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Giant negative magnetoresistance in semiconductors doped by multiply charged deep impurities

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A giant negative magnetoresistance has been observed in bulk germanium doped with multiply charged deep impurities. Applying a magnetic field the resistance may decrease exponentially at any orientation of the field. A drop of the resistance as much as about 10 000% has been measured at 6 T. The effect is attributed to the spin splitting of impurity ground state with a very large g factor in the order of several tens depending on impurity.

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It is surprising that in well investigated transport properties of bulk semiconductors, particularly in the best known material germanium, until now new and previously not observed phenomena can be found. Here we report on a giant negative magnetoresistance in Ge which shows sizable effects already at very small magnetic-field strengths. An exponential drop of the resistance with rising magnetic field, which may be more than two orders of magnitudes, occurs in a *parallel* as well in perpendicular orientation of current and magnetic field.

Negative magnetoresistance has attracted much interest in the last decades due to the large variety of physical phenomena causing a drop of the resistance of semiconductors in an external magnetic fields. One of the striking effects is the low temperature giant negative magnetoresistance observed in disordered structures in magnetic fields with a variable range hoping regime due to quantum interference leading to weak localization.[1–6] Other important mechanisms of giant negative magnetoresistance in semiconductors are magnetic-field controlled metal-insulator transitions,[7] removal of a minigap in a semiconductor superlattice,[8] and magnetic-field suppression of spin-disorder scattering.[9,10] A similar giant change in resistance has been observed in Ge:Cu as a result of stress. A drop of the resistance by up to 12 orders of magnitude at liquid-helium temperature has been attributed to the formation of an impurity band in the band gap of Ge.[11] The application of a magnetic field on magnetic perovskites aligns the spins in different magnetic domains thereby lowering the energy barrier for carriers and yielding a colossal negative magnetoresistance.[12] A negative magnetoresistance occurs also in carbon nanotubes which has been shown to exhibit ballistic electron transport,[13] the increase of conductivity has been attributed to a magnetic-field-induced increase of the density of states in the vicinity of the Fermi level.[14] The giant negative magnetoresistance reported here has only been observed in samples doped with multiply charged impurities and could not be detected in materials with only singly charged impurities.

The experiments have been carried out on Ge:Hg, Ge:Cu, and Ge:Ga. In germanium Hg and Cu are deep acceptors which can bind two and three holes, respectively, whereas Ga is a shallow acceptor which binds one hole.

The binding energies of holes on Hg are 90 and 230 meV for detachment of the first and the second hole, respectively. From Cu three holes may be removed with the binding energies 40, 320, and (E_g-260) meV where E_g is the energy gap. The hydrogenlike shallow impurity Ga has an ionization energy of about 10 meV. The doping levels were in the range from 10^{14} to 3×10^{15} cm^{-3}. The typical size of the samples was $5\times3\times1$ mm^3. One pair of Ohmic contacts were prepared on opposite faces. The samples were fixed in a temperature variable cryostat. The resistance of the samples in the dark has been obtained from the low voltage Ohmic range of current-voltage characteristics. A magnetic field B up to 6 T could be applied parallel and perpendicular to the current flow by a superconducting magnet.

The conductance, $\sigma=1/\rho$, where ρ is the sample resistivity, measured at zero magnetic field is shown as a function of the inverse temperature, $1/T$, is plotted in the insets of Figs. 1 and 2 for Ge:Hg and Ge:Cu, respectively. At low

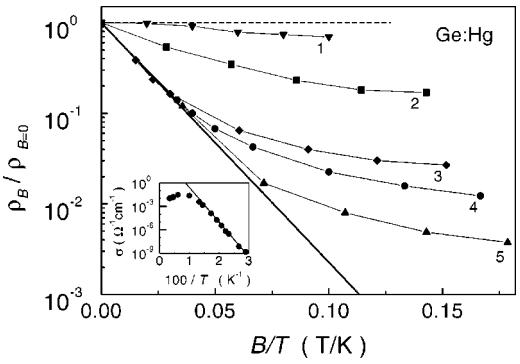

FIG. 1. A log-lin plot of the magnetoresistance $\rho_B/\rho_{B=0}$ of Ge:Hg as a function of the magnetic-field strength B normalized by the temperature T in the range $B=0$–6 T and for various temperatures: 1–55 K, 2–40 K, 3–38 K, 4–35 K, 5–33 K. The full is a fit to $\exp(-aB/k_BT)$ with $a=5.8$ meV/T. The inset shows an Arrhenius plot of the conductivity at zero B.

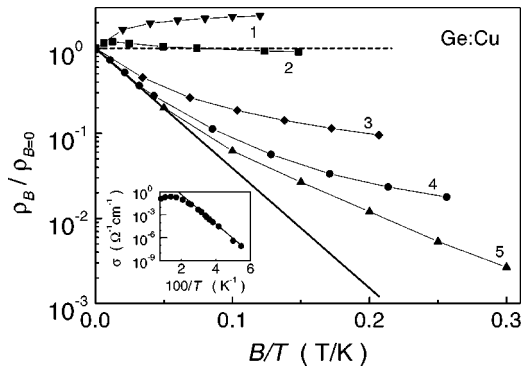

FIG. 2. A log-lin plot of the magnetoresistance $\rho_B/\rho_{B=0}$ of Ge:Cu as a function of the magnetic field strength B normalized by the temperature T in the range $B=0-6$ T and for various temperatures: 1–50 K, 2–40 K, 3–29 K, 4–25 K, 5–20 K. The full is a fit to $\exp(-aB/k_BT)$ with $a=2.8$ meV/T. The inset shows an Arrhenius plot of the conductivity at zero B.

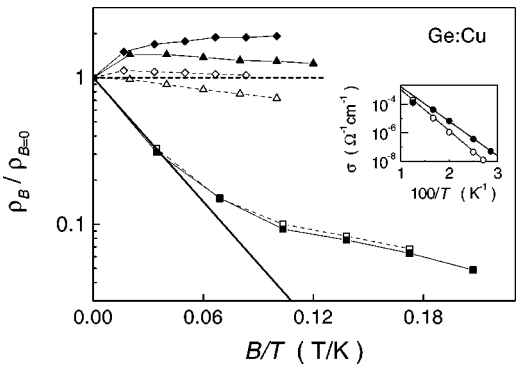

FIG. 3. A log-lin plot of the magnetoresistance $\rho_B/\rho_{B=0}$ of Ge:Cu as a function of the magnetic field strength B normalized by the temperature T in the range $B=0-6$ T and for various temperatures and for two compensation ratios. Diamonds, triangles, and squares correspond to $T=60$, 50, and 29 K, respectively. Full symbols: $N_A=1\times10^{15}$ cm^{-3}, $N_D/N_A=0.18$; open symbols: $N_A=3\times10^{15}$ cm^{-3}, $N_D/N_A=0.6$. The full is a fit to $\exp(-aB/k_BT)$ with $a=2.8$ meV/T. The inset shows an Arrhenius plot of the conductivity at zero B for both materials.

temperatures the temperature dependences exhibit a clear Arrhenius behavior determined by the corresponding binding energies. All magnetoresistance measurements have been carried out in these temperature ranges.

In Fig. 1 the resistance of a Ge:Hg sample is shown as a function of the magnetic field B normalized by the temperature T for various, but for each measurement constant temperatures. At low temperatures (curves 5, 4, and 3) and small magnetic-field strengths (~ 2 T) the resistance drops exponentially with the same slope for different temperatures. At higher field strength the resistance saturates. At higher temperatures (curves 1 and 2 in Fig. 1) the magnetic-field dependence gets weaker and finally the negative magnetoresistance changes to positive magnetoresistance. In the case of the perpendicular geometry, the negative magnetoresistance is still present at low temperatures but it is substantially smaller than in the parallel geometry. This is caused by a compensation due to the ordinary positive magnetoresistance in transverse magnetic fields.

The analogous measurements on Ge:Cu are shown in Fig. 2. The results are qualitatively the same with the difference that the slope is here only one third of that of Ge:Hg.

The strength of the negative magnetoresistance is independent on compensation ratio in the investigated range $N_D/N_A=0.18$ to 0.6 at low temperatures but gets dependent at higher temperatures where a substantial free carrier density exists in the band. This is shown in Fig. 3 where the resistance as a function of B/T at constant T for various temperatures and for two compensation ratios is plotted. The inset show the Arrhenius plot of the conductivity.

The negative magnetoresistance has only been observed in the dark and in a temperature range where only a small fraction of the impurities were ionized. If the samples were irradiated by visible or infrared light with photon energies larger than the impurity binding energies, the negative photoconductivity vanished. In the case of positive magnetoresistance (at high temperatures) irradiation did not affect the resistance ratio $\rho_B/\rho_{B=0}$.

With the singly charged shallow acceptor Ga in germanium only positive magnetoresistance could be detected down to liquid-helium temperature. This shows that at higher temperatures when almost all impurities are ionized the magnetic field increases the resistance by affecting the mobility. At low temperatures when almost all carriers are bound to acceptors the effect of the magnetic field on both mobility and binding energy causes a positive magnetoresistance, too. Thus, the influence of the magnetic field on the mobility cannot explain a negative magnetoresistance. This conclusion is supported by the fact that at high temperatures also the magnetoresistance of Ge:Cu ($T>40$ K) and Ge:Hg ($T>70$ K) is positive.

The observations that a giant negative magnetoresistance occurs only in materials doped with multiply charged impurities and that the resistance decreases exponentially with rising magnetic field in a significant range of temperature and magnetic field strength give a key for a qualitative understanding of the phenomenon. The exponential drop of the resistance indicates a decrease of the impurity binding energy being linear as a function of the magnetic field. The different behavior of singly (Ga) and doubly (Hg) charged impurities showing positive and negative magnetoresistance, respectively, will be discussed on the basis of a comparison with magnetic-field dependence of the ionization energy of neutral hydrogen and helium atoms.[15] The analog of the also investigated Cu in Ge is halogenlike corresponding to a triply occupied four fold degenerate shell (three holes on one Γ_8^+ state[16]) which is more complex and will not be considered in detail in the following discussion. In the cases of Ga and Hg the low-energy edge of the continuum states does not depend on magnetic field because the Landau diamagnetism ($\Delta\varepsilon_L=\Delta\varepsilon=\hbar\omega_c/2$) is compensated by the Pauli spin paramagnetism ($\Delta\varepsilon_P=-\Delta\varepsilon=-\mu_BB=-\hbar\omega_c/2$). Here μ_B and ω_c are the Bohr magneton and the cyclotron frequency, respectively. For hydrogen atoms in relatively low magnetic fields the energy of the ground-state level, $E_H(B)$, goes

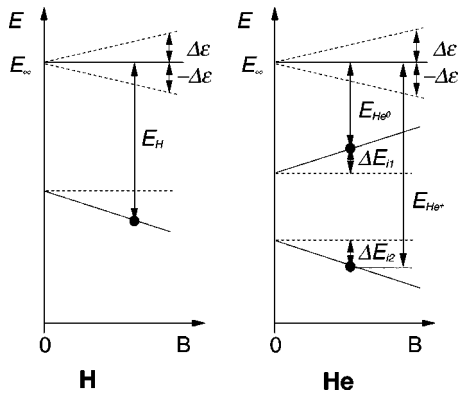

FIG. 4. Scheme of the energy levels of H-like and He-like atoms in magnetic field. E_A is the continuum edge, $E_H(B)$, $E_{He^0}(B)$, and $E_{He^+}(B)$ are ionization energies. ΔE_{ij} $(j=1,2)$ are changes of ionization energies in a magnetic field. $\Delta\varepsilon$ is the magnitude of paramagnetic and diamagnetic shifts of the continuum edge compensating each other.

down due to spin paramagnetism. The diamagnetic contribution is vanishingly small. Thus, the ionization energy of hydrogen atoms linearly increases with rising magnetic field. For helium atoms the situation is just the other way round, the binding energy decreases. The reason is that there are now two electrons with zero total spin on the $1s$ shell. Hence, the energy of this pair of electrons is independent of magnetic-field strength. After ionization of the first electron, one electron remains on the shell whose ground-state energy level goes down in the same way like that of the H atom. Thus, the ionization energy of the first electron, E_{He^0}, decreases by the value of ΔE_{i1} and that of the second electron, E_{He^+}, increases by the value of ΔE_{i2} as a function of the magnetic field. Therefore, $\Delta E_{i1}=-\Delta E_{i2}=-\hbar\omega_c/2$. The scheme of the energy levels involved in this discussion is sketched in Fig. 4.

This simple picture seems to apply to singly and multiply charged acceptors in semiconductors with rather complicated valence band where free holes are characterized by spin 3/2. For singly charged impurities, as in the case of hydrogen atoms, the ionization energy increases with rising magnetic field due to spin paramagnetism of holes in the ground state. Thus with rising magnetic-field strength the density of free holes decreases yielding a freezing out of free carriers. This is in good agreement to the positive magnetoresistance observed in Ge:Ga. For centers with two holes (doubly charged impurities) the ionization energy of the two-particle ground state can decrease linearly with the magnetic field as in the case of atomic helium. In contrast to the atomic situation, however, the edge of the continuum is not independent of the magnetic-field strength and increases the binding energy.[17] Thus, in order to obtain the decrease of the binding energy which results in the observed exponential increase of free carrier concentration, the paramagnetic shift of the second hole $|\Delta E_{i2}|$ must override the shift of the bottom of the valence band ΔE_0 and the ground-state shift of the acceptor with two holes.

The halogenlike model of Ge:Cu is also expected to yield a negative magnetoresistance as the binding of the triply occupied four fold degenerate ground state decreases with rising magnetic field.

The analysis of the measurements in the range of exponential decrease of the resistance (low temperatures and $B=0-2$ T) using $\Delta E_{i1}=-g\mu_B B$, where ΔE_{i1} is the change of the impurity binding energy, leads to a g factor $g=100$ for Ge:Hg and $g=48$ in the case of Ge:Cu (note Ge:Cu is triply charged). Therefore the effect of such a large g factor overrides any shift of the band edge and the ground state of acceptor with two holes in the magnetic field.

The origin for such giant g-factors remains unclear. Measurements using standard methods like EPR (ESR) are not known for deep acceptors in Ge (Ref. 18) because of large random fluctuations of the deformation potential and the degeneracy of the valence band yielding broad lines. This experimental difficulties were pointed out by Kohn.[19] Calculations based on the effective-mass approximation after Refs. 20,21 yield a ground-state g factor varying from about -1 for the shallow level ($E_A \ll \Delta_{so}$) to about 10 for deep centers ($E_A \sim \Delta_{so}$). Here E_A and Δ_{so} are the acceptor ground-state energy and spin-orbit energy splitting, respectively. For Ge:Cu these theoretical estimations are in a good agreement to Zeeman spectroscopy of transitions from the ground state to the first excited multiplet by Fisher and Vickers.[16] The g factor which is needed to fit our experimental results on Ge:Cu is much larger than observed by these optical measurements as well as calculations based on the effective-mass approximation. This drastic difference may be the result that in contrast to Zeeman spectroscopy, where the hole remains bound to the acceptor, in our case the acceptor is ionized in the final state. This causes a drastic change of the one-hole binding energy which increases from 40 meV of the first hole to 320 meV of the second hole. Thus, the effective-mass approximation breaks down and cannot be used to get proper values of g factors. Nevertheless the effective mass calculation yields the tendency that the g value increases with rising ground-state energy, which is qualitatively in agreement with our experimental data.

The strength of the present negative magnetoresistance in Ge:Cu is comparable to the resistance change observed under high axial stress by Dubon *et al.*[11] (two orders of magnitude at 20 K in both cases). This work shows that stress of 4 kbar leads to a deformation splitting of the acceptor levels which results in a decrease of the binding energy of the first hole by 25 meV. As the present measurements reveal that the hole binding energy drops by the same magnitude at 6 T, the approach of Dubon *et al.* should be taken into account at least at high magnetic fields. Note that also this approach requires unusual large g factors in the present situation.

The experimentally observed deviation from the exponential drop of the resistance at high magnetic fields and intermediate temperatures (Figs. 1 and 2) is due to a large increase of free carrier concentration which show a positive magnetoresistance. The same effect of free carriers causes the influence of compensation ratio on the magnetoresistance (Fig. 3).

In summary, in contrast to all established mechanisms of negative magnetoresistance, the giant negative magnetoresistance experimentally observed in germanium is due to a large shift of the thermal population of the band in a magnetic field. The exponential decrease of resistance requires a linear splitting of the impurity ground state in the magnetic field with an astonishingly large g factor. The large magnitude of g factor needs further investigation in order to explain it.

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