Far-Infrared Reflectance Spectra of Si:P near the Metal-Insulator Transition

A. Gaymann and H. P. Geserich
Insititut für Angewandte Physik, Universität Karlsruhe, D-76128 Karlsruhe, Germany

H. v. Löhneysen
Physikalisches Institut, Universität Karlsruhe, D-76128 Karlsruhe, Germany

(Received 25 June 1993)

Far-infrared reflection measurements on Si:P both on the metallic and insulating side of the metal-insulator transition (MIT) were performed at low temperatures. In the metallic regime free-carrier absorption and, additionally, absorption peaks due to interband transitions from the impurity band to the conduction band and to transitions between the broadened valley-orbit split $1s$ states are observed. This gives clear evidence that the impurity band is formed by the overlap of the $1s(A_1)$ ground states and is well separated from the conduction band when the MIT occurs. Only far beyond the metallic limit the impurity band merges completely with the conduction band.

PACS numbers: 71.30.+h, 71.55.Cn, 78.50.Ge

The metal-insulator transition (MIT) in doped semiconductors continues to be a major field in solid state physics. The nature of the electronic states close to the critical doping concentration N_c is not completely understood. In particular, the question whether the MIT occurs in an impurity band well separated from the conduction band or inside the conduction band itself is a problem still under discussion [1]. Another open question is the influence of the valley-orbit splitting in many-valley semiconductors like Si and Ge on to the electronic density of states in the metallic regime. It has been suggested that the many-valley nature of tetrahedral semiconductors leads to the absence of a Mott-Hubbard gap in the single-particle excitation spectrum [2].

First evidence that the MIT in doped silicon and germanium occurs in an impurity band which merges with the conduction band only when the doping concentration N exceeds approximately $3N_c$ came from Knight shift measurements [3,4]. Later, this result was supported by calculations of the Knight shift and the specific heat in Si:P on the basis of a tight-binding model for the impurity band, which led to good agreement with experimental data [5]. More recently Rosenbaum *et al.* [6] observed a sharp feature in the low-temperature magnetoconductivity in Ge:Sb for a doping concentration above the MIT at a field corresponding to the central-cell splitting. This suggests that central-cell effects in the metallic phase persist and that the electronic states responsible for transport are derived from an impurity band.

Optical spectroscopy is a well-established method to probe the nature of these electronic states. The high energy resolution of absorption and reflection measurements provides information on the band structure over a wide energy range. The conductivity function $\sigma(\hbar\omega)$ reflects the joint density of states. Thus, from far-infrared spectroscopy on uncompensated Si:P with the well-known conduction band, detailed information of impurity states and the impurity band should be obtained. In fact, infrared absorption measurements on the single-valley system GaAs:Si near a magnetic-field induced MIT have shown evidence for an impurity band [7,8]. However, the many-valley nature of Si:P might strongly affect the electronic band structure near the MIT as mentioned above.

Several infrared absorption measurements on Si:P have been performed (see for example references in [9]), the most comprehensive and complete one by Thomas *et al.* [9]. All of them, however, are restricted to the insulating side of the MIT whereas optical measurements on metallic samples in the FIR regime are still missing, with the exception of two barely metallic samples very close to N_c [10,11]. In this paper, we report on far-infrared reflection measurements which allow us to investigate samples on the insulating as well as on the metallic side of the MIT with the same method, yielding directly the conductivity function $\sigma(\hbar\omega)$. On the other hand, a determination of $\sigma(\hbar\omega)$ from the absorption coefficient $\alpha(\hbar\omega)$ by transmission measurements via $\sigma(\hbar\omega) \sim \alpha(\hbar\omega)n(\hbar\omega)$ [12] requires the knowledge of the refractive index $n(\hbar\omega)$, which of course shows a different frequency dependence for insulators and metals. Our measurements thus demonstrate unambiguously that the MIT in Si:P occurs in the P-derived impurity band.

Phosphorus-doped single crystals were grown with the Czochralski method, yielding rods 54 mm in diameter. Taking advantage of a P concentration gradient along the axis of the rods, several samples with different N could be conveniently cut from a single rod using a diamond saw. N was determined by the room-temperature resistivity ρ_{295} using the calibration of Thurber *et al.* [13]. As usual, a fit of the resistance ratio $R(295\text{ K})/R(4.2\text{ K})$ vs ρ_{295} was employed for a more accurate concentration determination ($\approx 0.1\%$). The samples with typical dimensions of $9\times 9\times 4\text{ mm}^3$ were polished with diamond powder to obtain a clean and planar surface.

Far- and mid-infrared reflection measurements were performed using a Fourier transform spectrometer Bruker IFS 113v. The spectral range varied between

0031-9007/93/71(22)/3681(4)$06.00

2 meV and 620 meV (20 cm^{-1}–5000 cm^{-1}). A black polyethylene filter eliminated radiation above 1 eV.

The samples were mounted in a helium-flow cryostat with thin polyethylene windows. Sample cooling was achieved by helium exchange gas ($p \approx 10$ mbar). The temperature was measured with an AuFe-Cr thermocouple mounted on the sample holder. At each temperature the radiation reflected from the sample was compared with that reflected from a gold mirror. Identical positioning of sample and mirror was attained by laser adjustment and a special turning mechanism. The absolute photometric accuracy of the reflectance data was better than 1%. There was no heating of the sample by the incident radiation as determined by an additional platinum resistor mounted directly on a sample surface during a test run.

In order to check whether the broad spectrum of the incident radiation causes changes in the carrier distribution (e.g., by photogeneration of free carriers) we performed intensity dependent reflection measurements at low temperatures. No changes of the reflectance spectra occurred upon reduction of the intensity to a level of 5%.

Figure 1 shows the reflectance spectra $R(\hbar\omega)$ of samples with different doping concentrations measured at 10 K. The dielectric function $\epsilon(\hbar\omega)$ was obtained by performing a Kramers-Kronig analysis of the measured reflectance spectra extrapolated to lower and higher energies using a Drude-Lorentz model. Figure 2 shows the corresponding spectra of the optical conductivity $\sigma = \epsilon_2\epsilon_0\omega$.

First we discuss the conductivity spectra of the samples in the insulating regime, i.e., with doping concentrations N lower than $N_c = 3.52 \times 10^{18}$ cm^{-3}. All spectra show broad peaks near the ionization energy $E_I = 45$ meV of the P atom in Si. The inset in Fig. 2 gives an energetic scheme of the impurity levels in the dilute limit. With increasing doping concentration the maximum shifts to lower energy and broadens. A comparison of the absorption coefficient $\alpha(\hbar\omega)$ for $N = 1.8 \times 10^{18}$ cm^{-3}, derived from reflection measurements, with earlier absorption spectra [9] leads to an excellent agreement. In a simple picture these peaks in $\sigma(\hbar\omega)$ labeled with E_I can be explained by optical transitions from the broadened ground states to the conduction band, where the broadening is due to disorder and electronic correlations. These spectra were described by excitation processes in larger clusters of donors by Thomas *et al.* [9]. At a still lower donor concentration $N = 3.4 \times 10^{17}$ cm^{-3} optical transitions $1s(A_1) \rightarrow 2p_0$ and $1s(A_1) \rightarrow 2p_\pm$ in the reflectance spectrum are observed. The donor energy levels are in very good agreement with earlier data derived from absorption measurements as will be reported elsewhere [14]. For the concentrations of the present work these transitions are masked by the featureless broadband absorption due to larger clusters.

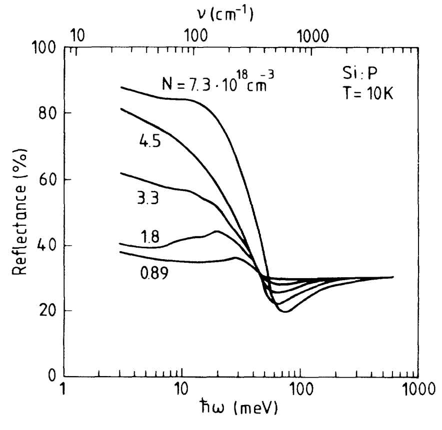

FIG. 1. Reflectance spectra $R(\hbar\omega)$ of insulating and metallic Si:P samples at 10 K.

At a concentration $N = 3.3 \times 10^{18}$ cm^{-3}, i.e., just below N_c, weak contribution of free-carrier absorption can be observed as deduced from the presence of a low energy tail of $\sigma(\hbar\omega)$. Even for $N = 1.8 \times 10^{18}$ cm^{-3} a weak tail corresponding to $\sigma \approx 2$ S cm^{-1} is seen. This is in qualitive agreement with specific-heat measurements showing a linear contribution in temperature even below N_c [15,16]. Generally, such a contribution is attributed to free carriers. However, since the dc conductivity is zero for $T \rightarrow 0$ the carriers are not delocalized over the entire crystal. Rather, quasifree carriers confined to clusters would be a possible explanation. However, the only qualitative agreement between "free" carrier concentration below N_c from specific heat and reflectivity calls for further investigations.

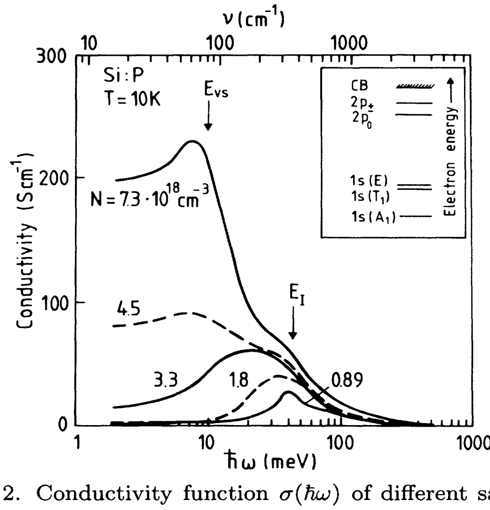

FIG. 2. Conductivity function $\sigma(\hbar\omega)$ of different samples obtained by Kramers-Kronig analysis. The inset gives a sketch of the level scheme of Si:P states in the dilute limit including valley-orbit splitting of 1s states; CB = conduction band; E_I = ionization energy of the impurity atom; E_{VS} = valley-orbit splitting between the $1s(A_1)$ and the closely spaced $1s(T_1)$ and $1s(E)$ levels.

For the metallic samples, three different features can be seen which are assigned to three different absorption mechanisms. First, intraband transitions are present as indicated by the occurrence of well-defined plasma edges in the reflectance spectra (Fig. 1). The spectral weight of this free-carrier absorption increases with increasing doping concentration. Extrapolating to the limit $\hbar\omega \rightarrow 0$ fairly good agreement with the values of the dc conductivity is obtained.

Second, weak absorption shoulders in $\sigma(\hbar\omega)$ around $E_I = 45$ meV clearly demonstrate that transitions into the conduction band persist even in the metallic state. We interpret these excitations as interband transitions from the impurity band to the conduction band. Thus, in addition to the free-carrier absorption these interband transitions can be observed in metallic samples, giving evidence that the metal-insulator transition in Si:P occurs in the impurity band and that the electronic transport at low temperatures is confined to this band which is well separated from the conduction band. The same interpretation was given by Lee *et al.* [7] and Romero *et al.* [8] who performed absorption measurements on single-valley n-type GaAs in the metallic state near the magnetic-field induced MIT. We add that temperature dependent reflection measurements on several metallic Si:P samples display that these interband transitions decrease with increasing temperature between 150 and 300 K [14]. This can be explained by the continuous thermal depopulation of the impurity band and the increasing occupation of the conduction band with increasing temperature. This additionally demonstrates that the excitations at about 45 meV are due to transitions of electrons in the impurity band to the conduction band and rules out the possibility that the observed transitions stem from a few isolated donors.

The third and most striking feature in the conductivity function is the absorption peak around 7 to 8 meV which is present in *metallic* samples only. This energy is close to the valley-orbit splitting $E_{VS} = 10$ meV between the $1s(A_1)$ and the closely spaced $1s(T_1)$ and $1s(E)$ levels for isolated donors well in the insulating regime (see inset in Fig. 2). At first sight, it appears surprising that a spectroscopic feature of isolated donors becomes clearly visible only in the metallic regime. However, in the isolated-donor regime, i.e., at very low doping concentrations this transition is dipole forbidden due to the angular momentum selection rule $\Delta l = \pm 1$. When the impurity atoms begin to interact the orbital angular momentum is no longer a good quantum number. Some indications for the weakening of the selection rule in the insulating regime were already observed by Thomas *et al.* [9]. In the metallic regime when impurity bands are formed by overlapping impurity ground states this selection rule should break down completely because there is no selection rule $\Delta l = \pm 1$ for extended states. The absorption peaks at about 10 meV constitute unambiguous evidence for transitions between the broadened valley-orbit split levels in the metallic state of Si:P. As can be inferred from Fig. 2 the oscillator strength of this transition becomes stronger with increasing doping concentration up to $N = 2N_c$ which is in agreement with the breakdown of the selection rule. Additionally, these peaks disappear with increasing temperature. This, again, can be explained by the continuous thermal depopulation of the impurity band formed from the impurity $1s(A_1)$ ground states. We add that another sample with $N = 7.0 \times 10^{18}$ cm^{-3} yielded exactly the same features as described here for the $N = 7.3 \times 10^{18}$ cm^{-3} sample.

Peaks in the absorption spectrum of two metallic samples very close to N_c were reported earlier [10,11]. It should be noted that the absorption coefficient $\alpha(\hbar\omega)$ shows a maximum even in the case of pure Drude-like intraband transitions at an energy determined by the concentration of free carriers. Hence, the $\alpha(\hbar\omega)$ peak cannot unequivocally be attributed to the transitions between the broadened valley-orbit split levels. However, our results clearly demonstrate the validity of the suggestion by Thomas [11]. In distinction to the previous work we observe that the absorption shoulder near E_I persists even rather deep in the metallic state $N \approx 2N_c$.

Valley-orbit transitions have been observed in Si:P by Jain *et al.* performing electronic Raman scattering experiments below the critical concentration N_c [17]. In these experiments it was found that the valley-orbit line $1s(A_1) \rightarrow 1s(E)$ broadens rapidly with increasing impurity concentration and disappears *before* the metallic regime is reached. This different behavior compared to infrared transitions can be understood by taking into account that the selection rules for optical transitions differ completely from those for electronic Raman scattering in the dilute limit. At very low doping concentrations the donor states are described by hydrogenlike wave functions with valley-orbit split $1s$ states and bound excited states, classified by angular momentum quantum numbers [18]. The selection rules for optical absorption are obtained by first order perturbation theory, whereas for electronic Raman scattering second order terms must be considered. As a result, optical transitions between the split $1s$ levels are strictly forbidden in the dilute limit, whereas in Raman scattering the transition $1s(A_1) \rightarrow 1s(E)$ is allowed [17]. The disappearance of the $1s(A_1) \rightarrow 1s(E)$ valley-orbit line in the Raman spectrum and the appearance of the optical transitions between the split $1s$ levels show that above the critical concentration N_c the hydrogenlike wave functions are no longer an adequate description of the impurity states.

In principle, a maximum in $\sigma(\hbar\omega)$ may also occur due to localization and Coulomb-interaction effects as demonstrated by Ng *et al.* in a low-mobility GaAs:Si superlattice [19]. However, since in bulk samples the electronic mean free path is much longer, such a maximum should appear in the microwave range, if at all.

Finally, we performed reflection measurements on a sample with a doping concentration deep inside the

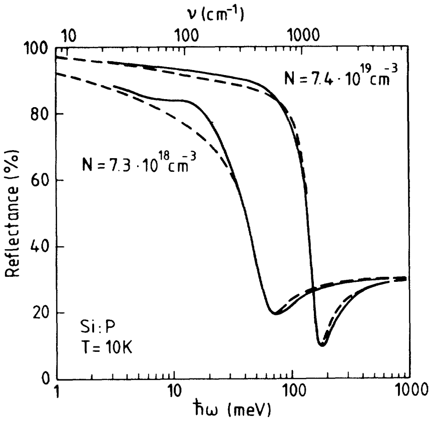

FIG. 3. Reflectance spectra (solid lines) of a metallic sample ($N = 7.3 \times 10^{18}$ cm^{-3} $\approx 2N_c$) when the impurity band is still separated from the conduction band and of one deep in the metallic regime ($N = 7.4 \times 10^{19}$ cm^{-3} $\approx 20N_c$) after merging of the two bands. A Drude fit (dashed lines) describes the data well only for $N \approx 20N_c$.

metallic regime ($N = 7.4 \times 10^{19}$ cm^{-3}). As already mentioned there are indications that the impurity band merges with the conduction band at a doping concentration $N \approx 3N_c$. After merging neither interband transitions from the impurity band to the conduction band nor transitions between the valley-orbit split 1*s* levels should be observable, only free-carrier absorption should persist. Figure 3 shows the reflectance spectrum of this sample at 10 K and that of the $N = 7.3 \times 10^{18}$ cm^{-3} sample for comparison, together with a fit describing the pure case of intraband transition by a Drude model. Only minor deviations of the reflectance spectrum for $N = 7.4 \times 10^{19}$ cm^{-3} from the Drude model are observed. Similarly, for GaAs:Si with $N = 6.5N_c$ the absorption spectrum could be described by a pure Drude response [8]. Our results on Si:P are in agreement with the observation that transport properties like the thermoelectric power for this sample obey perfect free-electron behavior when taking the conduction band effective mass and valley degeneracy into account [20]. In contrast, the reflectance spectrum of the $N = 7.3 \times 10^{18}$ cm^{-3} sample where impurity and conduction bands are still separated shows strong deviations from the pure case of intraband transition near 10 meV due to transitions between the broadened valley-orbit split levels.

In conclusion, our measurements demonstrate that the MIT in Si:P occurs in the impurity band which is formed by overlapping of the phosphorus $1s(A_1)$-derived ground states. Furthermore, they show directly by optical spectroscopy the persistence of central-cell effects in the metallic phase of doped semiconductors which was previously suggested for Ge:Sb from magnetoconductivity measurements by Rosenbaum *et al.* [6]. Finally, our measurements directly prove that even for $N = 7.3 \times 10^{18}$ cm^{-3} $\approx 2N_c$ transport at low temperatures occurs predominantly in the impurity band which merges with the conduction band at doping concentrations deep inside the metallic regime. No indications of a Mott-Hubbard gap are seen in our experiments, in agreement with theoretical predictions [2].

We thank Dr. W. Zulehner, Wacker Chemitronic, for providing the samples and M. Lakner for the concentration determination and helpful discussions. This work was supported partly by the Deutsche Forschungsgemeinschaft through Sonderforschungsbereich 195 and by the Commission of the European Communities under Contract No. CI1-0526-M(CD).

---

[1] N. F. Mott, *Metal-Insulator Transitions* (Taylor & Francis, London, 1990), 2nd ed.

[2] R. N. Bhatt and T. M. Rice, Phys. Rev. B **23**, 1920 (1981).

[3] M. N. Alexander and D. F. Holcomb, Rev. Mod. Phys. **40**, 815 (1968).

[4] D. Jérome, D. Ryter, H. J. Shultz, and J. Friedel, Philos. Mag. B **52**, 403 (1985).

[5] M. Kaveh and A. Liebert, Philos. Mag. Lett. **58**, 247 (1988).

[6] T. F. Rosenbaum, S. Pepke, R. N. Bhatt, and T. V. Ramakrishnan, Phys. Rev. B **42**, 11 214 (1990).

[7] Ming-Way Lee, D. Romero, H. D. Drew, M. Shayegan, and B. S. Elman, Solid State Commun. **66**, 23 (1988).

[8] D. Romero, S. Liu, H. D. Drew, and K. Ploog, Phys. Rev. B **42**, 3179 (1990).

[9] G. A. Thomas, M. Capizzi, F. DeRosa, R. N. Bhatt, and T. M. Rice, Phys. Rev. B **23**, 5472 (1981).

[10] T. F. Rosenbaum, K. Andres, G. A. Thomas, and P. A. Lee, Phys. Rev. Lett. **46**, 568 (1981).

[11] G. A. Thomas, in *High Temperature Superconductivity*, edited by D. P. Tunstall *et al.* (Adam Hilger Press, Bristol, 1991).

[12] F. Wooten, *Optical Properties of Solids* (Academic Press, New York, 1972).

[13] W. R. Thurber, R. L. Matthis, Y. M. Liu, and J. J. Filliben, J. Electrochem. Soc. **127**, 1807 (1980).

[14] A. Gaymann, H. P. Geserich, and H. v. Löhneysen (to be published).

[15] N. Kobayashi, S. Ikehata, S. Kobayashi, and W. Sasaki, Solid State Commun. **24**, 67 (1977).

[16] M. Lakner and H. v. Löhneysen, Phys. Rev. Lett. **63**, 648 (1989).

[17] K. Jain, S. Lai, and M. V. Klein, Phys. Rev. B **12**, 5448 (1976).

[18] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1957), Vol. 5.

[19] H. K. Ng, M. Capizzi, G. A. Thomas, R. N. Bhatt, and A. C. Gossard, Phys. Rev. B **33**, 7329 (1986).

[20] M. Lakner and H. v. Löhneysen, Phys. Rev. Lett. **70**, 3475 (1993).