for $N = 0.34 \times 10^{18}\ {\rm cm}^{-3}$ illustrates that an algebraic T dependence of $\chi_{\rm loc}$ is, in fact, not observed. In order to test more generally the validity of the Bhatt–Lee model we calculate $C_{\rm loc}$ from $\chi_{\rm loc}$ with the above equations and compare it in figure 6 to ΔC as measured directly (Lakner & von Löhneysen 1989; Lakner *et al.* 1994). Indeed, the decrease of ΔC with increasing T for $N = 0.34 \times 10^{18}\ {\rm cm}^{-3}$ is reproduced quite well by the calculation of $C_{\rm loc}$ and the absolute values of ΔC and $C_{\rm loc}$ coincide. Likewise, the data of ΔC for $N = 1.6 \times 10^{18}\ {\rm cm}^{-3}$—now increasing with increasing T—are reproduced almost quantitatively by the calculation. These findings indicate the validity of the Bhatt–Lee model in the insulating state. However, with increasing $N \geqslant 3.3 \times 10^{18}\ {\rm cm}^{-3}$, i.e. on the metallic side of the MI transition, the agreement quickly deteriorates. This clearly indicates that the Bhatt–Lee model is unsuited for the metallic state although its validity has often been tacitly assumed in this range.

The origin of localized moments in the metallic state has been investigated in a number of approaches, most of them starting with an Anderson–Hubbard model which is the simplest model Hamiltonian featuring the essential elements of disorder, through random hopping integrals t_{ij}, and on-site Coulomb interaction:

$$H = \sum_{i\sigma} (\varepsilon_i - \mu) n_{i\sigma} + \sum_{ij\sigma} t_{ij} c_{i\sigma}^{+} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}, \tag{3.3}$$

$c_{i\sigma}(c_{i\sigma}^{+})$ is the annihilation (creation) operator for an electron with spin projection, σ, in the 1s (A_1) groundstate of the dopant atom at site i, and $n_{i\sigma} = c_{i\sigma}^{+} c_{i\sigma}$. It is usually assumed that the five excited states generated by valley-orbit splitting are sufficiently far away (experimentally approximately 10 meV, see below) that a single-band model is applicable. The host semiconductor properties enter only through the fact that the positions, i, are the sites of the Si lattice and that the effective mass and interaction are renormalized. The various approaches differ in the type of mean-field model employed (Milovanović *et al.* 1989; Bhatt & Fischer 1992; Dobrosavljević & Kotliar 1993; Langenfeld & Wölfe 1995; Lakner *et al.* 1994). In the approach taken by Langenfeld & Wölfle (1995, see also Lakner *et al.* 1994) the starting point is the observation that the fraction of dopant atoms carrying a localized moment in the metallic state is relatively small, of the order of several percent at $N_{\rm c}$ (see figure 4). Therefore an isolated moment forming in an effective homogeneous medium is considered. The effective Hamiltonian is that of the Anderson magnetic-impurity

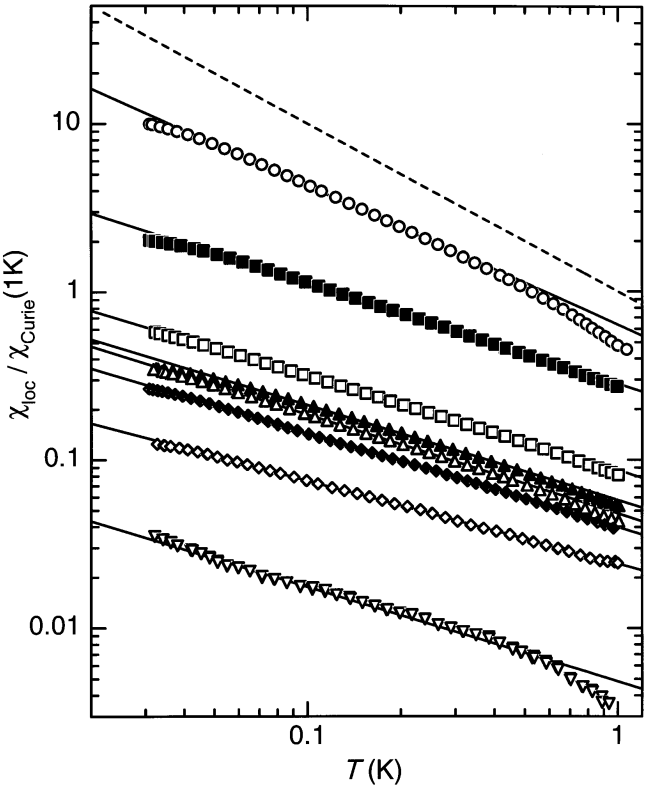

Figure 5. Magnetic susceptibility $\chi_{\rm loc}$ due to localized moments (normalized to the Curie susceptibility of N independent $S = \frac{1}{2}$ spins at 1 K) of Si:P. P concentrations N (in 10^{18} cm^{-3}) are from top to bottom: 0.34, 1.6, 3.3, 3.56, 3.62, 3.8, 4.2, 5.1 (after Schlager & von Löhneysen 1998).

model with the local spin occupation number of an impurity atom at site 0, which is proportional to the magnetization, to be determined self-consistently. The resulting concentration $N_{\rm M}$ of local moments (obtained applying the usual Anderson criterion for the stability of a local moment) is shown in figure 4 where good agreement between $N_{\rm M}$ and the experimentally determined values $N_{\rm S}$ and $N_{\rm Sch}$ on the metallic side is seen.

The coupling of the localized moments to the itinerant electrons by an effective exchange interaction $J_{\rm eff}$ gives rise to the Kondo effect. Because of disorder, both the density of states at the Fermi level $N(E_{\rm F})$ and the effective exchange interaction $J_{\rm eff} \approx \bar{t}^2/U$ where $\bar{t}$ is the average hopping amplitude from the local-moment site to the neighbouring sites, will fluctuate. This leads to a distribution $P(T_{\rm K})$ of Kondo temperatures $T_{\rm K} \sim \exp(-(1/N(E_{\rm F})J_{\rm eff})$. An approximate power-law behaviour $P(T_{\rm K}) \sim T_{\rm K}^{-\alpha_{\rm K}}$ is found with $\alpha_{\rm K} \approx 0.9$ (Lakner *et al.* 1994) which translates into a specific-heat contribution $C_{\rm K} \sim T^{1-\alpha_{\rm K}}$ because the Kondo specific heat is a universal function of $T/T_{\rm K}$. Attributing ΔC in the metallic state of Si:P to the Kondo effect, $\alpha_{\rm K} = 1 - \alpha_{\rm c} \approx 0.8$ is inferred experimentally, in rough agreement with the theoretical calculation. However, the Kondo susceptibility for the same distribution $P(T_{\rm K})$ should vary roughly as $\chi_{\rm K} \sim T^{-\alpha_{\rm K}}$ which is not observed (cf. figure 5). Further work is necessary to resolve this discrepancy. In the theory, interactions among

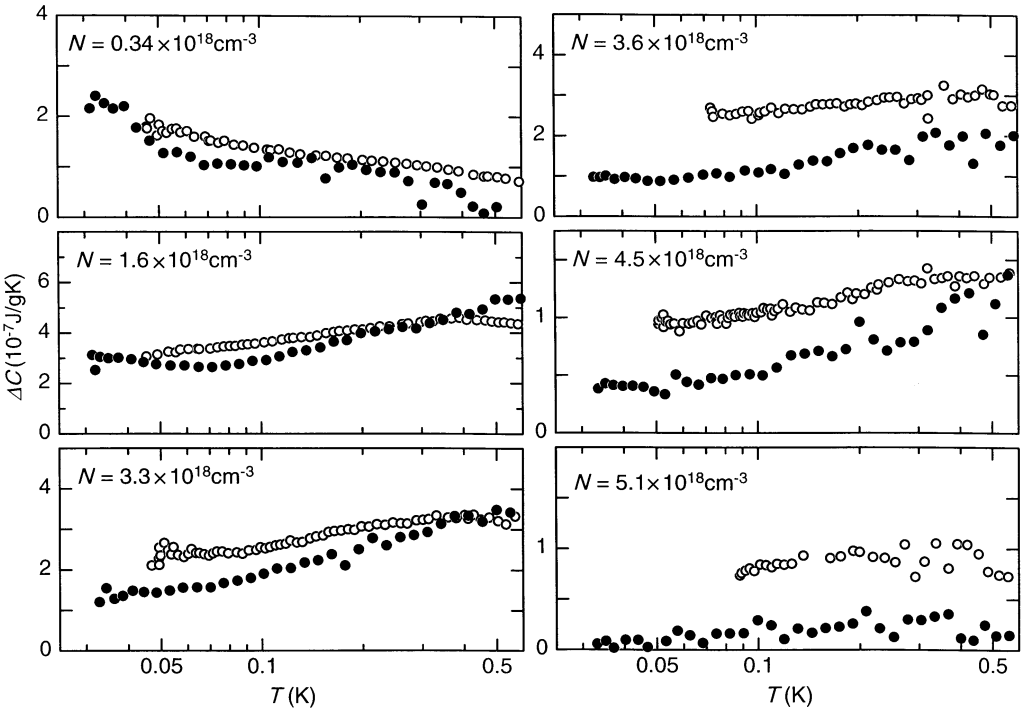

Figure 6. Excess specific heat contribution ΔC of Si:P with different P concentrations N as measured (○) and calculated from $\chi(T)$ (●) (after Schlager & von Löhneysen 1998).

localized moments (RKKY interaction) or a possible quenching of the Kondo effect by disorder have not been considered.

The effect of localized magnetic moments on the electrical resistivity via the process of spin-flip scattering has not been positively identified because $\rho(T, B)$ is dominated by weak localization, electron–electron interactions and wave-function shrinkage induced by a magnetic field, B. The strong influence of the two latter mechanisms, for instance, is directly borne out by the negative magnetoconductance observed in metallic Si:P (Rosenbaum *et al.* 1983; Sarachik 1995; von Löhneysen & Welsch 1991) while for spin-flip scattering (and also for weak localization) a positive magneto-conductance, i.e. negative magneto-resistance, is observed. Hence, while a direct effect of spin-flip scattering in $\rho(T, B)$ appears to be negligible, the recent discovery (Blaschette *et al.* 1996) of a shallow maximum in $\sigma(T)$ in Si:P for concentrations around $N \approx 1.1N_c$ (see figure 7) does suggest an indirect influence of local moments on the conductivity by virtue of their influence on electron–electron interactions. As pointed out by Paalanen *et al.* (1986) (see also Alloul & Dellouve 1978; Roy & Sarachik 1988), the contribution from the triplet particle-hole channel is suppressed if the electron spin-flip rate τ_s^{-1} becomes sufficiently large. The situation is analogous to the case of Si:P at higher concentrations in a magnetic field where it is well known that the sign change of the temperature coefficient m of the conductivity from $m < 0$ for $g\mu_B B < k_B T$ to $m > 0$ for $g\mu_B B > k_B T$ is due to spin-splitting of the triplet term where electron–electron interactions are cut off for $g\mu_B B > k_B T$ (Lee & Ramakrishnan 1985; Belitz & Kirkpatrick 1994; Rosenbaum *et al.* 1986; Sarachik 1995; von Löhneysen & Welsch 1991). In the concentration region

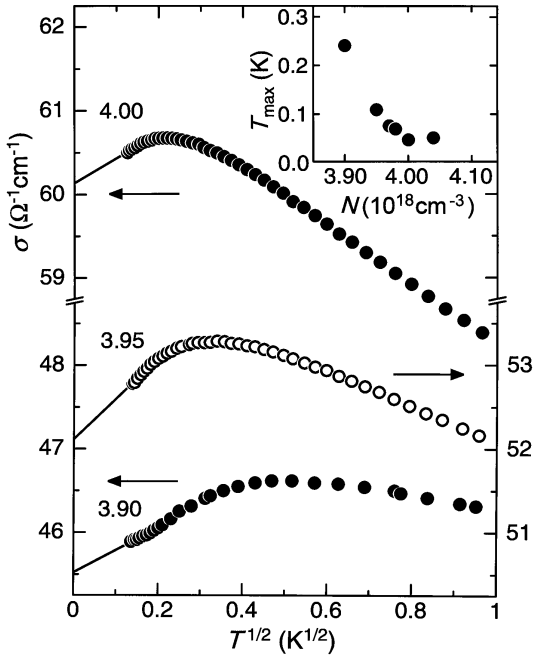

Figure 7. σ versus $\sqrt{T}$ for some Si:P samples. P concentrations N (in 10^{18} cm^{-3}) from top to bottom: 4.00, 3.95 and 3.90. The inset shows the temperature $T_{\max}$ of the conductivity maximum versus N (after Blaschette *et al.* 1996).

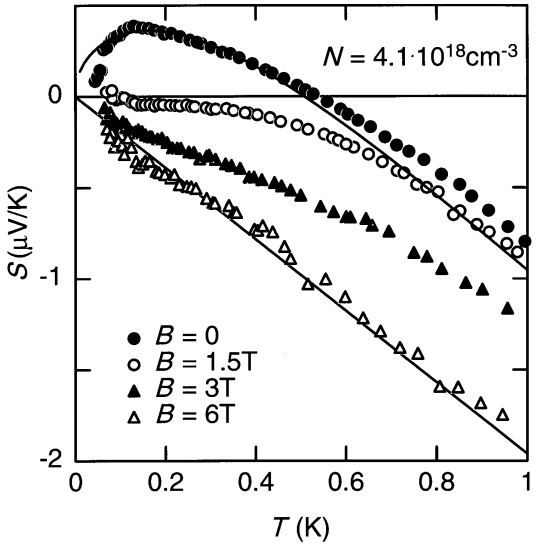

Figure 8. Thermoelectric power, S, versus temperature, T, for different magnetic fields, B, for Si:P. Solid line is the best fit of a Kondo thermoelectric power with $T_{\rm K} = 0.8$ K to the zero field data (after Lakner & von Löhneysen 1993).

of the $\sigma(T)$ maximum, an anomalously strong shift of $T_{\max}$ with field is observed (Blaschette *et al.* 1996).

The thermoelectric power, S, clearly indicates scattering by localized magnetic moments (Lakner & von Löhneysen 1993) because it is particularly sensitive to the

Kondo effect. Figure 8 shows $S(T)$ for a Si:P sample with $N = 4.1 \times 10^{18}\,\mathrm{cm}^{-1}$. The maximum of $S(T)$ is attributed to magnetic scattering since it is observed only for N slightly above N_c where an appreciable density of localized moments exists. (It is the same N range where the maximum in $\sigma(T)$ has been found.) Even more convincing is the suppression of the $S(T)$ maximum in large magnetic fields, also shown in figure 8. In $B = 6$ T we recover the negative diffusion thermoelectric power $S \sim -T$ observed for $N \gg N_c$ in zero field (Lakner & von Löhneysen 1993). A very similar behaviour of $S(T)$ has been found for compensated Si:(P,B) (Ziegler *et al.* 1996). Assuming a Kondo-derived thermoelectric power one can compare the $S(T)$ maximum to a corresponding single-ion expression derived by Maki (1969), cf. figure 8. The deviations between data and best fit might be due to the neglect of a T_K distribution in the fit where a single-valued $T_K = 0.8$ K is assumed. It is reassuring that the change of the conductivity due to Kondo scattering as calculated from the fit (Lakner & von Löhneysen 1993) is only a few percent of the total variation of $\sigma(T)$, in line with the lack of a sizable Kondo effect on $\sigma(T, B)$.

4. Electronic transport processes on the insulating side of the metal–insulator transition

Despite a number of important differences (critical region, exponent puzzle, etc.), transport processes of compensated versus uncompensated Si:P on the metallic side not too close to the MI transition are overall similar. For instance, we have seen above that the scattering by magnetic moments leads to a similar behaviour of the thermoelectric power in both types of materials. It has been demonstrated with infrared reflection measurements that the MI transition in Si:P occurs for electronic states in the impurity band which even for P concentrations $N \approx 2N_c$ is still energetically separated from the conduction band (Gaymann *et al.* 1993, 1995). This was inferred from features at 10 and 45 meV in the reflection spectra that could be attributed to optical transitions within the valley-orbit split impurity multiplet, i.e. from the 1s (A_1) state to the (nearly degenerate) 1s (E) or 1s (T) states, and to the conduction band at the MI transition was actually suggested long time ago by Mott (1990), based on some more indirect evidence. Again overall similar behaviour is found for the infrared reflection of compensated Si:(P,B) (Gaymann *et al.* 1993, 1995).

Therefore, the marked differences in transport properties between Si:P and Si:(P,B) well on the insulating side (Liu *et al.* 1996) are particularly interesting. Figure 9 shows the thermoelectric power plotted as $-S \cdot N$ versus T on a log–log plot. (Here the T range is above 1 K so that the Kondo anomaly in metallic samples, i.e. the positive thermoelectric power maximum superimposed on an overall negative diffusion thermopower with a concomitant sign change of $S(T)$, is not seen and should not be confused with the behaviour above 1 K.) For sufficiently high T ($\gtrsim 15$ K) S is always negative. While the $-S \cdot N$ curves for compensated Si:(P,B) fall on an almost universal curve for carrier concentration N between 1.5 and $2.95 \times 10^{18}\,\mathrm{cm}^{-3}$, such a scaling is seen for uncompensated Si:P only in the concentration range above $N_0 = 2.78 \times 10^{18}\,\mathrm{cm}^{-3}$. Below that concentration, $S(T)$ exhibits a sign change at a temperature $T_{S=0}$ which rapidly shifts to higher values with decreasing N. This sign change from $S < 0$ to $S > 0$ with decreasing T is visible in figure 9 as a precipitous drop of $-\log NS$ with decreasing T. A further strong difference is seen in the electrical resistivity $\rho(T)$ (figure 10). For low carrier concentration, $N < N_0$, ρ rises much faster with decreasing T for Si:P than for Si:(P,B), while the behaviour is similar

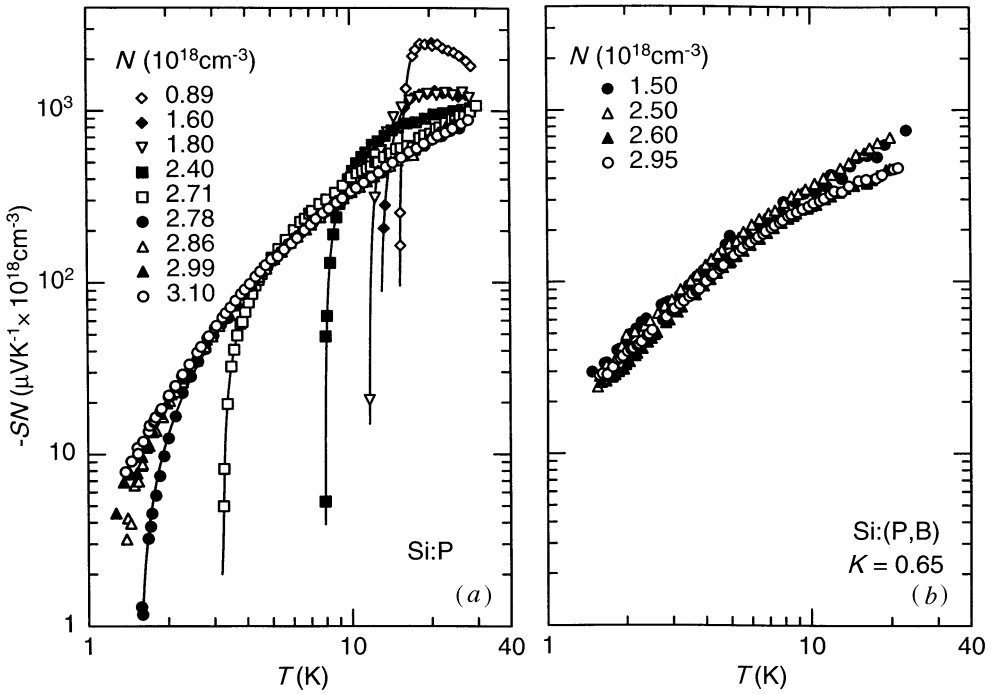

Figure 9. Negative thermoelectric power times carrier concentration $-SN$ versus temperature, T, on a log–log plot for (*a*) Si:P and (*b*) Si:(P,B) (after Liu *et al.* 1996).

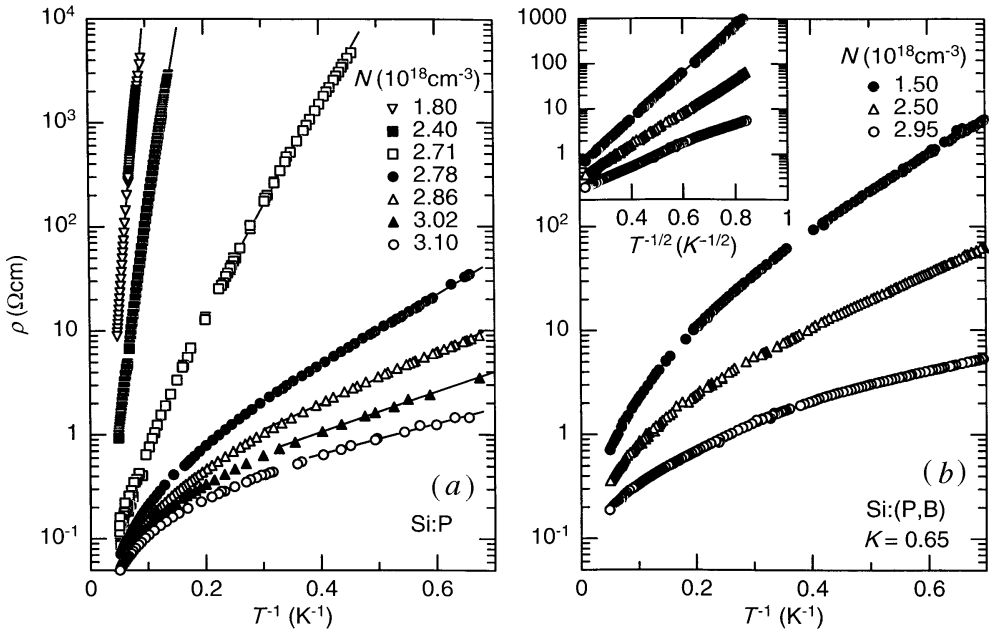

Figure 10. Electrical resistivity, ρ, plotted versus inverse temperature for (*a*) Si:P and (*b*) Si:(P,B). Straight lines in (*a*) indicate fits to obtain the activation energy E_2. Inset in (*b*) shows the Si:(P,B) data plotted as log ρ versus $T^{-1/2}$. Straight lines indicate Efros–Shklovskii hopping (after Liu *et al.* 1996).

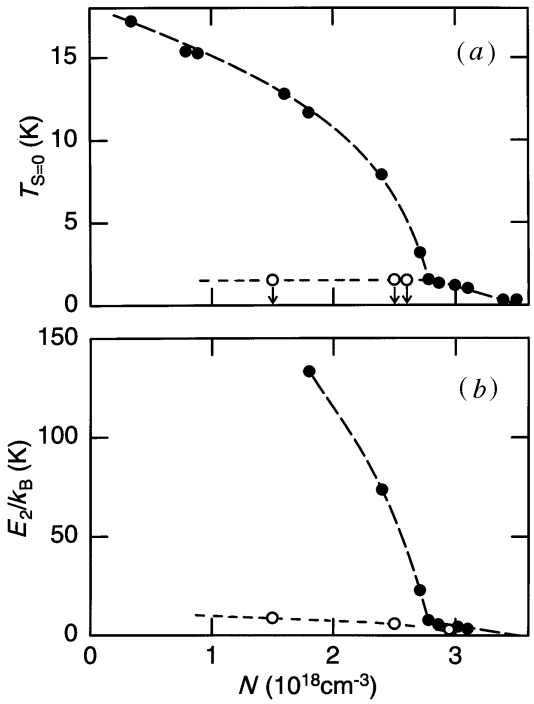

Figure 11. (a) Temperature $T_{S=0}$ of the thermoelectric-power zero and (b) activation energy E_2 versus carrier concentration, N, for uncompensated Si:P (closed circles) and Si:(P,B) (open circles) (after Liu *et al.* 1996).

for $N > N_0$. The strong qualitative difference in $S(T)$ and $\rho(T)$ below N_0 points to different dominant transport processes. Interpreting the steep $\rho(T)$ increase of Si:P below N_0 as an activated process, we can extract an activation energy E_2. Figure 11, shows a comparison of E_2 and $T_{S=0}$. Although there is an order-of-magnitude difference in absolute values of E_2/k_B and $T_{S=0}$, the similarity of the concentration dependence is striking. Hence we interpret the sign change of $S(T)$ as the onset of an activated process. If one were forced to assume an E_2 process also for Si:(P,B)—although the data actually suggest Efros–Shklovskii VRH with a hopping exponent $p = \frac{1}{2}$, see inset of figure 10—one would obtain the open circles in figure 11, i.e. no feature appears at N_0.

The sudden appearance of a hard gap only in Si:P at N_0 well below N_c suggests that we are observing the Hubbard gap due to the on-site Coulomb repulsion U. It has been speculated that the E_2 process is indeed due to the Hubbard gap (Mott & Davis 1979). Some time ago the Hubbard gap was inferred for very dilute samples ($N < 10^{17}$ cm^{-3}) from optical measurements (Norton 1976) while more recent infrared transmission (Thomas *et al.* 1981) and reflection (Gaymann *et al.* 1993, 1995) did not see any signature of a Hubbard gap closer to the transition. In fact, from a calculation of the electronic properties of P clusters in Si:P a stability of a negatively charged cluster of four P sites was found, indicating a lack of electronic repulsion (Bhatt & Rice 1981). On the other hand, the negatively charged isolated P donor in Si is barely stable (binding energy 1.7 meV), i.e. U is of the order of the ionization energy of 45 meV. Therefore it is very likely that the on-site electron repulsion weakens progressively as the P concentration (and carrier concentration) increases, until at $N_0 = 2.78 \times 10^{18}$ cm^{-3} the density of states of the two Hubbard bands starts to

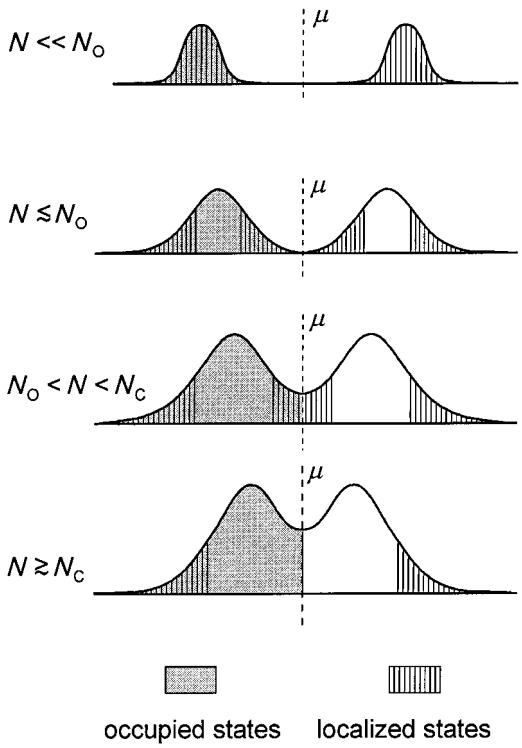

Figure 12. Qualitative sketch of the density of states of the impurity band of uncompensated Si:P indicating the splitting into lower and upper Hubbard band. See text for details.

overlap. Because of disorder, however, metallic behaviour does not incur immediately since the tail states of the Hubbard bands are localized. It is only at the critical concentration N_c that the Hubbard bands are so close that the chemical potential μ is within the range of extended states. This scenario is schematically depicted in figure 12. It gives a physical picture of how disorder and electron–electron interactions drive the MI transition in Si:P. Of course, the Hubbard features are absent in Si:(P,B) as they should because compensated semiconductors are away from half-filling.

5. Conclusions

Although considerable progress has been made in a number of areas in the field of metal–insulator transitions of doped semiconductors, notably in the understanding of localized magnetic moments and the difference of uncompensated and compensated materials, a number of important unresolved issues remain. The most fundamental problem is, of course, the nature of the MI transition itself. We are still far away from a theoretical understanding and therefore even better experiments are needed. It is hoped that the challenge and excitement of this long-standing problem will lead experimentalists and theorists alike to new initiatives.

The work reviewed here grew out of a very fruitful collaboration with students, post-docs and colleagues. Their contribution can be identified from the references cited. In particular, I acknowledge M. Lakner, X. Liu, H. G. Schlager, T. Trappmann and S. Wagner for their important contributions, enthusiasm in carrying out difficult experiments, and useful discussions. I am very grateful to P. Wölfle for numerous enlightening discussions on the theoretical aspects of the metal–insulator transition. I have enjoyed useful discussions with G. Kotliar, S. Sachdev and

M. P. Sarachik. I thank W. Zulehner, Wacker Siltronic, for the Si:P samples and D. F. Holcomb, Cornell University, for the Si:(P,B) samples.

References

Abrahams, E., Anderson, P. W., Licciardello, D. C. & Ramakrishnan, T. V. 1979 *Phys. Rev. Lett.* **42**, 673.

Alloul, H. & Dellouve, P. 1978 *Phys. Rev. Lett.* **59**, 578.

Belitz, D. & Kirkpatrick, T. R. 1994 *Rev. Mod. Phys.* **66**, 261.

Bhatt, R. N. & Fischer, D. S. 1992 *Phys. Rev. Lett.* **68**, 3072.

Bhatt, R. N. & Lee, P. A. 1982 *Phys. Rev. Lett.* **48**, 344.

Bhatt, R. N. & Rice, T. M. 1981 *Phys. Rev.* B **23**, 1920.

Blaschette, A., Ruzzu, A., Wagner, S. & von Löhneysen, H. 1996 *Europhys. Lett.* **36**, 527.

Castner, T. G. 1994 *Phys. Rev. Lett.* **73**, 3600.

Castner, T. G. 1995 *Phys. Rev.* B **52**, 12 434.

Dai, P., Zhang, Y. & Sarachik, M. P. 1993 *Phys. Rev. Lett.* **70**, 1968.

Dai, P., Zhang, Y. & Sarachik, M. P. 1994 *Phys. Rev.* B **49**, 14 039.

Dai, P., Bogdanovich, S., Zhang, Y. & Sarachik, M. P. 1995 *Phys. Rev.* B **52**, 12 439.

Dobrosavljević, V. & Kotliar, G. 1993 *Phys. Rev. Lett.* **71**, 3218.

Field, S. B. & Rosenbaum, T. F. 1985 *Phys. Rev. Lett.* **55**, 522.

Gaymann, A., Geserich, H. P. & von Löhneysen, H. 1993 *Phys. Rev. Lett.* **71**, 3681.

Gaymann, A., Geserich, H. P. & von Löhneysen, H. 1995 *Phys. Rev.* B **52**, 16 486.

Hornung, M., Ruzzu, A., Schlager, H. G., Stupp, H. & von Löhneysen, H. 1994 *Europhys. Lett.* **28**, 43.

Kobayashi, N., Ikehata, S., Kobayashi, S. & Sasaki, W. 1977 *Solid State Commun.* **24**, 67.

Koon, D. W. & Castner, T. G. 1988 *Phys. Rev. Lett.* **60**, 1755.

Lakner, M. & von Löhneysen, H. 1989 *Phys. Rev. Lett.* **63**, 648.

Lakner, M. & von Löhneysen, H. 1993 *Phys. Rev. Lett.* **70**, 3475.

Lakner, M., von Löhneysen, H., Langenfeld, A. & Wölfle, P. 1994 *Phys. Rev.* B **50**, 17 064.

Langenfeld, A. & Wölfle, P. 1995 *Ann. Phys.* **4**, 43.

Lee, P. A. & Ramakrishnan, T. V. 1985 *Rev. Mod. Phys.* **57**, 287.

Liu, X., Sidorenko, A., Wagner, S., Ziegler, P. & von Löhneysen, H. 1996 *Phys. Rev. Lett.* **77**, 3395.

Madel, O., Schlager, H. G. & von Löhneysen, H. 1997 *Z. Phys.* B **102**, 473.

Maki, K. 1969 *Prog. Theor. Phys.* **41**, 586.

Marko, J. R., Harrison, J. P. & Quirt, J. D. 1974 *Phys. Rev.* B **10**, 2448.

Milovanović, M., Sachdev, S. & Bhatt, R. N. 1989 *Phys. Rev. Lett.* **63**, 82.

Mott, N. F. 1990 *Metal–insulator transitions*. London: Taylor & Francis.

Mott, N. F & Davis, E. A. 1979 *Electronic processes in non-crystalline materials*, 2nd edn. Oxford: Clarendon.

Norton, P. 1976 *Phys. Rev. Lett.* **37**, 164.

Ootuka, Y. & Matsunaga, N. 1990 *J. Phys. Soc. Jpn.* **59**, 1801.

Paalanen, M. A., Rosenbaum, T. F., Thomas, G. A. & Bhatt, R. N. 1982 *Phys. Rev. Lett.* **48**, 1284.

Paalanen, M. A., Sachdev, S., Bhatt, R. N. & Ruckenstein, A. E. 1986 *Phys. Rev. Lett.* **57**, 2061.

Rosenbaum, T. F., Andres, K., Thomas, G. A. & Bhatt, R. N. 1980 *Phys. Rev. Lett.* **45**, 1723.

Rosenbaum, T. F., Milligan, R. F., Paalanen, M. A., Thomas, G. A., Bhatt, R. N. & Lin, W. 1983 *Phys. Rev. B* **27**, 7509.

Rosenbaum, T. F., Thomas, G. A. & Paalanen, M. A. 1994 *Phys. Rev. Lett.* **72**, 2121.

Roy, A. & Sarachik, M. P. 1988 *Phys. Rev.* B **37**, 5531.

Sarachik, M. P. 1995 In *Metal–insulator transitions revisited* (ed. P. P. Edwards & C. N. R. Rao), p. 79. London: Taylor & Francis.

Schlager, H. G. & von Löhneysen, H. 1998 *Europhys. Lett.* (In the press.)

Shlimak, I., Kaveh, M., Ussyshkin, R., Ginodman, V. & Resnick, L. 1996 *Phys. Rev. Lett.* **77**, 1103.

Stupp, H., Hornung, M., Lakner, M., Madel, O. & von Löhneysen, H. 1993 *Phys. Rev. Lett.* **71**, 2634.

Stupp, H., Hornung, M., Lakner, M., Madel, O. & von Löhneysen, H. 1994*a* *Phys. Rev. Lett.* **72**, 2122.

Stupp, H., Hornung, M., Lakner, M., Madel, O. & von Löhneysen, H. 1994*b* *Phys. Rev. Lett.* **73**, 3601.

Thomas, G. A. 1985 *Phil. Mag.* B **52**, 479.

Thomas, G. A., Paalanen, M. A. & Rosenbaum, T. F. 1983 *Phys. Rev.* B **27**, 3897.

Thomas, G. A., Capizzi, M., DeRosa, F., Bhatt, R. N. & Rice, T. M. 1981 *Phys. Rev.* B **23**, 5472.

Trappmann, T., Sürgers, C. & von Löhneysen, H. 1997 *Europhys. Lett.* **38**, 177.

von Löhneysen, H. 1990 *Festkörperprobleme/Adv. Solid State Phys.* **30**, 95.

von Löhneysen, H. & Welsch, M. 1991 *Phys. Rev.* B **44**, 9045.

Wagner, S., Lakner, M. & von Löhneysen, H. 1997 *Phys. Rev.* B **55**, 4219.

Wang, X.-F., Wang, Z., Kotliar, G. & Castellani, C. 1992 *Phys. Rev. Lett.* **68**, 2504.

Ziegler, P., Lakner, M. & von Löhneysen, H. 1996 *Europhys. Lett.* **33**, 285.

Discussion

S. V. Kravchenko (*City College of the City University of New York, USA*). We have studied the temperature dependence of resistivity, ρ, for a two-dimensional system of strongly interacting electrons at the surface of silicon at low electron densities (n_s), near the conductor–insulator transition. The resistivity was empirically found to scale with temperature and electric field so that $\rho(T, n_s) = f_1(T/T_0(n_s))$ (see figure 13) and $\rho(E, n_s) = f_2(E/E_0(n_s))$ both in conducting ($n_s > n_c$) and insulating ($n_s < n_c$) regions (n_c is the electron density at the transition). This behaviour is very reminiscent to *superconductor–insulator* transition in thin Bi films (see, for example, Liu *et al.* 1991). We have also observed a remarkable symmetry between the resistivity and conductivity on opposite sides of the transition, which implies that the transport mechanisms on the two sides are related. These behaviours, along with other observations (Kravchenko *et al.* 1994, 1995, 1996), suggest a true conductor–insulator transition in the two-dimensional electron system in silicon at $B = 0$, in contrast to the predictions of the well-known scaling theory.

Additional references

Liu, Y., McGreer, K. A., Nease, B., Haviland, D. B., Martinez, G., Halley, J. W. & Goldman, A. M. 1991 Scaling of the insulator-to-superconductor transition in ultrathin amorphous Bi films. *Phys. Rev. Lett.* **67**, 2068–2071.

Kravchenko, S. V., Kravchenko, G. V., Furneaux, J. E., Pudalov, V. M. & Dioro, M. 1994 Possible metal–insulator transition at $B = 0$ in 2 dimensions. *Phys. Rev.* B **50**, 8039–8042.

Kravchenko, S. V., Mason, W. E., Bowker, G. E., Furneaux, J. E., Pudalov, V. M. & Dioro, M. 1995 Scaling of an anomalous metal–insulator transition in a 2-dimensional system in silicon at $B = 0$. *Phys. Rev.* B **51**, 7038–7045.

Kravchenko, S. V., Simonian, D., Sarachik, M. P., Mason, W. E. & Furneaux, J. E. 1996 Electric-field scaling at a $B = 0$ metal–insulator transition in 2 dimensions. *Phys. Rev. Lett.* **77**, 4938–4941.

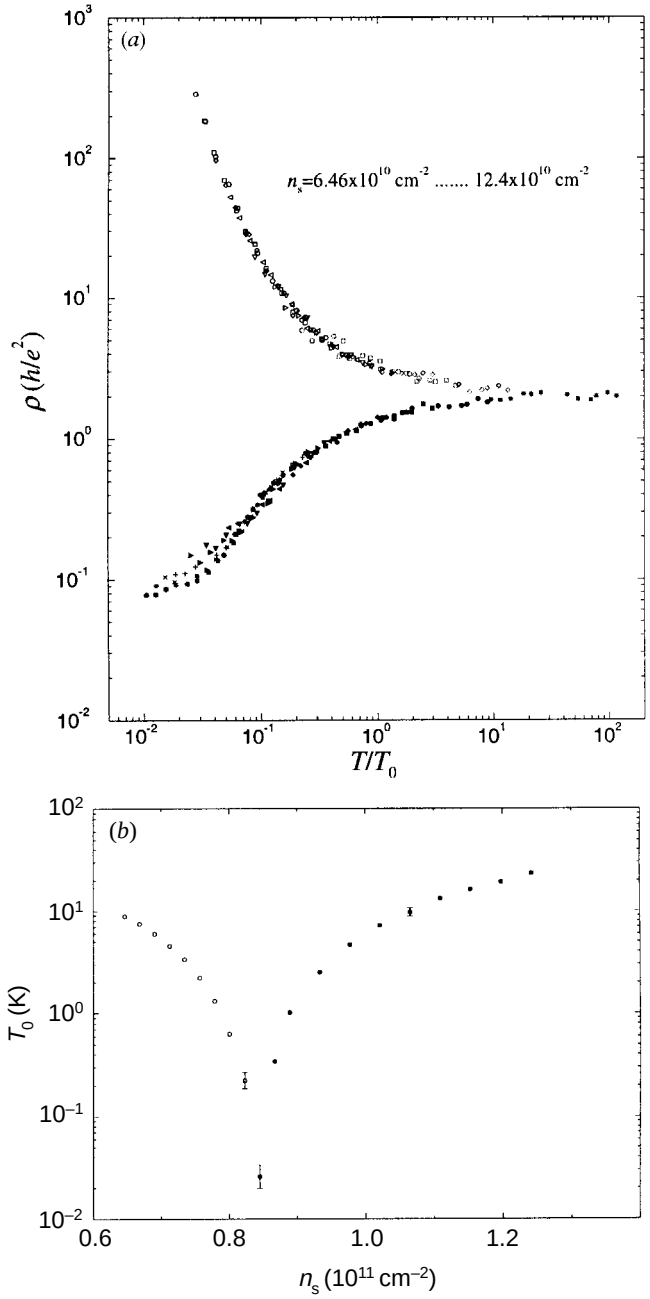

Figure 13. Resistivity versus T/T_0 (a) and scaling parameter, T_0, versus electron density (b). Open symbols correspond to the insulating side of the transition, closed to the metallic one.