Influence of Magnetic Dopants on the Metal-Insulator Transition in Semiconductors

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InSb:Mn and InSb:Ge reveal differences in their resistivity near the metal-insulator transition although both are acceptors of comparable depth. InSb:Ge shows the commonly observed behavior whereas InSb:Mn exhibits a strong enhancement of the resistivity below 10 K and pronounced negative magnetoresistance effects at 1.6 K. Both effects increase by applying hydrostatic pressure. The different behavior arises from the differences in the filling of the $3d$ shell, half filled $3d^5$ for Mn with a total spin of $S = 5/2$ and entirely filled $3d^{10}$ for Ge with total angular momentum of $J = 0$. The exchange interaction between the hole spin of the Mn acceptor and the $S = 5/2$ spin of its $3d^5$ shell is the dominant correlation effect leading to the formation of an antiferromagnetic alignment of the Mn $3d^5$ spins along the percolation path which inhibits hopping of holes between neighboring Mn sites.

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By incorporating magnetic impurities into semiconductors one immediately enters interesting intermediate areas between the fields of magnetism and semiconductor physics. One example is the area of so called dilute magnetic and magnetic semiconductors, where currently one main interest lies on obtaining ferromagnetic semiconductors with Curie temperatures above room temperature which may be employed as spin injectors or spin aligners in future III-V semiconductor spintronics or spin optoelectronics [1–3]. To achieve this aim one usually attempts to raise the magnetic ion content within the semiconductor to a few percent, i.e., to obtain magnetic semiconductor alloys. Another hot topic is the interaction of carriers or excitons with single Mn ions which can be probed by studying individual Mn-doped III-V and II-VI quantum dots [4–6]. Such experiments shed light on the fundamental interaction mechanisms and may be useful in the context of spin quantum information processing. Here, we focus on Mn-doped InSb samples with somewhat intermediate Mn concentrations to study the effect of these magnetic impurities on the metal-insulator transition (MIT). The MIT is a fundamental problem of semiconductor physics. It deals with the transition from an insulating state towards a metallic state with increasing impurity (i.e., acceptor or donor) concentration in a semiconductor host crystal [7,8]. It is well known today that carrier-carrier interactions play a fundamental role in this metal-insulator transition (MIT), as first pointed out by Neville Mott [9]. The Pauli principle allows two carriers of different spin to be located at the same impurity site, which makes these levels two-fold spin degenerate. However, the two carriers will experience a Coulomb repulsion. This strong Coulomb interaction yields an energy gap separating low-lying states with one electron per atom from states with two electrons per atom. A simple and widely used approach that takes these correlation effects into account is the Hubbard model [10]. It is well known that the system undergoes the so-called Mott transition from a metallic to an insulating state when the on-site interaction between the electrons exceeds some threshold. The corresponding localization of the electron wave functions is known as Mott localization.

So far, the theories describing the MIT, such as the Hubbard model [10] or the Anderson model [11], make no distinction between magnetic (e.g., Mn) and nonmagnetic impurities (e.g., Ge). However, it can be anticipated that in the case of magnetic impurities additional correlation effects, such as the exchange interaction between the localized magnetic moment of the $3d^5$ shell of the Mn acceptor and the magnetic moment of the acceptor hole, will have a significant impact on the transport behavior at the MIT.

In this Letter, we will compare the transport behavior of InSb doped with nonmagnetic Ge with InSb doped with magnetic Mn. Both Mn and Ge form shallow acceptor levels in InSb with identical acceptor activation energies of $E_{\mathrm{Mn}} = E_{\mathrm{Ge}} = 9.5$ meV [12,13]. Consequently, the MIT occurs at the same critical impurity concentration of $N_{\mathrm{cr}} = N_{\mathrm{Ge}} = N_{\mathrm{Mn}} \approx 2 \times 10^{17}$ cm^{-3} and the two systems are directly comparable. Any differences in their transport properties can be related to the different magnetic nature of the impurities. It is important to note that the magnetic impurity Mn serves both as the source of a large localized magnetic moment due to its half filled inner $3d$ shell and as the source of a loosely bound hole due to its acceptor character. We study the resistance and magnetoresistance in InSb:Ge and InSb:Mn crystals close to the MIT within the temperature range of 1.6 to 280 K, in magnetic fields of up to 10 T and at hydrostatic pressures of up to 14 kbar. We demonstrate that magnetic impurities such as Mn provoke dramatical changes in the character of the MIT which need to be accounted for in respective theories.

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The InSb crystals were grown by the Czochalsky method. The samples ($3 \times 1 \times 1$ mm^3 in size) were cut from single crystal ingots perpendicular to the growth axis to minimize the impurity-concentration gradient along their length. Ohmic contacts were made with an In solder. The measurements under hydrostatic pressure were performed in a nonmagnetic clamp pressure cell, that allowed hydrostatic pressure of up to 16 kbar at low temperature. The resistivity and Hall effect have been measured either in van der Pauw or Hall bar geometry.

Figure 1 displays an Arrhenius plot of the temperature dependence of the resistivity of both InSb:Mn and InSb:Ge. From the perspective of the experimental uncertainty in determining the MIT, the two samples can be considered as having carrier concentrations close to, but below $N_{\rm cr} \approx 2 \times 10^{17}$ cm^{-3}. For each sample three curves are shown corresponding to different values of the applied hydrostatic pressure. At ambient pressure, both InSb:Ge and InSb:Mn exhibit almost metallic behavior, i.e., constant resistivity at low temperatures. In the case of InSb:Ge, pressure-induced changes are negligible at high temperatures and only a minor increase of the resistivity with pressure is observed at 1.6 K. The general qualitative behavior of $\rho(T)$ hardly changes by applying hydrostatic pressure. In the case of InSb:Mn, applying pressure also does not influence the resistivity at room temperature, but causes significant changes at low T. A huge increase of the resistivity at 1.6 K by more than 4 orders of magnitude occurs with increasing pressure, leading to a rise of the activation energy E_A from 0.1 meV at ambient pressure to 1.6 meV at 12 kbar. This is a first indication of a completely different transport situation at low temperatures in samples doped with *magnetic* impurities compared to those doped with conventional *nonmagnetic* impurities.

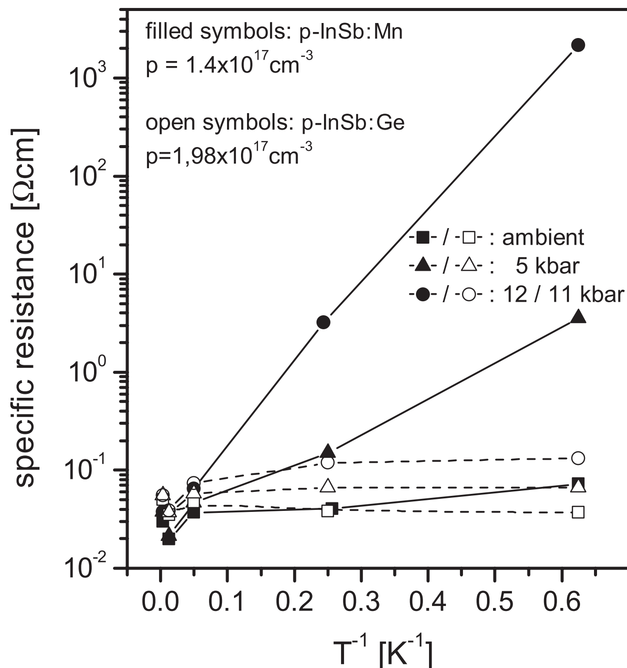

FIG. 1. Arrhenius plot of the resistivity of InSb:Mn and InSb:Ge crystals for various hydrostatic pressures (ambient, 5.2 kbar both InSb:Mn and InSb:Ge, 12.2 kbar and 11.1 kbar for InSb:Mn and InSb:Ge, respectively). InSb:Mn shows a dramatic increase of the activation energy in contrast to InSb:Ge.

The magnetoresistance measurements yield differences of similar distinctness. In the case of Ge doping [Fig. 2(b)], a small positive magnetoresistance (MR) effect (possibly due to wave function shrinkage) is observed at 1.6 K. Under hydrostatic pressure the MR curves remain positive and do not change significantly in magnitude. In contrast, large negative magnetoresistance effects dominate the curves for InSb:Mn. Already at ambient pressure, the sample shows a very large negative MR effect with a minimum of the relative MR of -35% at 3 T. With increasing pressure the negative contribution becomes even more pronounced up to 8 kbar with a minimum of -97%. Simultaneously the positive contribution loses strength or is shifted towards higher magnetic fields as no significant positive MR is found up to 10 T. With even higher hydrostatic pressure, the negative MR becomes less pronounced again and the steep decrease of the resistivity at low fields is smeared out. Still only a very weak positive MR is found up to 10 T. The extremely strong negative MR effects are too large to be explained by standard theories of MR (Weak Anderson localization [14], spin dependent hopping [15]) and do not arise in Ge doped InSb. Therefore the origin of the effect has to be connected to the magnetic nature of the Mn impurities.

A qualitative explanation of these unusual transport properties in InSb:Mn can be given in the Mott picture [16] accounting for additional correlation effects due to the p-d exchange between the localized Mn $3d^5$ spins and the hole spins of the Mn acceptor. At the MIT a significant overlap of the wave functions of neighboring acceptors can be assumed and the hole transport follows a percolation path through the acceptor system. The situation along the percolation path corresponds to the transport along a one-dimensional chain of impurity atoms. Since the acceptor wave functions are symmetric in space, the significant overlap between the wave functions of acceptors forces an antiparallel alignment of the hole spins of neighboring acceptors and the system forms an antiferromagnetic insulator [16]. This is the case for both Mn and Ge doped InSb [see Fig. 3(a)]. The difference between the two systems arises due to the additional p-d exchange coupling of the Mn localized magnetic moment and the spin of the hole localized at a Mn site. This coupling has two consequences: First, if the temperature is low enough, the antiferromagnetic order of the hole spins on neighboring Mn sites leads via p-d coupling to an antiferromagnetic order of the localized Mn $3d^5$ spins along the acceptor chain. The antiferromagnetic alignment of neighboring $S = 5/2$ spins is mediated through the localized holes (which must not be

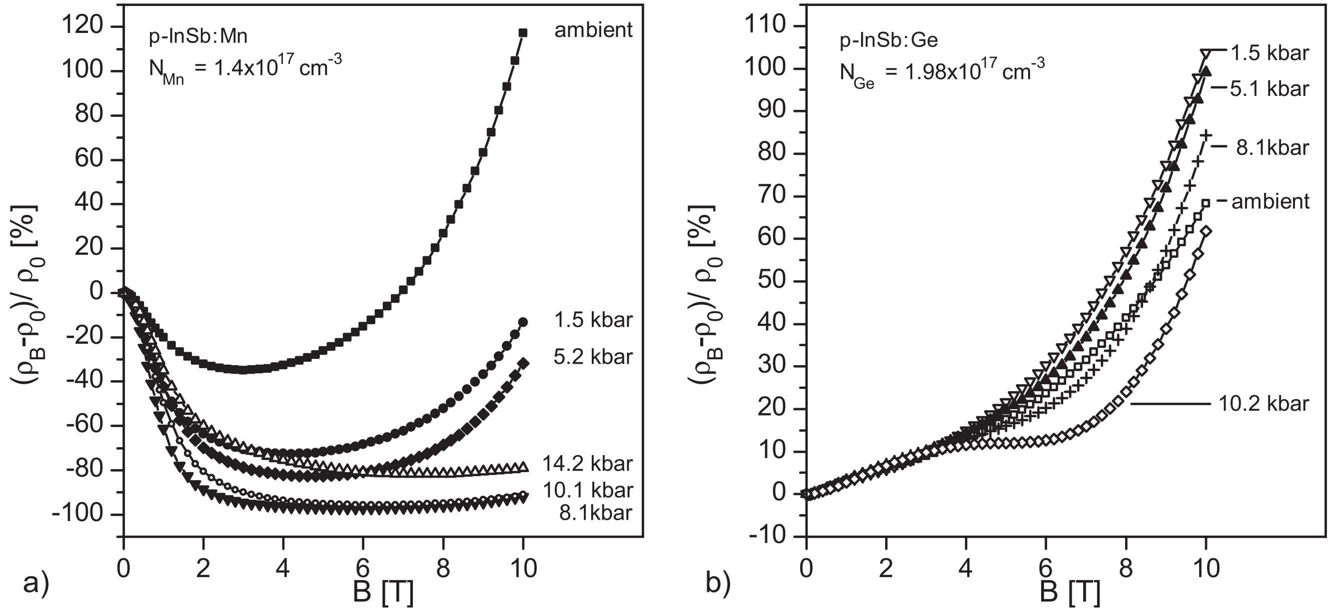

FIG. 2. Magnetoresistance in (a) p-InSb:Mn and (b) p-InSb:Ge as a function of magnetic field shown for various pressures at $T = 1.6$ K.

mistaken with the RKKY interaction between two Mn ions which is mediated by a free carrier plasma). Second, the p-d coupling lifts the spin degeneracy of acceptor levels, i.e., the energy level of the hole will depend on the relative orientation of its spin to that of the localized $S = 5/2$ Mn $3d^5$ spin. The corresponding spin Hamiltonian of the form $H_{pd} = -J_{pd}\vec{S} \cdot \vec{s}$ leads to the exchange splitting Δ of the acceptor hole levels [see Fig. 3(b)], where J_{pd} is the p-d exchange constant, $\vec{S}$ and $\vec{s}$ are the localized Mn $3d^5$ spin and the hole spin, respectively. The p-d exchange splitting Δ is much larger than the effects due to hole-hole interaction. The corresponding energy states are defined locally, with the low energy state given by an antiparallel alignment of hole and Mn spins and a high energy state characterized by parallel alignment. This corresponds to an antiferromagnetic coupling $J_{pd} < 0$ as reported by Schneider *et al.* [17] for GaAs:Mn and by Kudelski *et al.* [6] for InAs:Mn [18]. These authors report typical values $|J_{pd}|$ of about 1 meV which is also the order of magnitude of the exchange splitting Δ. The activation energies E_A, which we observe in InSb:Mn but not in InSb:Ge, are also in this range (see discussion of Fig. 1).

Below the Néel temperature, the transport path in InSb: Mn at the MIT is along an antiferromagnetically ordered chain of Mn spins. The hole states of the same spin orientation on neighboring Mn sites of the chain will differ by the p-d exchange splitting $\Delta \gg kT$ and thus inhibit hopping between these states. In InSb:Ge, neglecting hole-hole correlations, the two hole states on the acceptor will be degenerate. Obviously the hole-hole correlation as an on-site interaction only slightly lifts this degeneracy. The corresponding splitting is much smaller than the p-d-exchange induced splitting Δ. Therefore hopping along the Ge chain will be much easier than along a Mn chain.

Crucial for the differences in transport between a Mn and Ge chain is the establishment of the antiferromagnetic order of the Mn $3d^5$ spins along the chain. This antiferromagnetic ordering requires low temperatures, i.e., above the corresponding Néel temperature the $3d^5$ Mn spins are randomly arranged and hopping between neighboring Mn ions is no longer fully inhibited. This explains why the transport results of InSb:Mn and InSb:Ge differ significantly at low temperatures $T < T_N$ only. In this case the activation energy E_A in InSb:Mn is of the order of the exchange splitting Δ.

Within the above picture, one can also explain the observed dependence on hydrostatic pressure [see Fig. 3(c)] and on magnetic field [see Fig. 3(d)]. Hydrostatic pressure leads to an increase of T_N. It compresses the crystal enhancing the wave function overlap of holes located at neighboring impurity sites and also enhancing exchange coupling J_{pd} leading to a pressure-induced increase of Δ which is reflected in the increase of E_A in InSb:Mn under pressure and a corresponding strong reduction of the number of free holes (determined by Hall measurements) which is not observed in InSb:Ge. For example, the p-d exchange between localized Mn spins and free hole spins in (Zn, Mn) Te increased linearly by almost 70% by increasing hydrostatic pressure from ambient conditions to 30 kbar [19].

By applying an external magnetic field, the antiferromagnetic ordering of the Mn $3d^5$ spins can be overcome and a ferromagnetic alignment may be established

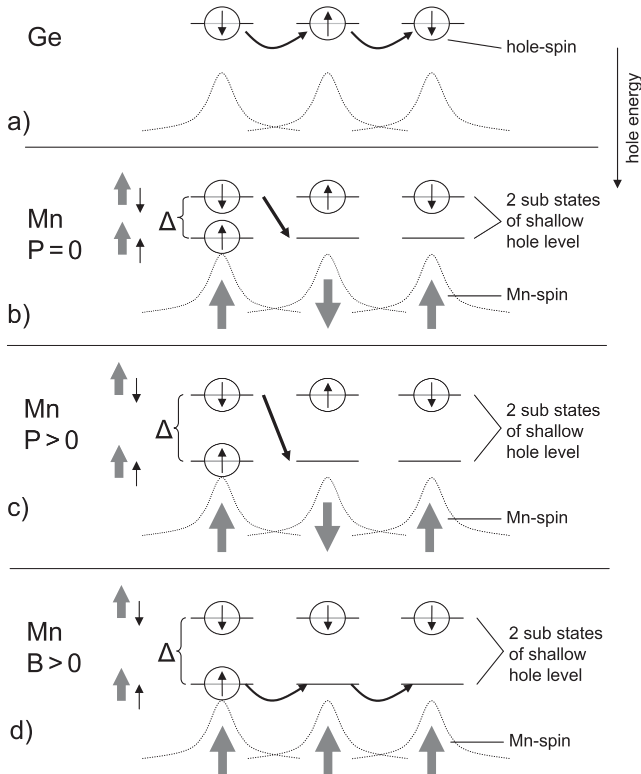

FIG. 3. Schematic illustration of hopping between impurity (hole) levels along the percolation chain in (a) InSb:Ge (b) InSb:Mn at zero magnetic field and ambient pressure (c) InSb:Mn under the influence of hydrostatic pressure (d) InSb:Mn with applied magnetic field. For simplicity, we assume a hole spin $s = 1/2$ in this illustration.

[Fig. 3(d)]. Consequently, an additional (spin-up) hole on a Mn site finds unoccupied spin-up hole states of the same energy on the neighboring sites [in contrast to the situation without magnetic field, Figs. 3(b) and 3(c)] allowing for hopping between sites of equal energy. With an increasing magnetic field, the situation changes from that described in Fig. 3(b) to that depicted in Fig. 3(d), i.e., from hopping with an activation energy of $E_A \approx \Delta$ to hopping with zero activation energy. Consequently, one observes a negative MR effect with increasing magnetic field which saturates at higher field. As Δ increases with hydrostatic pressure the corresponding negative MR must also increase as observed in the experiment. In InSb:Ge none of the mentioned effects are present due to the nonmagnetic nature of Ge.

Furthermore, it should be noted that the differences in electric transport of InSb:Mn and InSb:Ge are most pronounced in the vicinity of the MIT [20]. The reasons for this are the following. For $N_{\mathrm{Mn}} \ll N_{\mathrm{cr}}$, no continuous percolation path consisting of overlapping Mn acceptor wave functions is formed as the main transport path. Thus, no fully antiferromagnetically ordered Mn chain is established, which was the prerequisite for the observed effects. For $N_{\mathrm{Mn}} \gg N_{\mathrm{cr}}$, a Mn ion along the transport is likely to have more than two Mn neighbors with overlapping acceptor wave functions. Because of competing interactions between Mn spins, the formation of the one-dimensional antiferromagnetically ordered Mn chain will also be perturbed leading again to a degradation of the corresponding transport effects compared to the MIT situation.

In conclusion, we have proven that magnetic dopants can significantly influence the metal-insulator transition in semiconductors. Correlation effects between the localized magnetic moments and the loosely bound carriers of the magnetic dopant can be significantly stronger than on site carrier-carrier correlations leading to new interesting phenomena in an area between magnetism and semiconductor physics.

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