Localization of electrons and negative magnetoresistance of nondegenerate germanium containing deep charged impurities

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Localization of electrons excited optically to the conduction band from deep centers was observed at the random Coulomb potential of charged impurities in compensated germanium. A negative magnetoresistance was observed and attributed to the influence of the magnetic field on quantum corrections to the conductivity.

Fluctuations of the potentials of impurity centers in crystals containing charged impurities may result in localization of electron states with energies below a certain value ε_c (Ref. 1). This limiting energy ε_c is known as the mobility edge. The nature of the conduction process in a degenerate electron gas is governed by the position of the Fermi level ε_F relative to ε_c: if $\varepsilon_F > \varepsilon_c$, the conduction process is metallic, but if $\varepsilon_F < \varepsilon_c$, the crystal behaves as an insulator and at $T = 0$ its conductivity vanishes. The metal–insulator transition which occurs when the Fermi level crosses the mobility edge is known as the Anderson transition. In nondegenerate semiconductors the Anderson transition may not be observed in its pure form (at $T = 0$), but in principle we can observe the "freezeout" of electrons in a potential relief if the temperature T is sufficiently low, so that $kT < \varepsilon_c$. We investigated compensated germanium with deep-level repulsive impurities and observed localization of electrons in the Coulomb relief formed by these impurities under conditions when the total density of electrons in the conduction band was created by optical release from deep centers.

1. We investigated n-type germanium crystals with the upper copper level partly compensated by antimony. The copper concentration was $N \sim 10^{15}$ cm^{-3} and the occupancy of the upper level of copper was 0.1–0.8. At low temperatures T the conductivity was ensured by illumination with impurity-absorbed light. Cooling from room temperature resulted in an exponential reduction of the conductivity with an activation energy equal to the ionization energy of triply charged copper amounting to 0.26 eV. At $T \lesssim 100$ K the electron density was controlled by their optical release from impurities and as a result of further cooling (region I in Fig. 1) the conductivity σ increased because of a change in the cross section for the capture of electrons by the repulsive copper ions.[2] We have plotted in Fig. 1 σ as a function of temperature in the optical generation region for different intensities of the exciting light. At $T \lesssim 20$ K we observed an exponential fall of σ with an activation energy of ~ 8 meV (region II). The Hall effect measurements indicated that the reduction in σ was due to an exponential reduction in the electron density (curve 5). Low-temperature activation-like reduction in the density was due to the Anderson localization of electrons from the conduction band in the random Coulomb potential of the charged centers; the activation energy was associated with the mobility edge. Similar temperature and field (see below) dependences of the conductivity σ had been reported also[3] for another multiply charged impurity (gold) in germanium.

In principle, the activated $\sigma(T)$ dependence could be due to the freezeout of electrons at shallow (antimony) donors. However, the trapping by antimony ions at $T = 10$–20 K could not be significant because of the low density n of free electrons in the compensated material. Under steady-state conditions each impurity level should be in equilibrium with the conduction band, i.e.,

$$n = gN_3/\alpha N_2 = n_1 N_{Sb}^0/(N_{Sb} - N_{Sb}^0).$$

Here, N_3, N_2, N_{Sb}, and N_{Sb}^0 are the concentrations of doubly and triply charged copper ions, of antimony atoms, and of neutral (electron-filled) antimony atoms; g and α are the optical generation and capture coefficients of the copper ions; $n_1 = N_c \exp(-\varepsilon_D/kT)$ is the Shockley–Read factor (ε_D is the ionization energy of a donor and N_c is the effective density of states in the conduction band). Cooling did not alter N_3 or N_2 as long as $N_{Sb}^0 \ll N_3, N_2$ and the trapping by antimony could affect the temperature dependence of n only if $N_{Sb}^0 \sim N_3, N_2$. At 20 K the Hall effect measurements indicated that for the curves in Fig. 1 the density was $n \approx 10^{10}$–10^{12} cm^{-3}. Consequently, $n \ll n_1$ and $N_{Sb}^0 \approx N_{Sb} n/n_1 \ll N_3$, N_2, i.e., at these temperatures there was no significant transfer of charge from copper to antimony. Therefore, n was

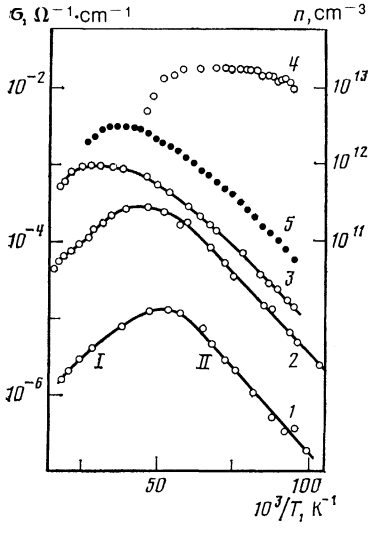

FIG. 1. Conductivity in a weak field obtained using different illumination intensities (1–3), maximum conductivity in a strong pulsed field (4), and Hall density of carriers (5) as functions of temperature. Curve 4 was obtained using the same illumination intensity as curve 1; curves 3 and 5 are related similarly.

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determined solely by the generation–recombination balance between the copper ions and the conduction band.

Throughout the range of temperatures investigated the conductivity σ increased with the illumination intensity (curves 1–3 in Fig. 1), which again indicated that the exponential part of the dependence $\sigma(T)$ was not associated with the trapping of electrons by antimony. In fact, since the exponential dependence $\sigma(T)$ in the case of capture by donors could appear only because of the temperature dependence of n_1, in the present case the value of σ should be determined solely by the thermal ionization of antimony atoms.

Thus the low-temperature activation-type fall of the conductivity was due to the freezeout of photoexcited electrons below the mobility edge ε_c. Electrons of energies $\varepsilon < \varepsilon_c$ were localized and did not participate in the conduction process, so that cooling, when kT became less than ε_c, changed the number of electrons participating in the conduction process in accordance with the law

$$n \approx n_0 \exp(-\varepsilon_c/kT), \qquad (1)$$

where n_0 is the total photocarrier density.

An electric field reduced the mobility edge ε_c and increased the density of free electrons. Figure 2 shows how the conductivity of a crystal depends on the applied voltage U. These dependences were determined using short ($\sim 10\,\mu$s) voltage pulses in order to avoid a change in the total electron density n_0 because of an increase, in a strong field, of the probability of capture by copper ions; pulses were also used in order to avoid the Joule heating of a crystal. It is clear from Fig. 2 that the conductivity rose strongly with the electric field (at ~ 11 K by more than four orders of magnitude) and the dependence $\sigma(U)$ was practically unaffected by a change in the intensity of the impurity-absorbed light (curves 1 and 2). When T was increased, the rise of $\sigma(U)$ became slower (curves 3–5). These curves were obtained at a fixed illumination intensity and the values of σ in weak fields represented by curves 3–5 corresponded to curve 1 in

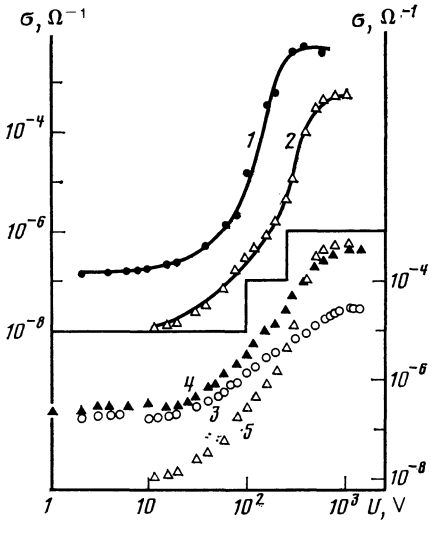

FIG. 2. Dependence of the conductance on the pulsed voltage applied to a sample subjected to illumination of different intensities (curves 1 and 2) at different temperatures T (3–5). Curves 1, 2, and 5 were obtained at $T = 10.9$ K; curve 3 was obtained at $T = 25$ K; curve 4 was obtained at $T = 17.3$ K.

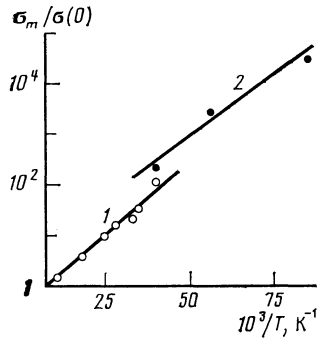

FIG. 3. Temperature dependence of the ratio of the conductivities in strong and weak fields recorded for two samples.

Fig. 1. Curve 3 corresponded to region I in Fig. 1 and it demonstrated that the localization of electrons occurred in a wider range of temperatures than that in which the dependence $\sigma(T)$ was activated.

Figure 3 shows the dependence of $\log[\sigma_m/\sigma(0)]$ on $1/T$ obtained for two samples [σ_m is the maximum conductivity reached in a field $E_m = U_m/L$, L is the length of the investigated crystal, and $\sigma(0)$ is the conductivity in a weak field]. Clearly, this dependence obeyed well the exponential law of Eq. (1).

Localization of electrons occurred in the Coulomb potential of the charged impurities. A rough estimate of the spatial scale of the random potential could be obtained from the maximum field E_m in which $\sigma(U)$ ceased to rise. Assuming that at $U = U_m$ all the electrons from the conduction band were delocalized, i.e., assuming that $eE_m l_c \approx \varepsilon_c$, we found that $l_c \sim 10^{-5}$ cm for $\varepsilon_c \approx 8$ meV and $E_m \approx 10^3$ V/cm. This quantity was found to be of the order of the average distance between impurities, which was to be expected because at low temperatures T there was no large-scale potential when the impurity level was approximately half-filled,[4] since the screening radius was limited to the average distance between the charged impurities.

The measured dependence $\sigma(U)$ could include a contribution from the field dependence of the mobility $\mu(E)$. Therefore, in order to estimate more accurately the value of l_c, we determined how the conductivity depended on the pulsed voltage in weak fields when the heating of electrons was still unimportant. We plotted in Fig. 4 the dependence $\log\sigma(U)$ at $T = 10.9$ K. Clearly, in weak fields the value of σ depended exponentially on U, i.e., an increase in the conduc-

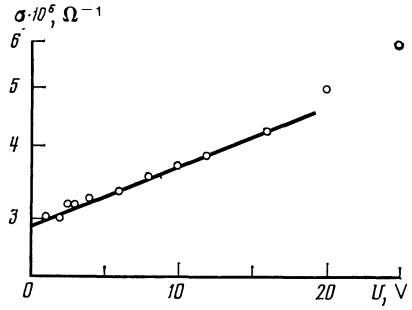

FIG. 4. Dependence of the conductance on the pulsed voltage.

tivity occurred because electrons "poured out" from the lower wells of the Coulomb relief on application of an external potential. As long as U was low, so that $el_c U/L \ll \varepsilon_c$, we could assume that the current percolation paths in the random potential were not affected. For a Boltzman distribution of the energies of localized electrons, we could assume that $n(E) \propto \exp(eEl_c/kT)$ [as indicated also by the exponential dependence of $\sigma_m/\sigma(0)$ on $1/T$]; then, the slope of the dependence $\log \sigma(U)$as shown in Fig. 4 yielded $l_c \approx 2\times 10^{-5}$ cm. Therefore, localization of conduction electrons occurred in the random potential of the charged impurities with a scale on the order of the average distance between the impurities.

It is clear from Eq. (1) that the activated dependence $\sigma(T)$ with a slope corresponding to the mobility edge ε_c could be observed only when the total photocarrier density n_0 depended weakly on T, i.e., if for $T \lesssim 20$ K there was practically no temperature dependence of the probability of the capture of electrons by the copper ions. This was confirmed by the temperature dependence of the conductivity σ_m in a field E_m in which the conduction band electrons were fully delocalized and their density was equal to n_0. The dependence $\sigma_m(1/T)$ is represented by curve 4 in Fig. 1. At temperatures below ~ 20 K the values of σ_m and, consequently, of n_0 were independent of T. The disappearance of the temperature dependence of the electron lifetime could be due to the fact that an electron could not be located farther from a center than the average distance between the impurities. Therefore, the position of the turning point governing the tunnel passage of an electron of energy $\sim kT$ across the Coulomb barrier of a repulsive impurity[5] ceased to depend on T at low temperatures. The critical temperature could be estimated from the condition $kT \sim Ze^2 N^{1/3}/\varkappa$ (Z is the charge of the center and is the permittivity), so that for $Z = 2$ and $N \approx 10^{15}$ cm^{-3} we should have $kT \approx 1.8$ meV, i.e., precisely $T \approx 20$ K.

2. Localization of the conduction band electrons manifest itself also in the anomalous magnetoresistance. The magnetoresistance measurements were made by placing a sample in a helium optical cryostat and subjecting it to a constant magnetic field H up to ~ 4 kOe. Additional coils were used to create an alternating magnetic field $\tilde{H} = 8.7$ Oe such that $\tilde{H} \ll H$. Measurements were made of a constant current i in a sample and of the alternating current $\tilde{\imath} = \tilde{H} di/dH$ caused by modulation of the magnetic field. The dependence $\tilde{\imath}(H)$ was used to reconstruct the dependence of the relative magnetoconductance $\Delta\sigma(H)/\sigma(0)$ on H. A modulation method made it possible not only to increase the sensitivity, but also to reduce significantly the influence of temperature instability, which was particularly important in the exponential part of the dependence $\sigma(T)$. In fact, the change in σ because of the instability of T was given by $\Delta\sigma(T)/\sigma \approx (\Delta T/T)(\varepsilon_c/kT)$ and in measurements of $\Delta\sigma(H)/\sigma$ in a static magnetic field we had to satisfy the condition $\Delta\sigma(H)/\sigma \gg \Delta\sigma(T)/\sigma$, i.e., in order to achieve $\Delta\sigma(H)/\sigma \sim 1\%$ when $\varepsilon_c/kT \approx 10$, a high temperature stability amounting to $\Delta T/T \ll 1.0\%$ was needed.

Figure 5 shows the dependence of the relative magnetoresistance $\Delta\rho(H)/\rho$ on H obtained at different temperatures. Clearly, the magnetoresistance was negative in the range of classically weak magnetic fields ($\mu H/c \ll 1$; the mobility μ deduced from the magnetoresistance had a maximum at $T \approx 70$ K and it amounted to $\sim 6.5\times 10^3$ cm$^2\cdot$V$^{-1}\cdot$s^{-1}) The magnitude of the negative magnetoresistance in the range of magnetic fields where it was observed decreased with increasing temperature. The negative magnetoresistance was observed not only in the low-temperature activated part of the dependence $\sigma(T)$, but also at temperatures where $d\sigma(T)/dT < 0$ (curve 5).

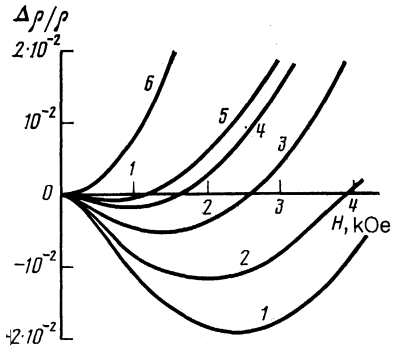

FIG. 5. Dependence of the relative magnetoresistance on the magnetic field at different temperatures (K): 1) 10.9; 2) 12.6; 3) 15.2; 4) 20.4; 5) 26; 6) 35.

Figure 6 shows the dependence of $\tilde{\imath}/i$ on the magnetic field in the range $H \lesssim 1$ kOe. Clearly, in weak fields the differential magnetoconductance di/dH increased linearly with H and then reached a plateau, i.e., we found initially that $\Delta\sigma/\sigma \propto H^2$ and then $\Delta\sigma/\sigma \propto H$. The slope of the initial region $\tilde{\imath}(H)/i$ and the value on the plateau decreased with increasing T. In the range $H > 1$ kOe the ratio $\tilde{\imath}/i$ decreased proportionally to H (see Fig. 1 in Ref. 6) and the slope of the field at the dependence of $\tilde{\imath}(H)/i$ in the range of "high" H was practically independent of temperature.

The negative magnetoresistance, observed long ago in heavily doped semiconductors and metals (see, for example, Ref. 7 and references given there to previous investigations), is currently attributed to a reduction in the quantum interference corrections to the conductivity in a magnetic field.[8] However, the existing theory applies to a degenerate electron gas in which the Fermi energy is considerably higher than the mobility edge. In our samples the conductivity was

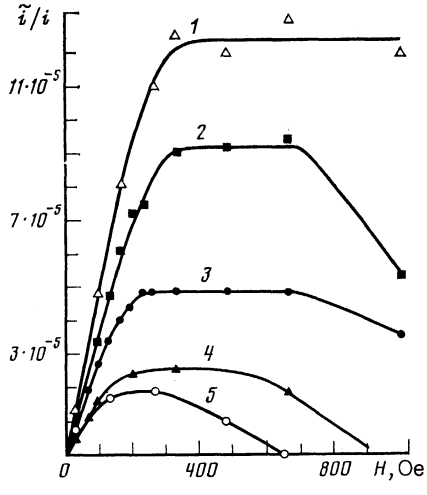

FIG. 6. Dependence of the ratio $\tilde{\imath}/i$ on the magnetic field at different temperatures T (K): 1) 10.9; 2) 12.6; 3) 15.2; 4) 20.4; 5) 26.

due to electrons excited optically from deep impurities to the conduction band where their energy distribution was of the Boltzmann type and the quasi-Fermi level was well below the mobility edge ε_c. Since in our case the condition $kT \ll \varepsilon_c$ was obeyed, electrons of energy $\varepsilon \approx \varepsilon_c$ participated in the conduction process. No calculations have yet been made of the quantum corrections to the conductivity and of their change in the magnetic field in this specific case. Nevertheless the negative magnetoresistance of our samples was clearly also due to quantum corrections to the conductivity. This point of view was confirmed by the observation that the negative magnetoresistance of our samples existed in classically weak magnetic fields when the usual magnetoresistance was weak. A necessary condition for the observation of the negative magnetoresistance was $\tau_\varphi \gg \tau$, where τ is the mean free time and τ_φ is the time for dephasing of an electron wave, governed by the inelastic scattering processes. In our case of low temperatures and a high concentration of multiply charged impurities the value of τ was governed by the scattering on ionized impurities and τ_φ by the scattering on acoustic phonons. Since $\tau_\varphi \geqslant \tau_{ph}$ (Ref. 9), where τ_{ph} is the time for the dissipation of momentum by acoustic phonons, the condition $\tau_\varphi \gg \tau$ is clearly satisfied. In weak magnetic fields [$H \ll c\hbar/4eD\tau_\varphi$ (Refs. 8 and 9), where D is the diffusion coefficient] the magnetoconductance obeys $\Delta\sigma(H) \propto H^2$, which is confirmed by the experimental results. An increase in H should saturate the interference part of $\Delta\sigma(H)$, changing to the classical dependence $\Delta\sigma/\sigma \propto -(\mu H/c)^2$. Therefore, the slope $di(H)/dH$ in "strong" magnetic fields is governed by the value of the mobility, which in our case was $\sim 6\times 10^3$ cm$^2\cdot$V$^{-1}\cdot$s^{-1} and was independent of T in the interval 10–20 K. The high value of μ (of the order of the mobility at 70 K) and the absence of the temperature dependence were again due to the fact that the measured mobility was due to electrons of energy $\sim \varepsilon_c \gg kT$.

The origin of the plateau in the dependence of di/dH on H [$\Delta\sigma(H) \propto H$] is not clear. It should be pointed out that a linear dependence $\Delta\sigma(H)$ has been reported also for heavily doped semiconductors (see, for example, Ref. 10), although the current in this case was due to the hopping conduction process and not due to the band process, as in our samples.

According to Refs. 8 and 9, the relative magnetoconductance is given by $\Delta\sigma(H)/\sigma = f(L_\varphi/L_H)$, where $L_\varphi^2 = D\tau_\varphi$ and $L_H^2 = c\hbar/eH$ is the magnetic length. Therefore, the change in the negative magnetoresistance with temperature is due to the temperature dependences of D and τ_φ. In our case the value of D was governed solely by the energy ε_c and was independent of temperature as long as $\varepsilon_c \gg kT$. Consequently, only τ_φ depended on temperature.

In spite of the fact that the existing theory does not deal with a nondegenerate electron gas near the mobility edge, we tried to find τ_φ from the expression[11]

$$\frac{\Delta\sigma}{\sigma} = \frac{1}{12\cdot 3^{1/2}}\left(\frac{\tau_\varphi}{\tau}\right)^{3/2}(\omega_c\tau)^2,$$

where $\omega_c = eH/mc$ is the cyclotron frequency and m is the effective mass of an electron. This expression is valid in the case of weak fields H, so that we determined τ_φ from the initial part of the dependence $\tilde{i}(H)$ in Fig. 6. The value of τ was deduced from the mobility. We then plotted τ_φ in Fig. 7 as a function of $1/T$. We found that, firstly, $\tau_\varphi \propto 1/T$ and,

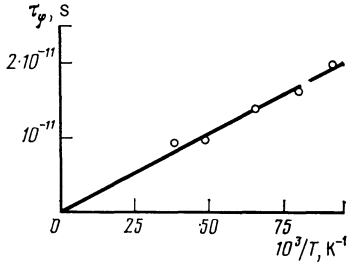

FIG. 7. Temperature dependence of τ_φ.

secondly, that the value of τ_φ was the same as τ_{ph}, which was the mean free time in the scattering by acoustic phonons. This was to be expected for the following reasons. It is shown in Ref. 9 that the dephasing time is $\tau_\varphi = \tau_{ph}$, if the condition $\tau_{ph}\bar{\varepsilon}\delta/\hbar \ll 1$ is not obeyed, where $\bar{\varepsilon}$ is the characteristic electron energy and δ is the scattering inelasticity parameter. In our case, we have $\varepsilon = \varepsilon_c$ and $\delta = (2ms^2\varepsilon_c)^{1/2}/kT$ (s is the velocity of sound), which yields $\tau_{ph}\varepsilon_c\delta/\hbar \sim 1$. Moreover, in the case of electrons of energy $\varepsilon \approx \varepsilon_c$, we find that $\tau_{ph} \propto T^{-1}\varepsilon_c^{-1/2}$, which accounts for the linear dependence of τ_φ on the reciprocal of temperature. The surprising agreement between τ_φ and τ_{ph}, not only in the temperature dependence but also in the magnitude, suggests that the theory of Ref. 11 is not restricted to the case of a degenerate gas. This may be due to the fact that in our crystals, as in the degenerate case, the electrons participating in the conduction process have practically the same energy ε_c, which is considerably greater than kT representing the average thermal energy.[1)]

3. Therefore, localization of electrons from the conduction band occurs in a nondegenerate semiconductor and the density of these electrons is controlled by their photoexcitation from deep impurities. Localization occurs in a random Coulomb potential of charged impurities with a spatial scale of the order of the average distance between the centers and is manifested in the anomalous temperature and field dependences of the conductivity. These anomalies are explained by the fact that the conductivity is due to an exponentially small number of delocalized electrons with an energy above the mobility edge. The results obtained demonstrate also that in the case of a nondegenerate electron gas we observe a negative magnetoresistance which can be explained by existing theoretical concepts of quantum interference corrections to the conductivity.

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[1)] A. Ya. Shul'man drew our attention to the analogy between the conductivity of a degenerate electron gas with $\varepsilon_F \gg kT$ and of nondegenerate electrons near the mobility edge at $\varepsilon_c \gg kT$.

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