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 10000% 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.

71.55.-i, 71.70.Ej, 72.20.-i, 75.30.Vn

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 as much as about 10000% 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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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 $B = 0 \ldots 6$ T and for various temperatures: 1- 5 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 Arhenius plot of the conductivity at zero $B$. 

The experiments have been carried out on Ge:Hg, Ge:Cu, and Ge:Ga. In germanium Hg and Cu are deep acceptors doubly and and triply charged, respectively, whereas Ga is a singly charged shallow acceptor. The binding energies of holes on Hg are 90 meV 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 meV, 320 meV, and $(E_g - 260)$ meV where $E_g$ is the energy gap. The hydrogen-like shallow impurity Ga has an ionization energy of about 10 meV. The doping levels were in the range from $10^{12}$ to $3\times10^{15}$ cm$^{-3}$. The typical size of the samples was 5 x 3 x 1 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 \( \rho \) 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 Fig. 1 and 2 for Ge:Hg and Ge:Cu, respectively. At low temperatures the temperature dependencies exhibit a clear Arhenius behaviour determined by the corresponding binding energies. All magnetoresistance measurements have been carried out in these temperature ranges.

![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 \( B = 0 \ldots 6 \) 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 \( \exp(\alpha B/k_B T) \) with \( \alpha = 2.8 \) meV/T. The inset shows an Arhenius plot of the conductivity at zero \( B \).](image)

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 (\( \sim 2 \) 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 Arhenius plot of the conductivity.

![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 \( B = 0 \ldots 6 \) T and for various temperatures and for two compensation ratios. Diamonds, triangles, and squares correspond to \( T = 60 \) K, 50 K and 29 K, respectively. Full symbols: \( N_A = 1 \cdot 10^{15} \) cm\(^{-3} \), \( N_D/N_A = 0.18 \); open symbols: \( N_A = 3 \cdot 10^{15} \) cm\(^{-3} \), \( N_D/N_A = 0.6 \). The full is a fit to \( \exp(\alpha B/k_B T) \) with \( \alpha = 2.8 \) meV/T. The inset shows an Arhenius plot of the conductivity at zero \( B \) for both materials.](image)

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.

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 behaviour of singly and doubly 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. In both cases the low energy edge of the continuum states does not depend on magnetic field because the Landau diamagnetism (\( \Delta \varepsilon_L = \Delta \varepsilon = \))
The origin for such giant g-value remains unclear. Calculations based on the effective-mass approximation after [13] 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 \(\Delta_{so}\) are the acceptor ground state energy and spin-orbit energy splitting, respectively. These theoretical estimations show that the g-value increases with the ground state energy, which is qualitatively in agreement with the experimental data.

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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