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N.B.: When citing this work, cite the original publication.

Original publication available at:
https://doi.org/10.1063/1.5125882

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Heavily $n$-doped Ge: low-temperature magnetoresistance properties on the metallic side of the metal-non-metal transition

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We report here an experimental and theoretical study on the magnetoresistance properties of the heavily phosphorous doped germanium on the metallic side of the metal-nonmetal transition. An anomalous regime, formed by negative values of the magnetoresistance, was observed by performing low-temperature measurements and explained within the generalized Drude model, due to the many-body effects. It reveals a key mechanism behind the magnetoresistance properties at low-temperatures and constitutes, therefore, a path to its manipulation in such materials of great interest of fundamental physics and technological applications.

I. INTRODUCTION

The advent of doped semiconductors stands for a milestone in the development of the semiconductor devices. Since the seminals, with p-n junction transistors and solar cells, until the current trends, with mid-infrared sensors and plasmonic devices, the doped semiconductors has provided a fertile ground for fundamental research and applied physics. Among the possibilities, such materials can be used in energy-efficient windows, because they can act as a metal for low photon energies and as a semiconductor (or insulator) for high photon energies. In comparison with ordinary metals, for which the carrier densities are discrete and limited to a narrow range, doped semiconductors constitute more flexible systems, allowing a continuous variation of the carrier concentration over a wide range. In particular, such flexibility is even larger in $n$-doped many-valley semiconductors, like Si and Ge. On the one hand, Si has six equivalent band minima in the $(100)$-directions within the Brillouin zone (BZ); on the other, Ge has eight in the L-points (the intersection of the $(111)$-directions with the zone faces). Since the conduction-band valleys are strongly anisotropic, when electrons are filling up the states at the bottom of the conduction-band minima, they do not form Fermi spheres, but cigar-shaped Fermi ellipsoids. As a consequence, the contribution to transport and optical properties from each Fermi volume is anisotropic.

However, the sum of contributions from all volumes is isotropic since the overall symmetry is cubic; note that while the Si has six Fermi ellipsoids in the BZ, in the Ge the eight minima lie at the BZ boundary, leading to electrons effectively distributed within four Fermi ellipsoids.

It is well known that the application of uniaxial stress on the sample breaks the afore-described symmetry, such that part of the minima move upward in energy and part move downward, depending on the applied stress direction. There is a redistribution of electrons between the valleys and the applied stress results in piezoresistance and optical birefringence. Furthermore, it is also possible to modify the distribution of electrons by using an external magnetic field. Each of the (aforementioned) Fermi volumes is doubly degenerate and corresponds to spin-up and spin-down electrons. With the introduction of a magnetic field, the spin-up valleys move up in energy and the spin-down valleys move down - i.e., there is a redistribution of electrons where the Fermi level is the same for both valley types. The system remains isotropic, but important transport properties change, in particular, the electric current parallel to the magnetic field, which is expressed in terms of the longitudinal magnetoresistance, as will be here discussed in detail.

For all conducting pure single crystals, the acquired knowledge shows that, in general, the resistivity increases with the applied magnetic field, i.e., the magnetoresistance is positive. On the other hand, doped semiconductors require a detailed description at the critical concentration, $n_c$, when the system turns metallic. For densities much larger than $n_c$, if we place the donor electrons at the bottom of the host conduction band and treat them as a non-interacting electron gas, we found an unambiguous agreement with experiments. However, an anomalous regime arises when $n$ approaches $n_c$, in which, for example, the heat capacity and the spin susceptibility are enhanced. In particular, low-temperature magnetotransport properties are critically affected by this regime, being the negative magnetoresistance a critical signature. Theses so-called anomalies have attracted much attention with several models reported in the literature. With a peculiar interpretation, Sernelius and Bergreen proposed that the donor electrons end up in the conduction band of the host already at the critical concentration $n_c$ and suggested that the anomalous properties, on the metallic side of and close to the transition point, are caused by many-body effects. One step forward, we explore here such anomalous behavior of the magnetoresistance in heavily n-doped Ge, comparing results from low-temperature magnetotransport measurements...
with those obtained from the theory.

II. MEASUREMENTS AND SAMPLES

As illustrated in Fig. 1, Hall and longitudinal resistance measurements were performed in an Oxford cryostat with VTI (Variable Temperature Insert), under a perpendicular magnetic field provided by a superconducting coil. To prevent heating effect and provide a clear signal for our measurements, was employed the lock-in technique with frequencies 0.5-13 Hz in the temperature range of 1.5-4.2 K and bias current of 10 $\mu$A.

The samples were prepared in the following way: P-type, Ga doped (100)-oriented square, 7 $\times$ 7 mm$^2$, Ge samples with resistivity in the range of 1-10 $\Omega$cm were implanted with phosphorus at room temperature. In each sample, implantations with energies of 240, 140, 80, 40, and 20 keV were accumulated with appropriate doses to obtain a plateau-like profile of P, from the surface to the depth of about 0.40 $\mu$m, according to TRIM code simulation$^{25}$. In Fig. 2 we show the simulation for the concentration profile. To achieve a P atomic concentration of $1 \times 10^{19}$ cm$^{-3}$, the implanted P doses were $2.0 \times 10^{13}$ cm$^{-2}$ (at 240 keV), $6.0 \times 10^{12}$ cm$^{-2}$ (at 140 keV), $4.0 \times 10^{12}$ cm$^{-2}$ (at 80 keV), $2.0 \times 10^{12}$ cm$^{-2}$ (at 40 keV) and $1.1 \times 10^{12}$ cm$^{-2}$ (at 20 keV). The doses in the other samples were scaled to this sample, according to the ratio of the desired P concentration. Furthermore, the damage annealing and the electrical activation of P were performed at 600 C for 1 minute in argon atmosphere in a Rapid Thermal Annealing furnace to avoid high thermal budget; Van der Pauw structures$^{20}$ were fabricated by applied indium contacts at the corners of the samples and annealing at 80 C on a hot plate for 1 minute was performed to improve the contacts. The implantation process is described in Refs. $^{27-29}$.

III. THEORETICAL APPROACH

From the theoretical point of view, the conduction band of Ge has four equivalent valleys ($\nu = 4$); there are eight minima in the $(\pm 1, \pm 1, \pm 1)/\sqrt{3}$ directions, but they all are on the zone boundary so only half of each cigar-shaped Fermi volume is inside the Brillouin zone. In heavily $n$-type doped germanium, on the metallic side of the metal-non-metal transition (i.e., $n > n_c$), the donor electrons are up in the conduction band valleys. We consider that the electrons are distributed in $\nu$ Fermi spheres and neglect some known anisotropy effects on the resistivity$^{30}$; the relation between the radius of each sphere is then given as$^{29} k_0 = (3\pi^2 n/\nu)^{1/3}$ and the Fermi energy given by $E_0 = h^2 k_0^2/(2m_e)$, where $m_e$ is the electron rest mass and $m_{de}$ is the effective mass of the density of states in one valley of the conduction band. In particular, the contributions from the exchange and correlation energy, $E_{xc}$, due to the influence of ionized-donor potentials (the band-structure energy, $E_b$), affect the parabolic band dispersion and the density of states, i.e. our model starts from the density of states from one valley, i.e.

$$D_E = D_{k}/|dE(k)/dk| = \frac{k^2}{\pi^4 (dk^2/dk)},$$ (1)
and take into account that in each valley there are two states for each \( k \) (i.e., one for each spin, up and down). Since \( D_E^k = km^*/\pi^2 \hbar^2 \) is the density of states for non-interacting electrons, the density of states for interacting electrons can be expressed, in analogy, by introducing a wave-number dependent effective mass, i.e.

\[
D_E = km^*/\pi^2 \hbar^2, \tag{2}
\]

with the effective mass given by

\[
m^* (k) = m/[1 - \beta (k)], \tag{3}
\]

where \( \beta (k) \) gets a contribution from each of the interaction energies, \( \beta (k) = \beta_{xc} (k) + \beta_0 (k) \), such that

\[
\beta_{xc} (k) = -\frac{m}{\pi^2 k^2} \frac{\partial}{\partial k} \frac{\delta N_E}{\delta n(k)}, \quad \beta_0 (k) = -\frac{m}{\pi^2 k^2} \frac{\partial}{\partial k} \frac{\delta N_E}{\delta n(k)}. \tag{4}
\]

\( N \) is the total number of electrons and \( n(k) \) is the occupation number of the state with wave-vector \( k \). Specially important for this paper, one effect of the interactions is that around the Fermi level the effective mass and density of states are enhanced\(^{31}\).

We use the generalized Drude model\(^{32,33}\) to calculate the resistivity. For the static case, as here, the results agree with the so-called Ziman’s formula\(^{34}\),

\[
\rho = \frac{1}{ne^2 m}, \quad \frac{1}{\tau} = \frac{4 \nu e m}{\pi k^2 \kappa^2} \int dq \frac{1}{q^2}, \tag{5}
\]

where \( \rho \), \( \tau \) and \( \kappa \) are respectively the resistivity, transport time and dielectric constant (\( \kappa = 15.36 \) for Ge).

The presence of a static and spatially homogeneous magnetic field \( B \) leads to a redistribution of electrons between spin up and spin down bands, which affects the density of states, the effective mass at the Fermi level, the conductivity and the transport time. Let us introduce the spin-polarization parameter, \( s \), that varies from zero in absence of \( B \) to 1 at full polarization (all electrons have spin down),

\[
s = \frac{n^\uparrow - n^\downarrow}{n}. \tag{6}
\]

For spin up and down electrons, the density and Fermi wave-number are respectively,

\[
\begin{align*}
n^\uparrow &= n(1-s)/2, \\
n^\downarrow &= n(1+s)/2, \\
k_{0}^\uparrow &= k_0(1-s)^{1/3}, \\
k_{0}^\downarrow &= k_0(1+s)^{1/3}.
\end{align*} \tag{7}
\]

Therefore, the resistivity is now written as\(^{29}\)

\[
\rho (s) = \frac{m/e^2}{n^\uparrow \tau^\uparrow (1 - \beta^\uparrow) + n^\downarrow \tau^\downarrow (1 - \beta^\downarrow)}. \tag{8}
\]

Note that the magnetoresistance is given by \( \Delta \rho/\rho = [\rho (s) - \rho (0)]/\rho (0) \), i.e. it is a function of the spin polarization \( s \); however, the experimental results are given in terms of \( B \). When the modulus of the magnetic field is small enough, one can assume the following linear relation between \( B \) and \( s \):

\[
B [T] = \frac{2.64262 \times 10^{-11} (n \text{[cm}^{-3}] / \nu)^{2/3}}{m_{de} (\chi / \chi_0)} s. \tag{9}
\]

### IV. RESULTS AND DISCUSSION

We compare obtained theoretical and experimental results in Figs. 3 - 5. The spin-susceptibility enhancement-factor (\( \chi/\chi_0 \)) and effective mass (\( m_{de} \)) were adjusted\(^{35}\) to optimize the fit between theoretical and experimental curves; note, however, that this adjustment does not affect our main picture, with negative values for the magnetoresistivity as well as its signal inversion. In Fig 3 we show the results for the sample with the lowest doping concentration, which is closest to the metal-nonmetal transition (reminding that\(^{16}\) \( n \approx 2.5 \times 10^{17} \text{cm}^{-3} \)) and for which the magnetoresistance presents a minimum that becomes deeper when the temperature decreases. The black line shows the theoretical curve obtained for the spin-susceptibility enhancement-factor equal to 2 (and 0 K), and the blue and red lines correspond respectively to experimental results for 1.5 K and 4.2 K. Fig. 4 presents the results for the sample with the next lowest doping concentration; in comparison with the Fig. 3, we see a more shallow minimum for the theoretical curve and lit-
tle deeper minima for the experimental curves. Here, we use $\chi/\chi_0$ equal to 2.2.

In Fig. 5 we present the results for the sample with the highest doping concentration, where we use $\chi/\chi_0$ equal to 2.5. In this figure, the relatively high noise level is related to increased digital noise level due to a larger dynamic range used in lock-in amplification compared with measurements in Fig. 3 and Fig. 4. Analyzing the Figs. 3 - 5, we identify two competing effects: while the lowering of the doping density leads to deeper minima, the increment of the temperature leads to shallower minima. It is also important to note that, near and on the metallic side of the metal-nonmetal transition, the enhancement of the density of states at the Fermi level increases. Furthermore, the enhancement of the spin susceptibility also increases when the density comes closer to $n_c$; however, it is reduced when the temperature goes up\textsuperscript{11,12,37,38}. Using a log-log plot, in Fig. 6 we show how the maximum negative magnetoresistance decreases linearly when the doping concentration increases. Note that the maximum starts to decrease at a density that depends on the temperature. The higher the temperature, earlier the maximum starts to decrease, as also reported in Ref.\textsuperscript{13}.

Here we propose an explanation to the cause of the negative magnetoresistance observed at low temperatures in heavily phosphorous doped germanium on the metallic side of the metal-nonmetal transition. First, in the absence of magnetic fields, the density-of-states enhancement at the Fermi level contributes to the enhanced resistivity. Second, the presence of a magnetic field lifts the degeneracy of the electron dispersion, resulting in an upshifted spin-up band and a downshifted spin-down band. At the Fermi level, there is a redistribution of electrons between spin-up and spin-down bands, which leads spin-up and spin-down electrons to states with wave-numbers $k_{01}$ and $k_{02}$ respectively. Consequently, the peak corresponding to the density of states at the Fermi-level splits in $k_{01}$ and $k_{02}$: for electrons with $k_{01}$, one peak remains at the Fermi-level while the other moves down into the unoccupied part of the bands; instead, for electrons with $k_{02}$, while one peak remains at the Fermi-level, the other moves up into the occupied part of the bands. The en-

FIG. 4. (Color online) The same as Fig. 3, but here for the doping concentration $6.25 \times 10^{17}$ cm$^{-3}$.

FIG. 5. (Color online) The same as Fig. 3, but here for the doping concentration $1.17 \times 10^{18}$ cm$^{-3}$.

FIG. 6. (Color online) The depth of the magnetoresistance minima as function of doping concentration. The red thick solid straight line is the theoretical result for 0 K; the blue open squares are the experimental results at 4.2 K; the green filled triangles are the experimental results for 1.5 K; the thin solid curves are just guides for the eye. See the text for details.
V. CONCLUSIONS

To summarize and conclude, we have investigated the anomalous regime of the longitudinal magnetoresistance of heavily n-doped germanium on the metallic side of the metal-non-metal transition, by using magnetotransport measurements at low temperatures (1.5 K and 4.2 K) and comparing with obtained results from many-body theory, where the donor-electrons are assumed to reside at the bottom of the many-valley conduction band of the host. For doping densities above and close to $n_c$, we found a regime formed by negative values of the magnetoresistance that is drastically suppressed when the temperature increases and physically interpreted in terms of many-body effects. The obtained results show that the experiments support the model and can help in understanding the mechanism of magnetoresistance of heavily doped semiconductors. Besides, the presented results open the possibility to explore the interplay with other relevant conduction/resistance mechanisms at low-temperatures, like the weak localization. Additionally, more samples in the doping range of $10^{18} - 10^{19}$ cm$^{-3}$ would be helpful for further verification of the theory.

VI. ACKNOWLEDGEMENTS

The authors acknowledge financial support from the Brazilian agencies: CNPq (Proj. 303304/2010-3), CAPES (PNPD 88882.306206/2018-01), FAPESB (PNX 0007/2011 and INT 0003/2015) and FAPESP (Proj. 15/16191-5).


![Diagram](image-url)
We have enhanced the effective mass, $m_{de}$, characterizing the Fermi spheres with a factor of 1.5, i.e. it has been changed from .22 to .33. Also note that the adjustment of $\chi/\chi_0$ only affects the theoretical curves in the horizontal direction.