Unconventional Magnetotransport in Graphite

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It has recently been found that when high quality (highly-oriented pyrolitic) graphite is placed in a magnetic field directed along the c-axis and the temperature is lowered, the resistance increases as it does in an insulator but then saturates. At lower temperatures and stronger fields, the resistivity begins to decrease again into what appears to be a “re-entrant metallic state”. Using magnetotransport and Hall measurements, we show that this unusual behavior can be explained within a conventional multi-band model that takes into account the combination of unique features specific to semimetals, i.e., low carrier density, high purity, and an equal number of electrons and holes (compensation). More exotic explanations, such as a magnetic-field-induced excitonic insulator and superconductor, suggested earlier, are not necessary to describe the complete set of observations.

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Elemental semimetals, such as bismuth and graphite, are intriguing materials to study because of their high magnetoresistance, low carrier density, and high purity. Due to small values of \( n \), these materials can be driven into the ultraquantum regime, when only the lowest Landau level remains occupied, using magnetic fields from a few to ten Tesla. In addition, light cyclotron masses, for any field orientation in Bi and along the c-axis in graphite, result in higher cyclotron frequencies, \( eH/m \), which ensure that quantum magneto-oscillations can be observed at moderate temperatures. High purity enables the oscillations to survive the effects of disorder. These features have made bismuth and graphite perhaps the two most popular materials for studies of quantum magnetic-field effects in the past.

Recently, interest in magnetotransport in graphite has been renewed due to observation of an effect that looks like a magnetic-field-induced metal-insulator transition: the metallic \( T \)-dependence of the in-plane resistivity in zero field turns into an insulating-like one when a magnetic field of few hundred Oe is applied normal to the basal (ab) plane. Increasing the field to about 1 T produces a re-entrance of the metallic behavior. It has been proposed that the low-field effect is due to a magnetic-field-induced excitonic insulator transition of Dirac fermions, whereas the high-field one is a manifestation of field-induced superconductivity. It has been also suggested that the apparent metal-insulator transition in graphite is similar to that in 2D heterostructures (although the latter is driven by a field parallel to the conducting plane). To elucidate these issues, we performed detailed measurements of magnetoresistance in graphite and found data quite similar to the data reported in Refs. over comparable temperature and field ranges; however, our interpretation is significantly different from that suggested in Refs.

In this letter, we present magnetotransport data and show that a combination of unique features specific to elemental semimetals, i.e., low carrier density, high purity, and equal number of electrons and holes (compensation), suffices to explain all features of the unusual in-plane magnetoresistance within the conventional theory of multi-band magnetotransport. To illustrate the uniqueness of low-density semimetals, we compare them with conventional, high-density, uncompensated metals. To begin with, if the Fermi surface is isotropic a metal exhibits no magnetoresistance because the Lorentz force does not have a component along the electric current. In real, anisotropic metals the magnetoresistance is finite and proportional to \( (\omega_c \tau)^2 \) in weak magnetic fields, i.e., for \( \omega_c \tau \ll 1 \) (where \( \tau \) is the mean free time of charge carriers). In stronger fields \( (\omega_c \tau \gg 1) \), classical magnetoresistance saturates if the Fermi surface is closed. For an open Fermi surface, the magnetoresistance may continue to grow for certain orientations of the magnetic field.) In contrast, transverse magnetoresistance of a compensated metal (semimetal), grows as \( H^2 \) both in the weak- and strong-field regimes.

The magnetoresistance \( \rho(H) - \rho(0) \) is much larger in semimetals than in conventional metals. In addition to the saturation effect, described above, another important factor that limits the magnetoresistance in conventional metals is the higher scattering rates and thus smaller values of \( \omega_c \tau \) product. The impurity scattering rate in semimetals is smaller than in conventional metals simply because semimetals are typically much cleaner materials. The lower carrier density of semimetals also reduces the rates of electron-phonon scattering in semimetals compared to that of conventional metals. For temperatures above the transport Debye temperature, which separates the regions of the \( T \)- and \( T^5 \)-laws in the resistivity, \( \Theta_D^p = 2\hbar k_F s/k_B \), where \( k_F \) is the Fermi wavevector and \( s \) is the speed of sound (both properly averaged over the Fermi surface), one can estimate the electron-phonon scattering rate as \( \tau^{-1} \simeq (k_F a_0)/(m^*/m_0) k_B T/h \), where \( a_0 \) is the atomic lattice constant, and \( m^* \) and \( m_0 \) are respectively the effective and bare electron masses. In a con-
dependent quantities: the dependence of the resistivity comes from two temperature-temperature dependences of the Fermi level in graphite between $\bar{\Theta}$ and hole charge carriers. There is no wide interval between $\bar{\Theta}$ and $\bar{m}$.

In this interval, (a) the magnetoresistance is large, (b) the scattering rate is linear in $T$, and (c) quantum magneto-oscillations are still not resolved due to the thermal smearing of Landau levels. We argue that the unusual behavior of graphite is due to the existence of the inter-valence and conduction bands. The data in the inset, taken at $H = 10$ kOe, shows a pronounced decrease in resistivity at low temperatures due to the lack of perfect compensation.

The resistivity was measured using an ac (17 Hz) resistance bridge over the temperature range 5K-350K. In all the measurements, the magnetic fields were applied perpendicular to the graphite basal plane. Both $\rho_{xx}$ (Fig. 2) and $\rho_{xy}$ (Fig. 3) were measured in magnetic fields up to 2000 Oe. A small field-symmetric component due to misaligned electrodes was subtracted from the $\rho_{xy}(H)$ data.

FIG. 1: Temperature dependence of $\rho_{xx}$ at the indicated fields ranging up to 2000 Oe. The solid lines are the fits to the data using the six parameters derived from the three bands described in the text. The data in the inset, taken at $H = 10$ kOe, shows a pronounced decrease in resistivity at low temperatures due to the lack of perfect compensation.

FIG. 2: Longitudinal resistivity $\rho_{xx}$ plotted on a logarithmic axis versus applied field $H$ at the temperatures indicated in the legend. The solid lines are determined by a fitting procedure that simultaneously includes the $\rho_{xx}$ data of Fig. 1 using a three-band model described in the text.

The “unusual” behavior of the temperature and field-dependent resistance, shown in Fig. 1, can be described in a straightforward way by a simple multi-band model that takes into account contributions to the conductivity from the electron and hole carriers associated with the overlapping valence and conduction bands. The data of Fig. 1 are “unusual”, since on lowering the temperature the resistance increases, as it does in an insulator, but then saturates and at lower temperature begins to decrease again (Fig. 1 inset) into what appears to be a “re-entrant metallic state”. Similar behavior (without a pronounced re-entrant effect at low temperatures) is also seen in thin bismuth films [14, 15].

Standard 4-probe measurements were carried out on single-crystal highly oriented pyrolytic graphite (HOPG) sample with a 2° mosaic spread, as determined by X-rays. The resistivity was measured using an ac (17 Hz) resistance bridge over the temperature range 5K-350K. In all the measurements, the magnetic fields were applied perpendicular to the graphite basal plane. Both $\rho_{xx}$ (Fig. 2) and $\rho_{xy}$ (Fig. 3) were measured in magnetic fields up to 2000 Oe. A small field-symmetric component due to misaligned electrodes was subtracted from the $\rho_{xy}(H)$ data.

We used a standard multi-band model [8] to fit the data. Each band has two parameters: resistivity $\rho_i$ and Hall coefficient $R_i = 1/q_i n_i$, where $q_i = \pm e$ is the charge of the carrier. In agreement with earlier studies, we fix the number of bands to three [2]. Two of these are the majority electron and hole bands, and the third is the...
minority hole band [2]. Although the third band is not essential for a qualitative understanding of the data, it is necessary for explaining fine features in \( \rho_{xy} \). We fit \( \rho_{xx} \) and \( \rho_{xy} \) simultaneously by adjusting the six parameters independently, until differences between the fitting curves and the experimental data are minimized. Because the majority carriers in graphite derive from Fermi surfaces that have six-fold rotational symmetry about the c-axis, we only need to use the 2x2 magneto-conductivity tensor \( \hat{\sigma} \) with elements \( \sigma_{xx} = \sigma_{yy} = \rho_i / \left[ \rho_i^2 + (R_i H)^2 \right] \)

and \( \sigma_{xy} = -\sigma_{yx} = -R_i H / \left[ \rho_i^2 + (R_i H)^2 \right] \), where \( \rho_i = m_i^*/n_i e^2 \tau_i \). The total conductivity, \( \hat{\sigma} = \sum_{i=1}^3 \hat{\sigma}^i \), is simply a sum of the contributions from all the bands and the total resistance is \( \hat{\rho} = \hat{\sigma}^{-1} \).

Qualitatively, the unusual temperature dependence of displayed in Fig. II can be understood for the simple case of a two-band, compensated (\( R_1 = -R_2 \)) semimetal, where \( \rho_{xx} \) reduces to

\[
\rho_{xx} = \frac{\rho_1 \rho_2}{\rho_1 + \rho_2} + \frac{(\rho_1 R_2^2 + \rho_2 R_1^2)}{(\rho_1 + \rho_2)^2} H^2 .
\]  

Assuming that \( \rho_1,2 \propto T^a \) with \( a > 0 \), we get \( \rho_{xx} \propto T^a \) for \( H = 0 \) as well. In a finite field, the net temperature dependence of \( \rho_{xx} \) contains the contributions from both the first and second terms in Eq. [2]. The key implication is that the temperature dependence of the second term is \( T^{-a} \), i.e., insulating like. As the field increases, the metallic-like dependence of \( \rho_{xx} \) flattens out until the field is above the boundary of the classically strong range, and the \( T^{-a} \)-dependence of the second term starts to dominate. At lower temperatures, the \( T^{-a} \) increase of the resistivity saturates to a value determined by the residual (impurity) resistivities of the subbands. Note that this scenario does not depend on the value of \( a \), i.e., on a particular scattering mechanism. For electron phonon interaction \( T > \Theta_F^D, a = 1 \).

The actual situation is somewhat more complicated due to the \( T \)-dependence of the carrier concentration, the presence of the third band, and imperfect compensation between the majority bands. Results for the temperature-dependent fitting parameters are shown in Fig. III where band 1 corresponds to majority holes, band 2 to majority electrons and band 3 to minority holes. The insulating-like behavior of the carrier density with a tendency towards saturation at low temperatures is well reproduced. For the majority bands, 1 and 2, the carrier concentrations are approximately equal and similar in magnitude to literature values [2]. The slope of the linear-in-\( T \) part of \( \tau^{-1} = \alpha_{\text{exp}}k_B T / h \) with \( \alpha_{\text{exp}} = 0.065(3) \) (dashed line in Fig. III top panel) is consistent with the electron-phonon mechanism of scat-
tering. To see this, we adopt a simple model in which carriers occupying the ellipsoidal Fermi surface with parameters $m_{ab}$ (equal to $0.055 m_0$ and $0.040 m_0$ for electrons and majority holes, correspondingly), $m_c$ (equal to $3 m_0$ and $6 m_0$, correspondingly) interact with longitudinal phonons via a deformation potential, characterized by the coupling constant $D$ (equal to 27.9 eV). In this model, the slope in the linear-in-$T$ dependence of $\tau^{-1}$ is given by

$$\alpha_{\text{theor}} = \left(\frac{\sqrt{2}/\pi}{(m^*)^{5/2}} E_F D^2 / \rho_0 s_{ab} \hbar^3 \right),$$

where $m^* = (m^2_0 m_c)^{1/3} \approx 0.21 m_0$ both for electrons and holes, $\rho_0 = 2.27$ g/cm$^3$ is the mass density of graphite, and $s_{ab} = 2 \times 10^6$ cm/s is the speed of sound in the ab-plane. (The numerical values of all parameters are taken from the standard reference on graphite [2].) With the above choice of parameters, $\alpha_{\text{theor}} = 0.052$ for both types of carriers. This value is within 20% of the value found experimentally. Given the simplicity of the model and the uncertainty in many material parameters, especially in the value of $D$, such an agreement between theory and experiment is quite satisfactory.

The minority band describes well the abrupt features in $\rho_{xy}$ at very low fields (Fig. 4 inset) and makes a negligible contribution at higher fields, due to its low carrier concentration and a correspondingly large value of the $(R_0 H)^2$ term in the denominators of the expressions for $\sigma_{xx}$ and $\sigma_{xy}$. At higher fields we neglect the minority hole band due to its small conductivity contribution and find that the re-entrant behavior (Fig. 4 inset) is most likely due to incomplete compensation. In the presence of finite compensation, i.e., when $R_1 + R_2 \neq 0$, Eq. (2) changes to

$$\rho_{xx} = \frac{\rho_1 \rho_2 (\rho_1 + \rho_2) + (\rho_1 R_2^2 + \rho_2 R_1^2) H^2}{(\rho_1 + \rho_2)^2 + (R_1 + R_2)^2 H^2}.$$  (3)

For small compensation, i.e., when $\delta = |R_1 + R_2| / \max \{R_1, R_2\} \ll 1$, $\rho_{xx}$ in Eq. (3) has two characteristic field scales: $H_c$ and $H_{\text{comp}}$. Field $H_c$ is the boundary of the classically strong field: for $H \gg H_c$, the second term in the numerator dominates over the first one. $H_{\text{comp}}$ is a “decompensation” field: for $H \gg H_{\text{comp}}$, the second term in the denomiator dominates over the first one. Given that all the parameters of the two bands are similar, $H_{\text{comp}} \approx \delta^{-1} H_c \gg H_c$. For fields in the interval $H_c \ll H \ll H_{\text{comp}}$, we are back to the case of a compensated semiconductor, whose magnetoresistance is described by the second term in the numerator of Eq. (2). The $T$-dependence of this term is insulating-like. For fields $H \gg H_{\text{comp}}$, the $H^2$-terms in the numerator and denominator of Eq. (3) cancel each other, hence the magnetoresistance saturates, as it does for an uncompensated metal. In this limit the $T$-dependence of the resistivity at saturation is again of the same sign as at $H = 0$, i.e., metallic-like. Hence, the saturation of the magnetoresistance followed by a re-entrant metallic-like behavior at lower temperatures is predicted to occur at lower temperatures and higher fields, in agreement with the experiment.

The re-entrant behavior in the inset of Fig. 4 at $H = 10$ kOe (solid circles) is replicated (solid line) by assuming $\rho_i$ and $R_i$ to be roughly equal to the fitted values in the lower fields, and imposing a 10% decompensation: i.e., $\delta = 0.1$. A 10% decompensation means that the concentration of charged impurities (acceptors and donors) is about $3 \times 10^{17}$ cm$^{-3}$, which is consistent with the values cited in the literature [2]. We thus believe that the re-entrant effect can be explained without invoking field-induced superconducting fluctuations [4].

Subsequent to the completion of this study, we were informed of recent work [T. Tokumoto et al., Solid State Commun. 129, 599 (2004)] which reaches conclusions similar to that of our paper.

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[11] Inequality Eq. (1) can be satisfied in a typical metal for $T \ll \Theta_D^0$ when the inverse (transport) time $\tau_{\text{tr}}^{-1} \propto T^5 \ll k_B T/\hbar$. For an uncompensated metal with a closed Fermi surface, however, magnetoresistance saturates in this regime.