Metal-Insulator-Like Behavior in Semimetallic Bismuth and Graphite

Xu Du, Shan-Wen Tsai, Dmitrii L. Maslov, and Arthur F. Hebard

Department of Physics, University of Florida, P. O. Box 118440, Gainesville, FL 32611-8440

(Dated: October 23, 2018)

When high quality bismuth or graphite crystals are placed in a magnetic field directed along the c-axis (trigonal axis for bismuth) and the temperature is lowered, the resistance increases as it does in an insulator, but then saturates towards field-dependent constant values at the lowest temperatures. These similarities invite an interpretation that ascribes this interesting behavior to properties shared by both graphite and bismuth, namely low carrier density, high purity, and an equal number of electrons and holes (compensation), rather than to specific properties of graphite: almost 2D nature of transport and a Dirac-like spectrum, as suggested in Refs. [3, 4, 5, 6].

In this letter we demonstrate this connection by examining the magnitude and ordering of three characteristic energy scales: namely, the width of the energy levels $\hbar/\tau$ where $\tau$ is the electron-phonon scattering time, the cyclotron energy $\hbar \omega_c$, and the thermal energy $k_B T$. We provide theoretical justification for, and experimental confirmation of, the existence of a wide interval of temperatures and magnetic fields, defined by the condition,

$$\hbar/\tau \lesssim \hbar \omega_c \lesssim k_B T. \quad (1)$$

In this interval, (a) the magnetoresistance is large, (b) the scattering rate is linear in $T$, and (c) Shubnikov de Haas (SdH) oscillations are not resolved due to the thermal smearing of Landau levels. We argue that the unusual behavior of bismuth and graphite is due to the existence of a region, specified by the inequalities of Eq. (1), and also due to compensation between electron and hole charge carriers. Our experimental confirmation is centered on a detailed study of graphite in which we use the conventional theory of multi-band magnetotransport to extract the field-independent carrier density, $n(T)$, and scattering time, $\tau(T)$, from simultaneous fitting of the temperature and field-dependent longitudinal resistivity $\rho_{xx}(T, B)$ (magnetoresistance) and transverse resistivity $\rho_{xy}(T, B)$ (Hall effect). We then show from this analysis that the inequality (1), which is unique to semimetals, is satisfied over a broad temperature and field range.

To illustrate the uniqueness of low-carrier-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 anisotropic metals the magnetoresistance is finite and proportional to \((\omega_c\tau)^2\) in weak magnetic fields, i.e., for \(\omega_c\tau \ll 1\). In stronger fields \((\omega_c\tau \gg 1)\), classical magnetoresistance saturates, if the Fermi surface is closed. In contrast, transverse magnetoresistance of a semimetal grows as \(B^2\) both in the weak- and strong-field regimes.

The magnetoresistance \([\rho(B) - \rho(0)]/\rho(0)\) 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 the \(\omega_c\tau\) 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 \(T^2\)-laws in the resistivity, \(\Theta_D^\rho = 2\hbar k_F s/k_B\), 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 \(\tau^{-1} \simeq (k_F a_0) (m^*/m_0) k_B T/\hbar\), where \(a_0\) is the atomic lattice constant, and \(m^*\) and \(m_0\) are respectively the effective and bare electron masses. In a conventional metal, \(k_F a_0 \simeq 1\) and \(m^* \simeq m_0\). In this case, \(\Theta_D^\rho\) is of order of the thermodynamic Debye temperature \(\hbar s/k_B a_0 \simeq\) few 100 K and \(\tau^{-1} \simeq k_B T/\hbar\). In low-carrier-density materials \((k_F a_0 \ll 1)\), which typically also have light carriers \((m^* \ll m_0)\), \(\Theta_D^\rho\) is much smaller and thus \(\tau^{-1} \ll k_B T/\hbar\). Therefore, in a low-carrier-density semimetal there exists a wide interval of temperatures and magnetic fields, defined by the inequalities. In contrast, there is no wide interval between \(h/\tau\) and \(k_B T\) in a conventional metal.

An additional feature, crucial for interpreting the experimental data, is that the Fermi energies of graphite \((E_F = 22 \text{ meV})\) and bismuth \((E_F = 30 \text{ meV})\) are relatively low and the temperature dependence of the resistivity comes from two temperature-dependent quantities: \(n(T)\) and \(\tau(T)\). Purity of materials ensures that electron-phonon scattering is a dominant mechanism for resistance over a wide temperature range.

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 sample basal planes. Both \(\rho_{xx}\) and \(\rho_{xy}\) (Fig. 3) were measured in magnetic fields up to 1 T, although the analysis (solid lines) was limited to \(B \leq 200 \text{ mT}\). A small field-symmetric component due to misaligned electrodes was subtracted from the \(\rho_{xy}(B)\) data.

We used a standard multi-band model to fit the data. Each band has two parameters: resistivity \(\rho_i\) and Hall coefficient \(R_i = 1/q_i n_i\), where \(q_i = e\pm e\) is the charge of the carrier. In agreement with earlier studies, we fix the number of bands to three. Two of these are the majority electron and hole bands, and the third is the minority hole band. Although the third band is not essential for a qualitative understanding of the data, it is necessary for explaining the low-field fine features in \(\rho_{xy}\) shown in the inset of Fig 3. The minority band makes a negligible contribution at higher fields due to its low carrier concentration.

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 \(2\times2\) magneto-conductivity tensor \(\hat{\sigma}\) with elements \(\sigma_{xx} = \sigma_{yy} = \rho_i/\left[\rho_i^2 + (\rho_i R_i)^2\right]\) and \(\sigma_{xy} = -\sigma_{yx} = -R_i B/\left[\rho_i^2 + (R_i B)^2\right]\), where \(\rho_i = m_i^*/n_i e^2 \tau_i\). The total conductivity, \(\hat{\sigma} = \sum_{i=1}^3 \sigma_i\), is simply a sum of the contributions from all the bands and the total resistance is \(\rho = \hat{\sigma}^{-1}\).

Qualitatively, the unusual temperature dependence...
displayed in Fig. 1 can be understood for a simple two-band case where $\rho_{xx}$ reduces to

$$\rho_{xx} = \rho_1 \rho_2 (\rho_1 + \rho_2) + (\rho_1 R_1^2 + \rho_2 R_2^2) B^2 / (\rho_1 + \rho_2)^2 + (R_1 + R_2)^2 B^2. \tag{2}$$

Assuming that $\rho_{1,2} \propto T^a$ with $a > 0$, we find that for perfect compensation, $R_1 = -R_2 = |\bar{R}|$, Eq. 2 can be decomposed into two contributions: a field-independent term $\propto T^a$ and a field-dependent term $\propto R^2(T) B^2 / T^a$. At high $T$, the first term dominates and metallic behavior ensues. At low $T$, $R(T) \propto 1/n(T)$ saturates and the second term dominates, giving “insulating” behavior.

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. 4 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. 4, top panel) is consistent with the electron-phonon mechanism of scattering. 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) and $m_c$ (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 $\alpha_{\text{theor}} = (\sqrt{2}/\pi) \sqrt{(m^*)^3} E_F D^2 / \rho_0 s_{ab}^2 \hbar^3$, where $m^* = (m_{ab} m_c)^{1/3} \approx 0.21m_0$ both for electrons and holes, $\rho_0 = 2.27 \text{ g/cm}^3$ is the mass density of graphite, and $s_{ab} = 2 \times 10^5 \text{ cm/s}$ is the speed of sound in the ab-
by the relation reflects the rightmost inequality of (1) and is determined for temperatures of $3.0\,K$. The boundary between (I) and (II) is obtained from experimental fitting parameters (Fig. 4). In region (I) SdH oscillations is observed, while the upper boundary is determined from the standard reference on graphite [2]. With the above choice of parameters, $\alpha_{\text{theo}} = 0.052$ 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 solid lines through the data points in Fig. 1 are calculated from the temperature-dependent fitting parameters derived from our three-band analysis and plotted in Fig. 4. The shaded region (II) depicted in the inset of Fig. 1 represents those temperatures and fields that satisfy the inequalities in (1). In region (I) SdH oscillations can be seen at sufficiently low $T$. Our sample has a Dingle temperature of 3.0 K. The boundary between (I) and (II) reflects the rightmost inequality of (1) and is determined by the relation $T > \frac{h e B}{m^*}$. The boundary between (II) and (III) reflects the leftmost inequality of (1) and is determined by the relation $B > \frac{m^*}{e \tau(T)}$ where $1/\tau(T)$ is obtained from experimental fitting parameters (Fig. 4). In the main panel of Fig. 1 we superimpose region (II), again as a shaded area, on the $\rho_{xx}(T, B)$ data. Below the lower boundary $\omega_c \tau < 1$, and the magnetoresistance is relatively small. The upper boundary is determined by the locus of $(B, T)$ points satisfying the rightmost inequality of (1). Clearly region (II), constrained by the inequalities of (1), overlaps well with the metal-insulating like behavior of graphite. Since the majority bands of bismuth comprise three non-coplanar electron ellipsoids and one hole ellipsoid, a similar analysis for bismuth is more complicated and would require more space than available here.

We thus conclude that the semimetals graphite and, by implication, bismuth share the common features of high purity, low carrier density, small effective mass and near perfect compensation and accordingly obey the unique energy scale constraints that allow pronounced metal insulating behavior accompanied by anomalously high magnetoresistance. At magnetic fields higher than discussed in this paper ($B \geq 1\,T$) we believe that the multiband model is still appropriate and may provide an alternative explanation for the reentrant behavior observed by us and others.

Subsequent to the completion of this study, we were informed of recent work [T. Tokumoto et al., Solid State Commun. 129, 599 (2004)] which used a two-band model to explain the unusual behavior of $\rho_{xx}(T, B)$ in graphite.

This work was supported in part by the National Science Foundation under Grants No. DMR-0101856 (AFH) and DMR-0308377 (DLM) and by the In House Research Program of the National High Magnetic Field Laboratory, which is supported by NSF Cooperative Agreement No. DMR-0084173 and by the State of Florida. SWT and DLM acknowledge the hospitality of the Aspen Center for Theoretical Physics, where part of the analysis was performed. The authors are especially thankful to J. E. Fischer and R. G. Goodrich for supplying respectively the HOPG and Bi samples, J. Derakhshian for assistance with the Bi measurements, and J. S. Brooks for discussions.

---

[1] V. S. Edel’mann, Sov. Phys. Usp. 20, 819 (1977).
[2] N. B. Brandt, S. M. Chudnov, and Y. G. Ponomarev, Semimetals 1: Graphite and its compounds (North-Holland, 1988).
[3] Y. Kopelevich et al., Phys. Solid State 41, 1959 (1999).
[4] H. Kempa, et al., Solid State Commun. 115, 539 (2000), ibid., 121, 579 (2002).
[5] Y. Kopelevich et al., Phys. Rev. Lett. 90, 156402 (2003).
[6] D. V. Khveshenko, Phys. Rev. Lett. 87, 206401 (2001).
[7] E. Abrahams, S. V. Kravchenko, and M. P. Sarachik, Rev. Mod. Phys. 73, 251 (2001).
[8] N. W. Ashcroft and N. D. Mermin, Solid State Physics (Holt, Rinehart and Winston, 1976).
[9] A. A. Abrikosov, Fundamentals of the Theory of Metals (North-Holland, 1988).
[10] V. F. Gantmakher and Y. B. Levinson, Carrier scattering in metals and semiconductors (North-Holland, 1987).
[11] Inequality Eq. (1) can be satisfied in a typical metal for $T \ll \Theta_D^*$ when the inverse (transport) time $\tau^{-1} \propto T^5 \ll k_BT/h$. For an uncompensated metal with a closed Fermi surface, however, magnetoresistance saturates in this regime.

[12] J. W. McClure and W. J. Spry, Phys. Rev. 165, 809 (1968).

[13] G. E. Smith, G. A. Baraff, and J. M. Rowell, Phys. Rev. 135, A1118 (1964).

[14] S. Cho, Y. Kim, A. J. Freeman, et al., App. Phys. Lett. 79, 3651 (2001).

[15] F. Y. Yang, K. Liu, K. Hong, et al., Science 284, 1335 (1999).