Transport study of Berry’s phase, the resistivity rule, and quantum Hall effect in graphite

Aruna N. Ramanayaka\textsuperscript{1} and R. G. Mani\textsuperscript{1}

\textsuperscript{1}Department of Physics and Astronomy, Georgia State University, Atlanta, GA 30303.

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Transport measurements indicate strong oscillations in the Hall-, $R_{xy}$, and the diagonal-, $R_{xx}$, resistances and exhibit Hall plateaus at the lowest temperatures, in three-dimensional Highly Oriented Pyrolytic Graphite (HOPG). At the same time, a comparative Shubnikov-de Haas-oscillations-based Berry’s phase analysis indicates that graphite is unlike the GaAs/AlGaAs 2D electron system, the 3D n-GaAs epilayer, semiconducting $H_{90.8}Cd_{0.2}Te$, and some other systems. Finally, we observe the transport data to follow $B \times dR_{xy}/dB \approx -\Delta R_{xx}$. This feature is consistent with the observed relative phases of the oscillatory $R_{xx}$ and $R_{xy}$.

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Single layers of carbon atoms known as graphene are an interesting future electronic material.[1–4] At the same time, graphene is a novel Two-dimensional Electronic System (2DES) with remarkable features providing for a solid state realization of quantum electrodynamics, massless Dirac particles, an anomalous Berry’s phase,[5–7] and an unconventional quantum Hall effect in a strong magnetic field.[1–7] The ABAB bernal stacking of graphene helps to produce graphite, an anisotropic electronic material exhibiting a large difference between the in-plane and perpendicular transport. Since graphite may be viewed as stacked graphene, one wonders whether remnants of the remarkable properties of graphene might also be observable in graphite.

Graphite exhibits a $\approx 0.03eV$ band overlap, in contrast to the zero-gap in graphene.[8–10] In the recent past, concepts proposed for graphene have also been invoked for graphite. For example, ref.[11] argues for the observation of massive majoron electrons with a three dimensional (3D) spectrum, minority holes with a two dimensional (2D) parabolic massive spectrum, and majority holes with a 2D Dirac spectrum. Hall plateaus in $\sigma_{xy}$ extracted from van-der-Pauw measurements on highly oriented pyrolytic graphite (HOPG) have been cited as evidence for the integral quantum Hall effect (IQHE) in graphite in ref.[12]. Luk’yanchuk et al. in ref. [13] suggest simultaneous quantum Hall effects for the massive electrons and massless Dirac holes with Berry’s phase of $\beta = 0$ and $\beta = 1/2$, respectively. $\beta$ is given here in units of 2$\pi$.

Finally, an ARPES-study has reported massless Dirac fermions coexisting with finite mass quasiparticles in graphite.[14]

Plateaus at Hall resistance at $R_{xy} = h/ie^2$ with $i = 1, 2, 3, \ldots$ and $R_{xx} \rightarrow 0$ are typically viewed as a characteristic of IQHE in the 2DES. At the same time, a “thick” specimen consisting of quantum wells separated by wide barriers exhibits plateaus at $R_{xy} = h/ij e^2$, where $j$ counts the number of layers in the specimen. Indeed, introducing a dispersion in the $z$-direction does not modify the observability of IQHE.[15] Thus, IQHE can also be a characteristic of anisotropic 3D systems such as graphite. Here, in graphite, the IQHE can be of the canonical variety, or of the unconventional type reported in graphene. In addition, theory has predicted the existence of a single, true bulk 3D QHE in graphite in a large magnetic field parallel to the $c$-axis at $\sigma_{xy} = (4e^2/\hbar)(1/c_0)$, where $c_0 = 6.7\AA$ is the $c$-axis lattice constant.[16]

Thus, there are reasons for carrying out quantum Hall studies in graphite. The possibility of both the canonical and unconventional IQHE in graphite motivates also a study of the Berry’s phase. Finally, one wonders whether 3D graphite might also satisfy the resistivity rule observed in 2D quantum Hall systems.[17]

This magneto-transport study of HOPG shows strong oscillations in the Hall resistance, $R_{xy}$, and Shubnikov-de Haas (SdH) oscillations in the diagonal resistance, $R_{xx}$, while manifesting Hall plateaus at the lowest temperatures. A Fourier transform of the $R_{xx}$ SdH oscillations indicates a single set of carriers, namely electrons, in these HOPG specimens. A Berry’s phase analysis of the SdH data suggests that these carriers in graphite are unlike those in GaAs/AlGaAs heterostructures, n-GaAs epilayers, bulk semiconducting $H_{90.8}Cd_{0.2}Te$, the

| Material          | $n_0$       | $B_0(Te\text{esu})$ | $\beta$ |
|-------------------|-------------|---------------------|---------|
| Graphite          | 0.47 ± 0.02 | 4.52                | 1/2     |
| GaAs/AlGaAs       | 0.05 ± 0.01 | 6.45                | 0       |
| GaAs\textsuperscript{a} [20] | 0.06 ± 0.02 | 7.43                | 0       |
| $H_{90.8}Cd_{0.2}Te\textsuperscript{b}$ [21] | −0.003 ± 0.022 | 1.298                | 0       |
| HgTe\textsuperscript{c} [22] | 0.06 ± 0.03 | 26.14                | 0       |
| 3D AlGaN\textsuperscript{d} [23] | −0.01 ± 0.03 | 35.39                | 0       |
| InSb\textsuperscript{d} [24] | 0.05 ± 0.03 | 19.80                | 0       |
| $C_{9.8}AlCl_{3.4}$\textsuperscript{d} [25] | 0.48 ± 0.02 | 11.7                 | 1/2     |

\textsuperscript{a}2$\mu$m thick n-GaAs epilayer
\textsuperscript{b}bulk semiconducting $H_{90.8}Cd_{0.2}Te$
\textsuperscript{c}$n$-type HgTe quantum wells
\textsuperscript{d}1st stage graphite intercalation compound

TABLE I: Intercept $n_0$ and the slope $B_0$ of $n_0$ vs. $B^{-1}$ plot. $\beta$ is the suggested Berry’s phase in units of $2\pi$. 
HgTe quantum well, 3D AlGaN, and InSb systems. Further, a resistivity rule study of graphite indicates \( R_{xx} \sim -B \times dR_{xy}/dB \), in variance with observations in canonical quantum Hall systems, while a phase analysis suggests a new classification (“type-IV”)\(^\text{[18]}\) of the phase relation between the oscillatory \( R_{xx} \) and \( R_{xy} \). The latter observation is consistent with \( R_{xx} \sim -B \times dR_{xy}/dB \).

Our 25µm thick graphite specimens were exfoliated from bulk HOPG, and the measurements were carried out using standard lock-in techniques with the \( B \) parallel to the c-axis. Measurements of \( R_{xx} \) and \( R_{xy} \) are shown in Fig. 1(a) and (b) respectively for \( 1.5 \leq T \leq 154K \) and \( 0 \leq B \leq 5 \) Tesla. At low \( T \), SdH oscillations in \( R_{xx} \) and \( R_{xy} \), and plateaus in \( R_{xy} \), appear manifested, see Fig.1(a) & (b), as in Fig. 2 and Fig. 3 of ref.[19]. Three Hall plateaus are observable in Fig. 1(b). The Hall plateau resistance observed at \( B = 2.5T \) and \( T = 1.5K \) is consistent, within a factor-of-two, with viewing the specimen as a stack of uncoupled quantum Hall layers. Note that \( R_{xx} > 0 \) through the Hall plateaus. The finite tilt of the highest-B plateau at \( T = 1.5K \) might be due to the incipient \( R_{xy} \) saturation, possibly due to multi-band transport.

The SdH effect has been used to probe the Berry’s phase.\(^\text{[5, 6]}\) For the graphene system, the oscillatory \( R_{xx} \) has been written as \( R(B, T) \cos(2\pi(B_0/B + 1/2 + \beta))\)\(^\text{[7]}\), where \( R(B, T) \) is the SdH oscillation amplitude, \( B_0 \) is the SdH oscillation frequency, and \( \beta \) is the Berry’s phase in units of \( 2\pi \). The observation of an anomalous Berry’s phase in graphene has generated new interest in the study of the same in graphite. Hence, we set out to examine our data for graphite from a similar perspective.

Graphite is a semi-metal with majority electrons and holes exhibiting elongated Fermi surfaces along the c-axis.\(^\text{[9]}\) The Fermi surface of graphite has been studied via the oscillatory magnetization (de Haas -van Alphen [dHvA]) effect, and also the oscillatory magnetoresistance (SdH) effect.\(^\text{[9]}\) Graphite exhibits a strong dHvA effect, and the Fourier transform of the associated oscillatory magnetization readily exhibits two spectral peaks corresponding to the two sets of majority carriers. The SdH

FIG. 1: (color online). (a) The diagonal resistance \( (R_{xx}) \) and (b) Hall resistance \( (R_{xy}) \) of sample S1 are exhibited vs. the applied magnetic field, \( B \), between 154 \( \leq T \leq 1.5K \). \( R_{xy} \) plateaus and SdH oscillations in \( R_{xx} \) are manifested at low \( T \).

FIG. 2: (color online).(a) Shown here are plots of Landau level index \( (n) \)(left) of samples S1, S2, and S3, and \( R_{xx} \)(right) of sample S1, vs. \( B^{-1} \). The slope of the \( n vs.B^{-1} \) plot indicates the SdH frequency, \( F = 4.52T_{\text{tesla}} \), and the intercept, \( n(B^{-1} = 0) = 0.47 \). (b) This plot shows the spectral intensity of the Fourier transform of \( dR_{xx}/dB \) of sample S1. A single peak in the Fourier spectrum confirms that the SdH effect in these graphite specimens is basically dominated by one type of carrier with \( F = 4.52T_{\text{tesla}} \). (c) \( n \) and \( R_{xx} \) are shown vs. \( B^{-1} \) for the GaAs/AlGaAs 2D electron system. In (d) & (e) \( n \) and \( R_{xx} \) are shown for the 2µm thick n-GaAs epilayer and 3D \( H_{g0,sCd0.2Te} \) systems. Linear fit of \( n \) vs. \( B^{-1} \) intersects the ordinate at 0.47, 0.05, 0.06, and –0.04 for HOPG, GaAs/AlGaAs, 2µm thick n-GaAs epilayer, and bulk \( H_{g0,sCd0.2Te} \) systems, respectively.
data, on the other hand, can often exhibit just a single broad peak in the Fourier spectrum.\[13\] It has been suggested that the scattering lifetimes manifested by the carriers in the two experiments might not be the same.\[9\] Further, that one set of carriers might suffer more broadening, and as a consequence, the associated oscillatory contribution due to this band might vanish in the SdH effect.

The HOPG specimens examined in this study are also characterized by a single broad peak in the Fourier transform of the SdH data, see Fig. 2(b). This feature suggests that the SdH effect in our HOPG specimen is also dominated by one type of carriers, namely electrons, and this feature indicates that this single carrier-type may be subjected to a Berry’s phase analysis as in graphene.

In order to examine and compare the Berry’s phase, plots of the Landau level index, \(n\) (left axis), and \(R_{xx}\) (right axis) versus \(B^{-1}\) are shown in Fig. 2(a), (c), (d), and (e) for graphite, the GaAs/AlGaAs 2D electron system, an n-GaAs epilayer\[20\], and bulk semiconducting \(Hg_{0.8}Cd_{0.2}Te\)\[21\] respectively. For all four material systems, minima of oscillatory \(R_{xx}\) have been assigned with \(n\), and maxima of the oscillatory \(R_{xx}\) have been assigned with \(n + 1/2\), as in ref. [7]. In such an analysis, an intercept \(n_0 = 0\) would normally indicate a Berry’s phase \(\beta = 0\), while \(n_0 = 1/2\) would normally correspond to \(\beta = 1/2\), as in graphene.\[7\]. For the three graphite samples S1, S2, and S3 (see Fig. 2(a)), the Landau level index intercept of a linear fit to \(n\) vs. \(B^{-1}\) yields 0.47, i.e., 1/2.

**FIG. 3:** (color online). The oscillatory Hall- \(\Delta R_{xy}\) and diagonal- \(\Delta R_{xx}\) resistances are shown for samples (a) S1, (b) S2, and (c) S3, vs. \(B\). (d) \(\Delta R_{xy}\) and \(\Delta R_{xx}\) are shown vs. the normalized inverse magnetic field \(B_0/B\). This plot shows a \(\pi/2\) phase shift between \(\Delta R_{xx}\) and \(\Delta R_{xy}\).

Panels (c), (d), and (e) give intercepts of 0.05, 0.06, and \(-0.04\), i.e., zero, for the GaAs/AlGaAs, n-GaAs epilayer, and bulk \(Hg_{0.8}Cd_{0.2}Te\) systems. These fit-extracted intercepts, \(n_0\), and \(B_0\) have been summarized in Table 1.

A similar analysis was carried out with other data and these results are also summarized in Table 1 for the HgTe quantum well,\[22\] 3D AlGaN,\[23\] InSb,\[14\] and \(C_{9.3}AlCl_{3.4}\) - a first stage graphite intercalation compound.\[25\] Notice that the Table 1 represents eight different systems, yet only graphite and \(C_{9.3}AlCl_{3.4}\) show \(n_0 = 1/2\) in the \(B^{-1} \rightarrow 0\) limit as observed in graphene.\[7\] This is a principal experimental finding of this work.

**FIG. 4:** (color online). Panels (a) and (b) show that the phase of the oscillatory \(\Delta R_{xx}\) and \(B \times dR_{xy}/dB\) does not change with \(T\). (c) Comparison of \(\Delta R_{xx}\) and \(B \times dR_{xy}/dB\) at \(T = 1.5K\). (d) \(\Delta R_{xx}\) and \(B \times dR_{xy}/dB\) are shown vs. \(B_0/B\). Both (c) and (d) suggest a phase shift of approximately \(\pi\) between \(\Delta R_{xx}\) and \(B \times dR_{xy}/dB\).

Does this experimental finding signify an anomalous Berry’s phase for the observed carriers in graphite? If the experimental results shown here in Fig. 1 had indicated \(R_{xy} > R_{xx}\) as in ref. \(7\), then, certainly, the conclusion would immediately follow that electrons in graphite exhibit an anomalous Berry’s phase as in graphene. The fact that Fig. 1 indicates \(R_{xy} \ll R_{xx}\) complicates the issue since many would reason that \(R_{xy} \ll R_{xx}\) implies \(\rho_{xy} \ll \rho_{xx}\) given the geometrical factors in these graphite specimens, and as a consequence, \(n_0 = 1/2\) in graphite should be taken to indicate normal carriers,\[13\] not Dirac carriers. Some features should, however, serve as caution against following this line of reasoning. First,
strong SdH oscillations, as in Fig. 1, are typically observed only when \( \rho_{xy} > \rho_{xx} \), i.e., \( \omega T > 1 \), for the associated carriers. Thus, perhaps, the observation of \( R_{xy} < R_{xx} \) in graphite need not imply \( \rho_{xy} < \rho_{xx} \). Next, it appears worth pointing out that some experiments in the GaAs/AlGaAs system have clearly shown that there need not be a simple relation between \( R_{xx} \) and \( \rho_{xx} \).[27] Finally, it is also known that certain types of longitudinal specimen thickness variations, density variations, and/or current switching between graphene layers in graphite, can introduce a linear-in-B component into \( R_{xx} \) originating from the Hall effect; such an effect can produce experimental observations of \( R_{xx} > R_{xy} \) even in systems that satisfy \( \rho_{xx} < \rho_{xy} \). Due to such possibilities in graphite, the results shown Fig. 2 and Table 1 could plausibly identify an anomalous Berry’s phase for electrons in graphite, and \( C_{63}AlCl_{34} \).[25] Here, it is noteworthy that semiconducting \( Hg_{0.8}Cd_{0.2}Te \) specimens also exhibits \( R_{xx} > R_{xy} \)[21] and yet shows \( n_0 = 0 \), unlike graphite. Clearly, the experimental finding is unambiguous: the infinite field phase extracted from the SdH oscillations for graphite is unlike the results for a number of canonical semiconductor systems, see Table 1.

Next, we examine more closely the phase relation in the oscillations of \( R_{xx} \) and \( R_{xy} \) since this is a striking feature of the data. Thus, background subtracted \( R_{xx} \) and \( R_{xy} \), i.e., \( \Delta R_{xx} \) and \( \Delta R_{xy} \), are shown in the Fig. 3(a)- Fig. 3(c), for samples S1 - S3. Thus far, the phase relations between \( \Delta R_{xx} \) and \( \Delta R_{xy} \) have been classified into three types in the high mobility GaAs/AlGaAs system.[18] Namely, type-III, where the oscillations of \( \Delta R_{xx} \) and \( \Delta R_{xy} \) are approximately 180 degrees out of phase. Type-II, where the oscillation of the \( \Delta R_{xx} \) and \( \Delta R_{xy} \) are in-phase. And, type-I, where the peaks of \( \Delta R_{xx} \) occur on the low-B side of the \( \Delta R_{xy} \) peaks, with a \( \pi/2 \) phase shift. Fig. 3 shows, however, that the peaks of \( \Delta R_{xx} \) appear on the high-B side of the \( \Delta R_{xy} \) peaks, unlike the cases mentioned above. This suggests a fourth phase relation (“type-IV”) between \( \Delta R_{xx} \) and \( \Delta R_{xy} \) in (HOPG) graphite. In the \( B^{-1} \) plot, see Fig. 3(d), the peaks of \( \Delta R_{xx} \) are shifted towards the low \( B_0/B \) side with respect to the peaks of \( \Delta R_{xy} \), with an approximately \( \pi/2 \) phase shift between \( \Delta R_{xx} \) and \( \Delta R_{xy} \), confirming this conjecture.

For the resistivity rule study,[17, 18, 28, 29] the temperature dependence of \( \Delta R_{xx} \) and \( B \times dR_{xx}/dB \) are shown in Fig. 4(a) and Fig. 4(b) respectively. Fig. 4 indicates a progressive change, where the oscillatory amplitude increases with decreasing \( T \) while the \( B \)-values of the extrema remains unchanged with \( T \). Fig. 4(c) shows the \( \Delta R_{xx} \) (right axis) and \( B \times dR_{xx}/dB \) (left axis) for the sample S1 at 1.5K. A direct comparison (see Fig. 4(c)) reveals a \( \pi \) phase difference between \( B \times dR_{xx}/dB \) and \( \Delta R_{xx} \), i.e, \( B \times dR_{xy}/dB \approx -\Delta R_{xx} \). Plots of \( \Delta R_{xx} \) and \( B \times dR_{xy}/dB \) vs. \( B_0/B \), (see Fig. 4(d)) confirm an approximately \( \pi \) phase shift between \( \Delta R_{xx} \) and \( B \times dR_{xy}/dB \). This variance from the canonical resistivity rule is consistent with the observed Type-IV phase relation between the oscillatory \( R_{xx} \) and \( R_{xy} \), see Fig. 3.

In summary, a study of (HOPG) graphite indicates strong oscillatory \( R_{xy} \) and \( R_{xx} \), with Hall \( (R_{xy}) \) plateaus coincident with a non-vanishing \( R_{xx} \) at the lowest \( T \). On the other hand, a comparative SdH Berry’s-phase study of graphite with other systems such the GaAs/AlGaAs 2D electron system, the 3D n-GaAs epilayer, bulk \( Hg_{0.8}Cd_{0.2}Te \), HgTe quantum well, 3D AlGaAs, InSb, and \( C_{63}AlCl_{34} \) - a graphite intercalation compound- reveals a value of \( n_0 = 1/2 \) in the \( B^{-1} \) \( \longrightarrow \) 0 limit only for the graphene based systems. As in graphene, this feature might indicate that one-half of a conduction band Landau level is pinned together with one-half of a hole Landau level in graphite and might reflect a non-trivial Berry’s phase (\( \beta = 1/2 \)) and Dirac carriers in graphite.

A close study of the oscillatory diagonal- and Hall-resistances reveals also an anomalous (“type-IV”) phase relation between oscillatory \( R_{xx} \) and \( R_{xy} \), over the entire \( T \)-range. This result is consistent with the observation of \( B \times dR_{xx}/dB \approx -\Delta R_{xx} \) in the resistivity rule analysis of the transport.

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