Thermal diffusivity and conductivity measurements for Si:P near the metal - insulator transition

1996 J. Phys.: Condens. Matter 8 999

(http://iopscience.iop.org/0953-8984/8/8/011)

J. Phys.: Condens. Matter **8** (1996) 999–1009. Printed in the UK

Thermal diffusivity and conductivity measurements for Si:P near the metal–insulator transition

H Suderow†, J P Brison‡, Ch Marcenat† and B Salce†

† Dèpartement de Recherche Fondamentale sur la Matière Condensèe, SPSMS, CEA/Grenoble, 17, Rue des Martyrs, 38054 Grenoble Cédex 9, France

‡ Centre de Recherches sur les Très Basses Températures, CNRS, BP 166, 38042 Grenoble Cédex 9, France

Received 9 October 1995

Abstract. Silicon doped with phosphorus undergoes a metal–insulator transition (MIT) at a critical phosphorus concentration. We present here data for the thermal diffusivity D of an insulating sample of Si:P very near the MIT. We describe briefly our method for measuring the dependence on the magnetic field (H) of D at very low temperatures ($T \leqslant 100$ mK). We present also data for the magnetoresistivity $\rho(H)$ and the thermal conductivity κ of the same sample, and the calculated specific heat $C_p = \kappa/D$. We compare C_p with earlier direct measurements, and we try to explain the behaviour of D, C_p, κ and ρ taking into account the complex situation in Si:P. We show that the measurement of D at very low temperatures and under a magnetic field can be a fruitful way of extracting information about the physics of doped semiconductors.

1. Introduction

Si:P has been widely studied as a typical example of a system which undergoes a metal–insulator transition (MIT). There is now a commonly accepted description of the MIT in this system. The valence electrons of the P atoms (randomly distributed in the host Si crystal) have energy levels close to the conduction band energy of silicon, and a very large effective Bohr radius. The MIT occurs when the concentration of P impurities reaches a critical concentration N_c ($\approx 3.5 \times 10^{18}$ atoms cm^{-3}) for which the orbitals of the donors overlap and form an energy band (in fact, the transition occurs in the impurity band, i.e. when the impurity band is still energetically separated from the conduction band) [1]. For compositions near the MIT an applied pressure and/or a magnetic field can alter the state of the sample and may render a metallic Si:P sample insulating (due to the shrinking of the electronic wave functions) [2, 3]. Recently, some open questions regarding this and other heavily doped semiconductors have been re-examined, both experimentally and theoretically (see [4] and references therein). We have studied an insulating sample very near the MIT, which we use also as a very sensitive resistive thermometer. Indeed, the initial purpose of our experiment was to test the response time of our thermometer (used for specific heat measurements), by analysing the time evolution of the resistance after a short heat pulse. But we could also, in this experiment, separate the heat diffusion time *inside our sample* from the heat flow to the cryostat through the thermal link, and so measure the thermal diffusivity D. One peculiarity of this experiment is that the *lower* the temperature, the *easier* the separation of the different time constants. We have also measured the thermal conductivity κ, and the magnetoresistivity of the same sample of Si:P. The thermal conductivity $\kappa(T, H)$

0953-8984/96/080999+11$19.50

has a puzzling behaviour and will be extensively discussed. We will also compare the results with previous work on the specific heat [5, 6, 7, 8, 9] and the thermal conductivity [10, 11, 12].

2. Experimental details

2.1. Resistivity and thermal conductivity

The sample was cut from a wafer of Si:P grown by the Czochralski technique. Four ohmic contacts for the resistivity measurement were made by ionic implantation of highly doped (metallic) regions, gold evaporation and a subsequent annealing at 350 °C for 1 h. Gold wires of 50 μm diameter were bonded onto the gold pads on the Si:P sample. The concentration of P was determined by room temperature resistivity measurements using the calibration of Thurber *et al* [13], together with measurements of the resistivity ratio (300 K/4.2 K) made by Hornung and von Löhneysen (see [14]). We found that our sample had a concentration of $N = 3.3 \times 10^{18}$ atoms cm^{-3} (i.e. $N \approx 0.94N_c$). After calibration against a paramagnetic salt (CMN) and NBS fixed points (series 767 and 768), we could use our sample directly as a sensitive thermometer for very low temperatures (15 mK–1 K; see figure 2, later). The measurement of the thermal conductivity was performed in a dilution refrigerator, with two matched carbon thermometers (Matshushita) which were kept in good thermal contact with the gold (voltage) contacts and were measured with a differential AC bridge. The thermometers were calibrated in a field by comparison to reference thermometers (germanium and carbon) placed in the low-field compensated region of the magnet.

2.2. Thermal diffusivity

The thermal diffusivity D was evaluated by analysing the thermal response of the sample to a heat pulse. This is a non-steady-state method, which is normally used at high temperatures, when the direct measurement of the thermal conductivity κ or the specific heat C_p by conventional (stationary) methods becomes difficult due to the increasing importance of heat losses. The thermal diffusivity D is defined by the heat diffusion equation (without losses):

$$\frac{\partial T}{\partial t} = D\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)T. \tag{1}$$

Thus, the measurement of the time evolution of the temperature $T(t)$ is sufficient to determine D; no precise temperature calibration, or even knowledge of the absolute quantity of heat introduced into the sample is needed. For these reasons, the thermal response of some materials at low temperatures has been studied by diffusivity experiments [15], but, to our knowledge, this is the first measurement of D in doped semiconductors at very low temperatures. The sample was glued onto a copper support (together with a thin Kapton foil in order to avoid electrical contact), and was heated with an infrared diode located at the top of the cryostat. The power of the diode was transmitted to the sample with an optical fibre. A very short light pulse ($\approx$10 μs) was applied and the subsequent evolution of the average temperature of the sample was monitored by measuring the resistance of the Si:P itself (we used our sample as a thermometer). The main advantage of this technique is that long thermal coupling time constants due to possible bad thermal contacts between the heater or the thermometer and the sample are avoided. We did not

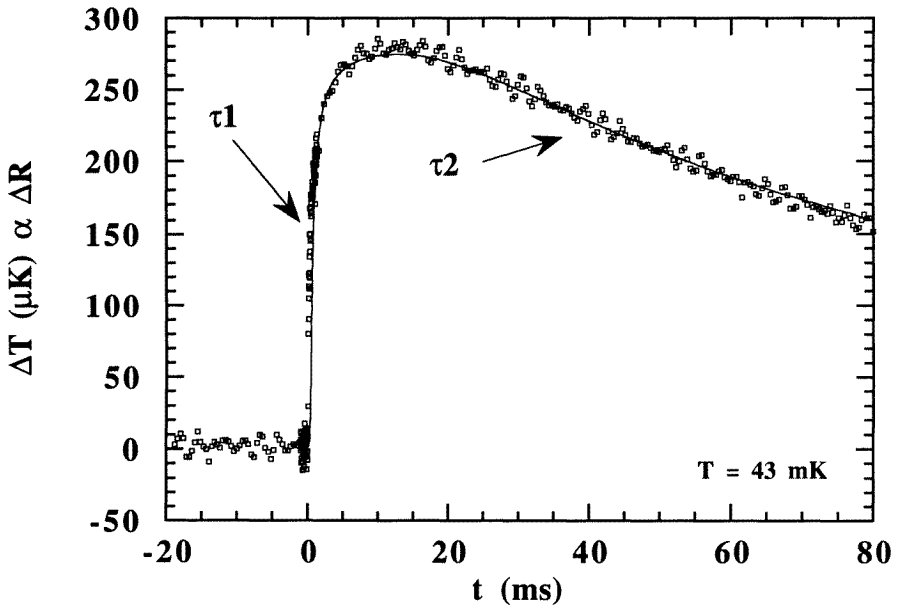
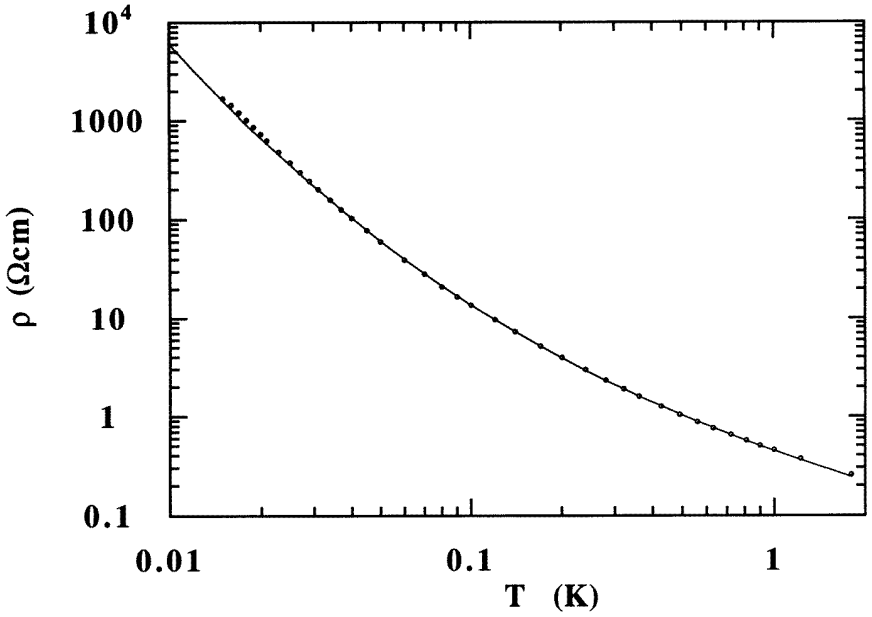


Figure 1. The response of our sample to a thermal pulse of 10 ms. We see the evolution of the average temperature of our sample after the pulse. Note that the resolution of our experiment permits us to have very small ΔTs. The fit to equation (2) is also shown. At higher temperatures (200 mK) and fields (5 T), the heat relaxation to the cryostat becomes comparable to the heat relaxation in the sample, and our simple model which led to equation (2) no longer holds.

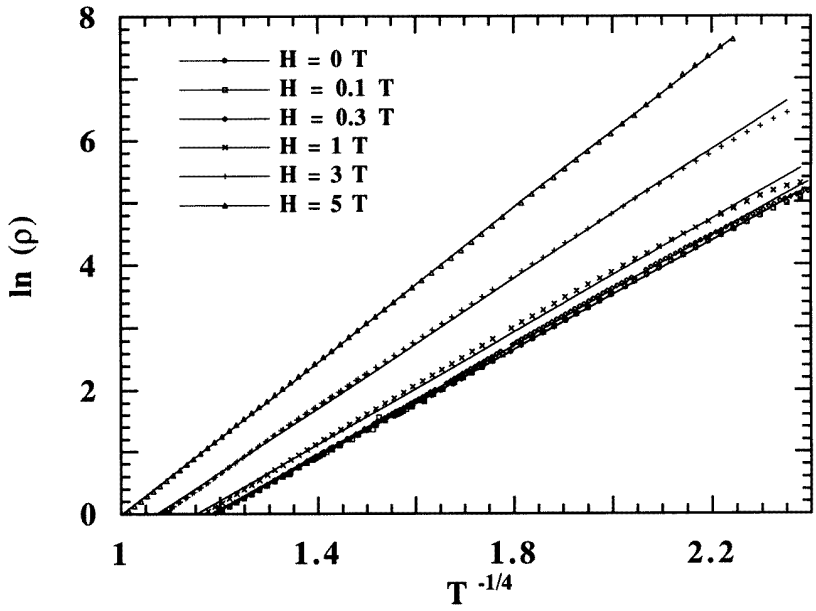
calibrate the quantity of heat injected into our sample, but we always checked that the temperature increase $\Delta T/T$ due to the heat pulse remained lower than 3% of the average temperature. As no precise temperature calibration was needed we could measure D in magnetic field without concerning ourselves with the field sensitivity of our thermometer (the Si:P sample itself). In fact, field measurements have an enhanced resolution due to the huge positive magnetoresistance of insulating Si:P. In order to be able to detect all of the Fourier components of the response (following the very short heat pulse), we had to measure the resistivity of the Si:P sample with a very large bandwidth (3 Hz–300 kHz). To avoid heating due to radiofrequency noise, special care was taken in the electrical shielding of the sample and the wires. It was possible to cool our sample down to the base temperature of the cryostat (35 mK). We note that in a preliminary stage, having directed the optical fibre directly onto the sample (and not the gold contacts), we saw a fast (as fast as the heat pulse, $\approx$10 μs) apparent variation of the temperature, which was superimposed onto a slower (thermal) variation of T. The fast signal disappeared when we directed the light onto one of the gold contacts, so we concluded that it was due to photoconduction in the Si:P sample. A typical pulse is shown in figure 1. In this figure we also see a fit to the response of the sample. This fit was obtained by a crude and simple model, solving equation (1) in two dimensions (we neglect the thickness of our sample) for a circular geometry, in which the heat pulse is a delta function at $x = y = 0$ and $t = 0$:

$$\Delta T \propto \Delta R \propto (\mathrm{e}^{-\tau_1/t} - \mathrm{e}^{-\tau_2/t}) \tag{2}$$

where ΔT and ΔR are the mean spatial variations for the temperature and the resistance, τ_1 is the time constant for the temperature increase (propagation of the heat up to the region between the voltage contacts of the resistivity measurements) and τ_2 is that for the heat



(*a*)



(*b*)

Figure 2. The temperature dependence of the resistivity for $H = 0$ T (a) and for some magnetic fields (b) is shown. Note that Mott's variable-range hopping law for $H = 0$ T is followed well. Full lines (in (a) and (b)) are fits to this law.

relaxation in the Si:P sample (heat propagation between the two contacts). The diffusivity D is proportional to $1/\tau_1$ and to $1/\tau_2$. As $\tau_2 \gg \tau_1$, we used τ_2 to determine D. From

figure 1 it can be seen that the simple functional (2) is able to reproduce quite accurately the measured temperature response. We did not try to calculate the proportionality constant between D and τ_2 or to use a more sophisticated and realistic model, because of the bad characterization of the boundary conditions (we therefore could not obtain an absolute value for D). This latter point becomes crucial at temperatures above 200 mK and at high magnetic fields ($H \geqslant 6$ T), where τ_2 is comparable to the time constant of the heat relaxation to the cryostat. Under these conditions no accurate measurements were possible. Extending our measurements to higher fields or temperatures, and determining the absolute value of D would require a more appropriate sample shape and thermalization.

3. Results and discussion

The resistivity was measured down to 15 mK and under a magnetic field. The best fit to the data was obtained with Mott's variable-range hopping law in three dimensions (VRH) for $T \leqslant 1$ K (see figure 2, and [16]):

$$\rho = \rho_0 \exp(-(T_0/T)^{-1/4}). \tag{3}$$

A low-temperature crossover between this Mott VRH law and Efros and Shklovskii's VRH law ($\rho = \rho_0 \exp(-(T_0/T)^{-1/2})$ which takes into account the electron–electron interactions was observed in some materials (see [16] and references therein). We did not observe this crossover in our Si:P sample: Mott's law is followed over a large range of temperature (one could even use this law for the calibration of the thermometer). Under a magnetic field, a very strong positive magnetoresistance is observed, explained qualitatively by the fact that the magnetic field reduces the spatial extension of the electron's wave function, and so the hopping probability. We do not observe any drastic change in the temperature dependence of the resistivity under a magnetic field (see, e.g., [17] for a more extensive discussion; see also [18]).

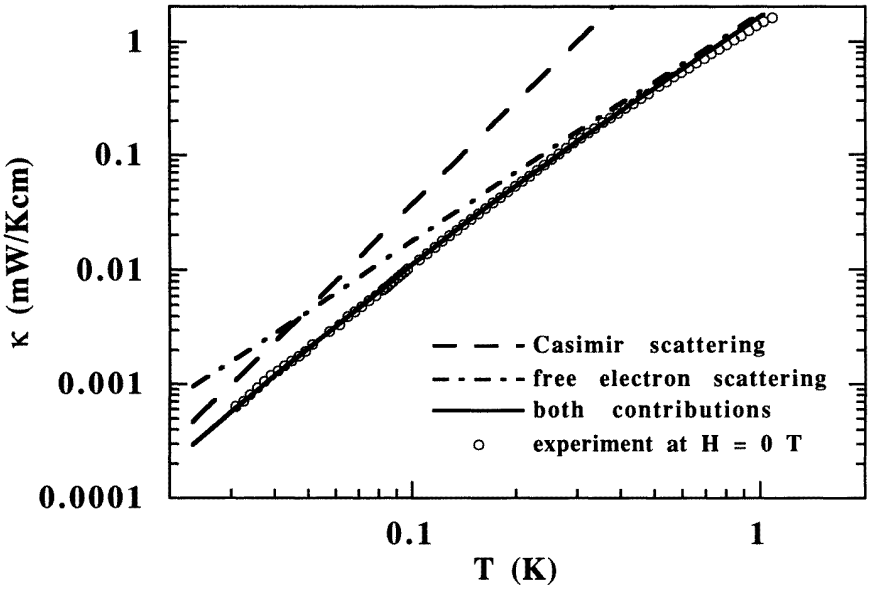
The thermal conductivity κ is shown in figure 3. It was measured down to very low temperatures ($T \approx 30$ mK) and under high magnetic fields ($H = 5$ T). The most striking feature of our measurement is that the thermal conductivity in all the temperature ranges that we have made measurements in does *not* vary under magnetic field (to within 10%). This is an anomalous and interesting situation, which we will now discuss. First, we should note that the conduction of heat by electrons is completely negligible in this sample. A crude estimation using resistivity data and the Wiedemann–Franz law (for metals) gives an electronic contribution five orders of magnitude smaller than that measured. The heat conduction is therefore dominated by the phonons, which is at first sight consistent with the fact that it does not significantly change in the field. The remaining problem is to understand the relaxation processes controlling κ in this temperature range. Several analyses have been carried out on κ for $T \geqslant 1$ K [10, 11]: they used a semi-phenomenological expression for the lattice conductivity given by

$$\kappa = \frac{k_B}{2\pi^2 v}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta/T} \frac{x^4 \mathrm{e}^x}{(\mathrm{e}^x - 1)^2}\, \mathrm{d}x\ \tau \tag{4}$$

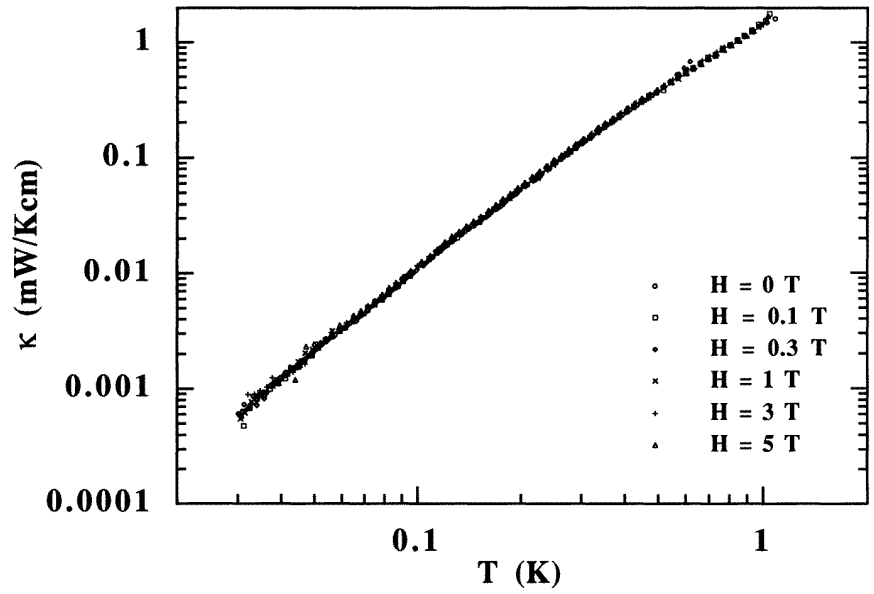
where τ, the relaxation time of the phonons, comprises many contributions and is written as

$$\tau^{-1}(x, T) = \tau_B^{-1} + \tau_{e-P}^{-1} + \tau_{Pt}^{-1} + \tau_{P-P}^{-1}. \tag{5}$$

v is the average velocity of the phonons, θ the Debye temperature and x the integration variable ($x = \hbar\omega/k_B T$). τ_B is the relaxation time for boundary scattering (the Casimir



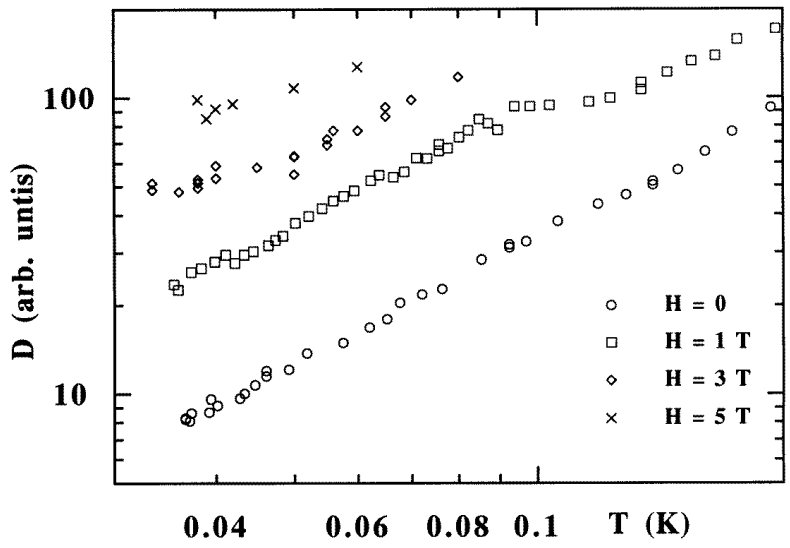
(*a*)



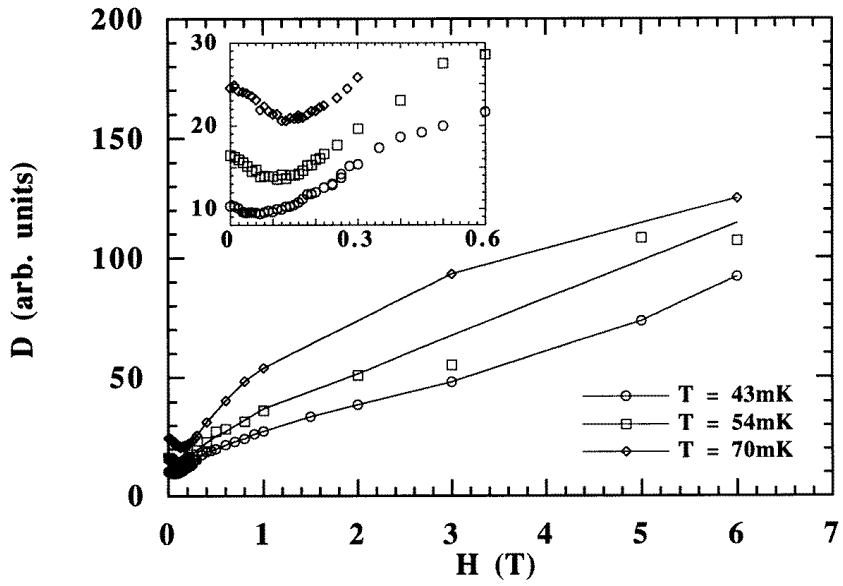
(*b*)

Figure 3. The thermal conductivity versus temperature for $H = 0$ T (a), and under a magnetic field (b); (a) also shows a fit (full line) of the thermal conductivity with an analysis detailed in the text. The chain line gives the thermal conductivity limited by free-electron–phonon scattering only, and the dashed line that limited by boundary scattering only.

mechanism), τ_{e-P} that for electron–phonon scattering, τ_{Pt} that for point defect scattering and τ_{P-P} that for phonon–phonon scattering. From [10, 11] we already know that τ_{P-P} and



(*a*)



(*b*)

Figure 4. The thermal diffusivity versus temperature (a) and magnetic field (b). The lines in (b) are guides to the eye. Note that our simple model does not permit us to determine an absolute absolute value for D, so the units are arbitrary. The inset in (b) shows the Schottky anomaly at low field and very low temperature.

τ_{Pt} which clearly dominate for $T \gg 2$ K do not contribute to τ for $T \leqslant 1$ K. There, only the boundary relaxation time τ_B and the electron–phonon scattering relaxation time τ_{e-P} have to be taken into account. τ_{e-P} needs more analysis: to calculate it, Radhakrishnan *et al* [11] used a two-component model, in which the electronic P impurity states form a

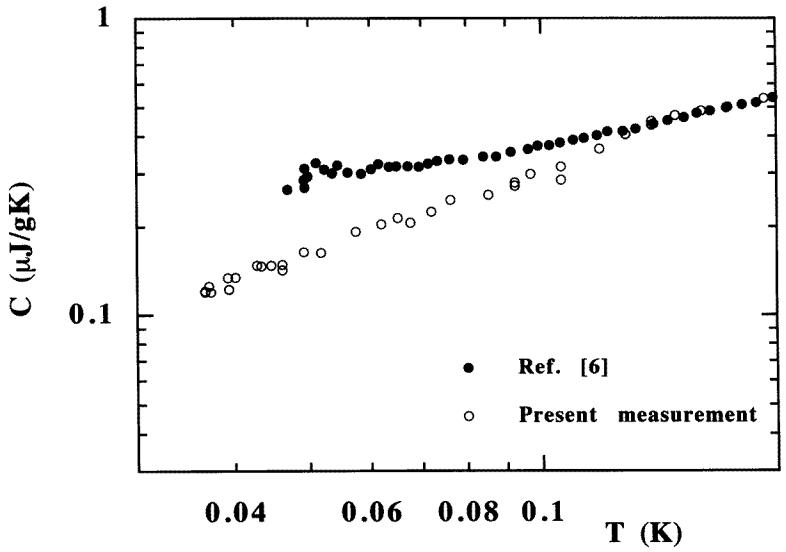
spatial mixture of localized and itinerant electrons. The proportion of each type of state is governed by the proximity of the MIT. The interactions between the two subsystems are not taken into account in the model. τ_{e-P} is then written as

$$\tau_{e-P}^{-1} = \tau_{e_{localized}-P}^{-1} + \tau_{e_{free}-P}^{-1}. \tag{6}$$

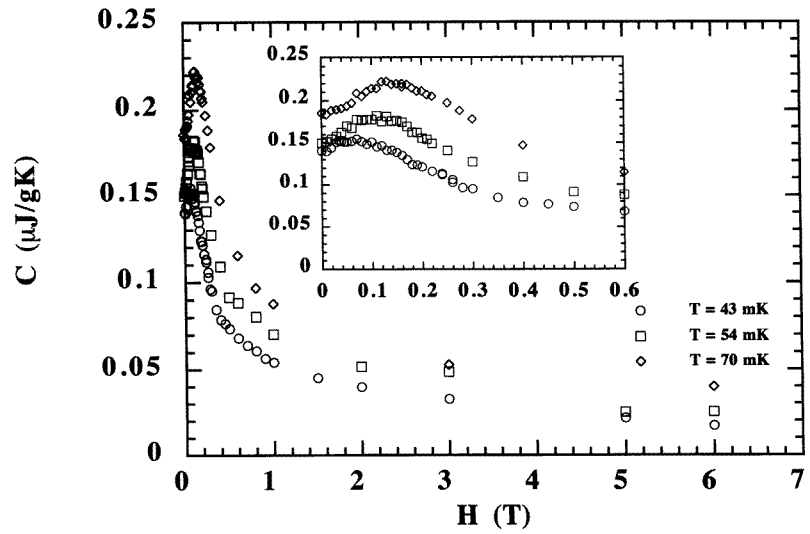
Again, with the parameters deduced in [10, 11], $\tau_{e_{localized}-P}^{-1}$ is negligible for $T \leqslant 1$ K. $\tau_{e_{free}-P}^{-1}$ depends on one parameter: m^*C, where m^* is the effective mass of the electrons (we took $m^* = 0.32\ m_0$ [19]), and C is a dilatation deformation potential constant [11]. We could then fit our curve for $\kappa(T)$ (figure 3) using equation (4) with $\tau^{-1} = \tau_B^{-1} + \tau_{e_{free}-P}^{-1}$. The thermal conductivity calculated using only the boundary scattering relaxation time, τ_B^{-1}, and only the free-electron–phonon scattering relaxation time, $\tau_{e_{free}-P}^{-1}$, are also shown. We adjusted the Casimir limit of boundary scattering to give good agreement with the data for $T \leqslant 100$ mK. The square of the effective cross section obtained from the fit was four times larger than our sample's cross section (this is consistent with the fact that one surface of our sample was polished, and could reflect the incoming phonons). The data for $T \geqslant 100$ mK fixed our value for C. Calculating the number of electrons in each subsystem (localized and itinerant) using a Poisson distribution for the phosphorus concentration and the same parameters as in [11] we found $C = 1.9$ eV. This is in good agreement with the results of [11] (for samples of lower concentration and $T \geqslant 2$ K) if we rescale C to our free-electron concentration ($C \propto N^{2/3}$) [19]. With such a dominant role of the free-electron–phonon scattering mechanism it is difficult to understand why no significant changes are observed in the thermal conductivity under a magnetic field. If one accepts the explanation given for the huge magnetoresistance of Si:P: the magnetic field diminishes the effective number of free carriers in Si:P, then one would expect a drastic decrease in the thermal conductivity under a magnetic field, mainly due to the relation $C \propto N_{free}^{2/3}$. This model fails to explain how the localization of free carriers under a magnetic field plays such an important role for the resistivity, but does not affect the free-electron–phonon scattering rate. It stresses the need for a more detailed understanding of the MIT in Si:P, with a model going beyond the phenomenological two-component picture and taking proper account of the disorder.

The thermal diffusivity is shown in figure 4. It was measured at very low temperatures (40–200 mK) and under a magnetic field (up to 5 T). We have recorded temperature ($D(T)$, figure 4(a)) as well as field ($D(H)$, figure 4(b)) sweeps. We note that the measurement of $\kappa(H)$ and $C_p(H)$ at these low temperatures is difficult due to the field dependence of the usual thermometers. For $D(T)$ in zero field we find a power-law behaviour with an exponent near 1.5 at $H = 0$ T in the temperature range of our measurement (40 mK–200 mK). With the $D(H)$ curves we could map out a marked anomaly at low field and very low temperature. Note that the heat diffuses better in the sample as H is augmented. At first glance, this is in contradiction to the fact that the electrical carriers diffuse less well under magnetic field and that the thermal conductivity is independent of the field. As we will see later, however, we can explain the behaviour of D qualitatively by comparison with the specific heat C_p.

With the thermal conductivity data for $T \leqslant 200$ mK and the heat diffusion time τ we have calculated the specific heat of our sample $C_p = \kappa/D \propto \tau\kappa$. Figure 5(a) shows this calculated $C_p(T)$ in zero field compared with the data of [5, 6] for a sample with a concentration close to ours ($N \approx 3.3 \times 10^{18}$ atoms cm^{-3}; see [5, 6] for further information, notably field measurements). The proportionality factor between D and τ was chosen in order to give agreement at $T \approx 200$ mK, and was of the order of magnitude of our sample dimensions (the bad characterization of the boundary conditions forced us to use a simple model from which we could not extract the absolute value for D). We find nevertheless



(*a*)



(*b*)

Figure 5. The calculated specific heat versus temperature (a) and magnetic field (b); (a) also shows the data of Lakner and von Löhneysen for a sample with $N \approx 3.3 \times 10^{18}$ atoms cm^{-3} [5, 6]. Note that in (a) our data are scaled to give agreement with Lakner and von Löhneysen's data at 200 mK, because we have not determined the absolute value of D. The inset in (b) shows the Schottky anomaly at low field and very low temperature.

some disagreement below 120 K. A possible explanation of this point could be the fact that the time-scale of our experiment ($\approx$ 80 ms at 40 mK, and $\leqslant$10 ms at 200 mK) is lower than that of the usual specific heat experiments. Due to the fact that the heat is propagated by the phonons, and that the thermal contact between phonons and electrons may be bad

at low temperatures, the electrons (localized or itinerant) in our system may not be able to follow such fast temperature variations: this would lead to a diminution of the electronic contribution of the specific heat, and hence a faster decay of C_p with temperature when calculated from diffusivity measurement. The time-scale of our experiment could also be a reason for the fact that we do not observe an upturn at the highest magnetic fields and the lowest temperatures on the calculated $C_p(H)$ which was observed by Lakner and von Löhneysen [5]. It was attributed to the Zeeman splitting of the ^{31}P nuclei, but the time-scale of their specific heat experiment ($t \approx 1$ s) was supposed to be of the order of magnitude of the (enhanced) Korringa relaxation rate for ^{31}P and was much larger than the time-scale of our measurement [20, 21, 22].

Nevertheless, the most striking feature of our thermal diffusivity measurements under field—the clear anomaly seen in figure 5(b)—can be explained qualitatively within a phenomenological two-component picture [5, 6]. The free electrons give the usual linear contribution to the specific heat while the spins of the localized electrons are responsible for a Schottky-like anomaly. The maximum of this anomaly will scale roughly like H/T, an effect which is clearly seen in the inset of figure 5(b) (or directly in D in figure 4(b)). This anomaly is also the reason for the better heat diffusion at high magnetic fields. At a fixed temperature κ almost does not change under a magnetic field but C_p is reduced as soon as the maximum of the Schottky-like anomaly is passed (in very low field). Our measurements of D allow for an extension of the literature data in that the anomaly is mapped out at very low temperatures as a function of H. They can only be understood qualitatively, and this stresses again the need for a model going beyond the two-component picture.

4. Conclusion

We have measured the thermal conductivity κ, the resistivity ρ, and the thermal diffusivity D, for an Si:P sample close to the metal–insulator transition at very low temperatures and under magnetic fields. Our measurements offer the possibility of comparing thermodynamic (C_p) and transport (κ, ρ) properties. The behaviour of the resistivity ρ can be explained by means of Mott's variable-range hopping mechanism of conduction. The temperature dependence of the thermal conductivity κ, as well as the comparison of C_p and D can be qualitatively understood in terms of a model which separates the electronic system into localized and itinerant electrons. But this model fails to explain the fact that κ does not vary under a magnetic field showing the lack of microscopic understanding of the MIT in silicon doped with phosphor. From an experimental point of view, we note that it would be interesting to measure D and κ across the MIT, not only in Si:P, but also in other materials with such a transition. For metallic or completely insulating samples, a thermometer other than the sample itself is needed, but the fact that only a time constant is measured eliminates the difficult problem of the magnetoresistance of the thermometer at low temperature.

Acknowledgments

We would like to thank J Flouquet, R Calemzuck, A Benoit and H von Löhneysen for stimulating discussions and continuous help, J Regolini (CNET, Grenoble) for providing the samples, and B Daudin, E Bedin and G Lapertot for making the contacts. We have also much appreciated the technical assistance of J M Martinod.

References

[1] Gaymann A, Geserich H P and von Löhneysen H 1993 *Phys. Rev. Lett.* **71** 3681
[2] Paalanen M A Rosenbaum T F, Thomas G A and Bhatt R H 1982 *Phys. Rev. Lett.* **48** 1284
[3] Hornung M, Ruzzu A, Schlager H G, Stupp H and von Löhneysen H 1994 *Europhys. Lett.* **28** 43
[4] Stupp H, Hornung M, Lakner M, Madel O and von Löhneysen H 1993 *Phys. Rev. Lett.* **71** 2634
[5] Lakner M and von Löhneysen H 1989 *Phys. Rev. Lett.* **63** 648
[6] Lakner M, von Löhneysen H, Langenfeld A and Wölfle P 1994 *Phys. Rev.* B **50** 17 064
[7] Kobayashi N, Ikehata S, Kobayashi S and Sasaki W 1977 *Solid State Commun.* **24** 67
[8] Marko J R, Harrison J P and Quirt J D 1974 *Phys. Rev.* B **10** 2448
[9] Kobayashi N, Ikehata S, Kobayashi S and Sasaki W 1979 *Solid State Commun.* **32** 1147
[10] Fortier D and Suzuki K 1976 *J. Physique* **37** 143
[11] Radhakrishnan V, Sharma P C and Singh M 1980 *Z. Phys.* B **39** 15
[12] Liu X 1995 *PhD Thesis* Karlsruhe University
[13] Thurber W R, Mattis R L, Liu Y M and Filliben J J 1980 *J. Electrochem. Soc.* **127** 1807
[14] Hornung M *Diploma Thesis* Karlsruhe University
[15] Danielson G C and Sidles P H 1969 *Thermal Conductivity* ed R P Tye (New York: Academic)
[16] Mott N F 1974 *Metal–insulator Transitions* (London: Taylor and Francis)
[17] Shklovskii B I and Efros A L 1984 *Electronic Properties of Doped Semiconductors* (Berlin: Springer)
[18] Dumoulin L 1991 *Proc. Detection de Rayonnement très Basses Temperatures (Aussois, 1991)*
[19] Ziman J M 1960 *Electrons and Phonons* (Oxford: Clarendon)
[20] Alloul H and Dellouve P 1987 *Phys. Rev. Lett.* **59** 578
[21] Paalanen M A, Ruckenstein A E and Thomas G A 1985 *Phys. Rev. Lett.* **54** 1295
[22] Paalanen M A, Graebner J E, Bhatt R N and Sachdev S 1988 *Phys. Rev. Lett.* **61** 597