High magnetic field induced charge density waves and sign reversal of the Hall coefficient in graphite

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Abstract

We report on the investigation of magnetic field induced charge density waves and Hall coefficient sign reversal in a quasi-two-dimensional electronic system of highly oriented pyrolytic graphite under very strong magnetic field. The change of Hall sign coefficient from negative to positive occurs at low temperature and high magnetic field just after the charge density wave transition, suggesting the role of hole-like quasi-particles in this effect. Angular dependent measurements show that the charge density wave transition and Hall sign reversal fields follow the magnetic field component along the $c$-axis of graphite.

(Some figures in this article are in colour only in the electronic version)

Graphite is a typical layered material made from stacked single atomic layers of carbon atoms, named graphene. A few years ago, it became possible to extract a graphene layer out of bulk graphite and to individually address its electronic properties [1]. The discovery of such an ultimate two-dimensional (2D) system has attracted tremendous interest in condensed matter physics, especially due to its distinctive band structure and potential applications in nano-electronic devices. In the meantime, such progress has also triggered a revival of interest in the mother material, graphite, pointing out its quasi-2D character which shares some similarities with graphene and which were skipped over in the past. The observation of massless electronic charge carriers (Dirac fermions) [2–4], quantum Hall effect [4, 5] or even possible fractional quantum Hall effects [6] in highly oriented pyrolytic graphite (HOPG) are just a few examples suggesting the unexplored physics of this material.

Graphite rapidly reaches the quantum limit at moderate magnetic field ($>8$ T) due to the in-plane light effective carrier mass and low carrier density. Beyond this magnetic quantum limit no drastic physical effects are expected to occur. However, earlier magneto-transport studies in graphite have clearly revealed an abrupt increase of the in-plane magneto-resistance ($R_{xx}$) when a very high magnetic field ($>25$ T) is applied parallel to the $c$-axis. The occurrence of this effect in a restricted temperature range ($1 \text{ K} < T < 10 \text{ K}$) [7–9] has been qualitatively explained in terms of a field induced electronic phase transition by Yoshioka and Fukuyama [10], later referred to as the YF model, where a charge density wave (CDW) instability develops along the $c$-axis, induced by the Landau level formation in the highly anisotropic energy band structure of graphite. The YF model describes well the phase transition boundary in the $(B, T)$ diagram, but fails to account for the magnitude and fine additional features of the magneto-resistance jump at the transition [8, 9]. Also, the discussion was enriched in [11] where the out-of-plane magneto-resistance exhibits a much larger change as compared to the in-plane magneto-resistance and suggests the occurrence of a spin density wave along the $c$-axis. So far, the high field induced anomaly in magneto-transport measurements is not fully understood and requires further development.

To date, most of the high magnetic field measurements have been reported on Kish or natural graphite and Hall measurements have not been discussed in detail. Simultaneous
measurements of longitudinal (in-plane) resistivity and Hall resistance are expected to give more insight into the physical phenomena that occur beyond the ultra-quantum limit in graphite. Indeed, the Hall effect is a very sensitive tool for investigating the charge carriers’ density, as well as their sign and dynamics. In this work, we report on transport and Hall resistance measurements on HOPG in pulsed magnetic field (57 T). The occurrence of a field induced resistance anomaly and the Hall sign reversal are investigated in a wide temperature range (1.6–300 K) and for different orientations of the magnetic field.

The HOPG used in this study is of type ZYB with small mosaic angle (≈0.80) and was supplied from SPI, USA [12]. The HOPG was cleaved into two separate samples of rectangular shape with typical lateral dimensions of hundreds of micrometers. We will refer to these samples as A and B, the former being slightly bigger in size than the latter. The thickness was roughly estimated to 10 μm by cross-sectional scanning electron microscopy (SEM) measurement for both samples. Five electrical contacts were glued onto the top face in the Hall bar geometry using conducting silver epoxy. Assuming a uniform distribution of the injected current through the sample, the typical samples’ resistivity is 0.33 ± 0.2 mΩ cm at room temperature and zero magnetic field. The uncertainty mainly comes from the imprecise lateral dimensions of the samples. The estimated resistivity is about 10–100 times higher than the best quality HOPG [5, 6] and Kish graphite [7]. Generally, a higher resistivity is expected in thin graphite flakes [13] or graphite with small grain size [14]. The high resistivity found in the present case may also be due to damage done to the sample during preparation (contamination, inhomogeneous cleavage or damage when making contacts). Magneto-transport experiments were repeated by reversing the magnetic field and averaging the signals asymmetrically in order to cancel the effects of voltage probe misalignment. A DC current of $i = 0.5 mA$ is injected through the device while the longitudinal and Hall voltages are simultaneously monitored during a magnetic field shot of total duration 300 ms. The reported experimental data have been numerically treated to reduce unwanted noise (sliding averaging algorithm), taking care that the main physical features are not affected.

Figures 1(a) and (b) show the in-plane longitudinal resistance ($R_{xx}$) and Hall resistance ($R_{xy}$) at different temperatures between 1.6 and 10 K, up to 57 T. We first focus on the low magnetic field regime ($< 9$ T) where the appearance of plateau-like features and Shubnikov–de Haas (SdH) oscillations can be seen in the Hall and longitudinal resistance, respectively (see inset of figure 1(b)). Both features are consistent with previously reported magneto-transport measurements in high quality HOPG [4, 5] and are attributed to the formation of Landau levels. When plotted against $1/B$, SdH oscillations are periodic with $\Delta(B^{-1}) = 0.2 \pm 0.02 T^{-1}$ in agreement with Kopelevich et al [6], yielding an estimated carrier density of $n = 2.4 \pm 0.2 \times 10^{11} \text{cm}^{-2}$.

At higher magnetic field, the longitudinal resistance tends to saturate before developing a noticeable kink. This saturation has been explained in terms of a freeze-out effect of the ionized impurity scattering centers in [8] whereas the formation of
CDWs accounts for the following resistance anomaly. The temperature dependence of the magnitude of the resistance jump as well as the following upturn are very similar to previous studies [9], although the smooth character of this anomaly is in contrast with the reported sharp sub-structures which are absent in our data. This effect is certainly related to disorder and/or voltage probe separation length which broadens the magneto-resistance fine details. Interestingly, the Hall resistance shows a sign change from negative to positive at magnetic field \( B_R \approx 40 \pm 1 \, \text{T} \), in the close vicinity of the magneto-resistance jump. However, in contrast to \( B_c \), the Hall resistance sign inversion \( B_R \) is temperature independent. Surprisingly, this effect continues to develop at temperatures higher than 10 K even when the CDW signatures in \( R_{xx} \) have totally disappeared, suggesting a independent origin for these two effects. However, in the low temperature regime and very high magnetic field, the Hall resistance shows an upturn which is tentatively associated with the onset of reentrant into the normal state.

In an attempt to improve the details of the magneto-resistance anomaly and motivated by the apparent non-correlation between the longitudinal and Hall resistances, a similar set of high field measurements have been performed with sample B, made from the same source of HOPG as sample A, but with reduced lateral dimensions. Similar results were observed and the experimental temperature range was extended to 300 K (figures 1(c) and (d)). The sign reversal of the Hall resistance is visible up to room temperature; however, the magnetic field at which it takes place is temperature dependent for \( T^* > 20 \, \text{K} \). Remarkably, \( T^* \) acts as a threshold temperature above which quantum effects (SdH oscillations and plateau-like features) as well as CDW signatures all vanish.

At low temperature and high magnetic field, the positive Hall resistance above \( (B_R) \) field suggests that transport is dominated by hole-like quasi-particles. Classically, in many such carrier systems, the Hall sign conversion mainly depends on the respective magnitude of the electron/hole density \( n_h \) and \( n_e \) as well as mobility \( \mu_e \) and \( \mu_h \) (\( \mu = e\tau/m^* \), where \( e \) is the electron charge, \( \tau \) is the scattering rate and \( m^* \) is the effective mass). Thus, one may reasonably suppose that the hole density and/or mobility takes over the electronic-like carriers at sufficiently large magnetic field and low temperature, thus accounting for the temperature dependent behavior of \( R_{xy}(B) \) and \( B_R \) above \( T^* \).

Recent studies suggest that it is very difficult to have defect-free graphite samples and the presence of impurities cannot be ruled out in experimental investigations [13, 15, 27, 28]. A detailed analysis [15] suggests that the typical carrier concentration is most probably not intrinsic to graphite, but comes from defects in the lattice structure or from impurities which act as electron/hole donors. However, earlier magneto-transport measurements on natural graphite and HOPG are very reproducible and have been explained considering the band structure evolution of graphite at moderate magnetic field. Also, the defect-free Slonczewski, Weiss and McClure (SWM) model has been recently used to describe very detailed magneto-transport data in bulk graphite at ultra-low temperature [16]. Therefore, we may reasonably expect that existing defect-free theoretical models for graphite can account, on average, for the macroscopic bulk magneto-transport effects in a disordered and micro-structured graphite sample. The presence of impurities and lattice defects would essentially act as charge donors, providing charge carriers without significantly perturbing the basic electronic properties of bulk graphite.

Earlier magneto-transport and theoretical calculations revealed that the Fermi surface of graphite consists of majority electrons as well as two hole pockets [20, 21]. The effective masses of electrons and two types of holes were estimated to be \( m_e^* \approx 0.056 \, m_0 \) [22], \( m_h^* \approx 0.084 \, m_0 \) [22] and \( m_\text{L}^* \approx 0.003 \, m_0 \) [23], respectively. The band structure and Landau level formation in a magnetic field applied perpendicular to the graphene planes were first investigated by Slonczewski, Weiss and McClure [24–26] for pure bulk graphite. In strong magnetic field, the SWM model predicts that only a few Zeeman-split Landau subbands are populated, specifically \( n = 0^\pm \) (electron) and \( n = -1^\pm \) (hole) bands (where \( \uparrow, \downarrow \) denote the up and down spin, respectively) and no drastic magneto-effects should be expected for magnetic fields higher than 20 T. The origin of the magneto-resistance anomaly in graphite, experimentally observed at \( B \approx 40 \, \text{T} \), cannot be accounted for within the SWM model. Later, this model was refined by Takada et al [29] by taking into account self-energy corrections and they concluded that the \( n = 0^\uparrow \) and \( n = -1^\downarrow \) Landau subbands cross the Fermi level upwards and downwards respectively and almost simultaneously at \( B = 53 \, \text{T} \). Although this model has been proposed to explain the observed reentrance at 53 T [9], it fails to describe properly most of the experimental features. Indeed, the transition-like behavior of the high field magneto-resistance anomaly stimulated Sugihara et al [30] to improve the YF theory and they concluded that the hole levels are responsible for the CDW formation. This last scenario is consistently supported by the experiment reported in this paper, where the magneto-resistance anomaly takes place in a finite low temperature range (1.6–10 K), only when hole-type carriers dominate transport.

Magneto-optical [2] and angle resolved photoemission spectroscopy (ARPES) [3] measurements suggest the existence of Dirac-like carriers very close to the H point and massive carriers at the K point of the electronic band structure of bulk graphite [2, 4]. Their contribution to transport using low temperature and low field magneto-transport measurements with advanced SdH oscillation analysis is still a matter of debate [4, 16–18]. On the other hand, this picture changes at very high magnetic field and according to Takada et al [29], one expects the hole Landau subband to lie close the Fermi level at the H point. These very light-mass hole carriers (Dirac fermions) at the H point may dominate electrical transport and be responsible for the Hall sign change at high magnetic field.

Figure 2 shows angular dependent \( R_{xx}(B) \) and \( R_{xy}(B) \) measurements for a wide range of angles from \( \theta = 0^\circ \) to \( 90^\circ \). In figure 2(a), the \( R_{xx}(B) \) resistance values have been normalized and successively shifted by 0.2 \( \Omega \) from \( \theta = 0^\circ \) to \( 40^\circ \) and by 1.2 \( \Omega \) for \( \theta = 90^\circ \) with respect to the reference curve at \( \theta = 0^\circ \) for clarity. It is noticed that the field at which
Figure 2. Angular dependence of the longitudinal (a) and the Hall resistance (b) at 4.2 K for sample A. In (a), the $R_{xx}(B)$ resistance values have been normalized and successively shifted by 0.2 $\Omega$ for $\theta = 0^\circ$–$40^\circ$ and by 1.2 $\Omega$ for $\theta = 90^\circ$ with respect to the reference curve at $\theta = 0^\circ$ for clarity.

CDWs occur ($B_c$) increases with increasing angle, at constant temperature (4.2 K). The Hall resistance shows a sign change from negative to positive at field ($B_c$) which also increases with increasing angle. When the magnetic field is parallel to the sample ($\theta = 90^\circ$) $R_{xx}(B)$ does not show any field induced CDW feature while the Hall resistance ($R_{xy}$) sign reversal is not observed up to the maximum field used in the present study. Theoretical calculations for the angular dependence of $B_c$ in graphite predicted that at constant temperature, $B_c(\theta)$ is approximately given by $B_c(0)/B_c(\theta) = \cos(\theta)$, as only the magnetic field component along the $c$-axis of graphite should contribute for the CDW instability [10]. This is confirmed by the inset figure 2(b). It is pointed out that both $B_c$ and $B_R$ follow the magnetic field component along the $c$-axis of graphite, within the experimental error. When the field is applied parallel to the graphene planes ($\theta = 90^\circ$), the Hall resistance is first zero for $B < 5$ T before increasing for higher magnetic field. This effect can be understood in terms of a spin-polarized electron system and has been extensively discussed in the literature for the case of a 2D electron gas [31–33].

Before concluding, we would like to discuss our results in more general terms, and attempt a comparison with other layered materials. We note that the Hall resistance sign change observed in graphite in the quantum limit is quite similar to the one reported in compounds such as NbSe$_3$, 2H-TaSe$_2$, 2H-Cu$_{0.2}$NbSe$_3$ [35, 36] and high temperature superconductors (HTSC) [37]. These highly anisotropic layered materials as well as quasi-one-dimensional organic conductors (TMTSF)$_2$X, where X is PF$_6$, ClO$_4$ [19, 40, 41]) are known to exhibit CDW transition under high magnetic field. All these CDW bearing compound materials exhibit a change in sign of the Hall coefficient soon after the CDW transition [19, 38, 39]. Theoretical calculations demonstrate that a strong magnetic field leads to the imperfect nesting of the Fermi surface and opens a gap in the electronic spectrum at the Fermi level [42] which may result in the Hall sign reversal in highly anisotropic conductors [36], as recently reported in [43]. All these common features (occurrence of CDWs, the pseudo-gap and Hall sign reversal) point towards a generic property of highly anisotropic layered materials to which graphite belongs.

To conclude, the present work reports on the magneto-resistance anomaly and Hall resistance sign reversal in HOPG under very high magnetic field. The experimental findings are consistent with the occurrence of CDWs involving the hole subband in the electronic spectrum of graphite. Most probably, the presence of very light hole charge carriers is responsible for the Hall sign change. The similarity with other layered materials exhibiting CDW formation, pseudo-gap and Hall resistance sign reversal is striking. In HOPG, the Hall resistance sign reversal is sustained up to room temperature while the CDW feature disappears above $T \approx 10$ K. Although these two phenomena take place at similar (but not exactly equal) magnetic field, the reported measurements suggest an independent origin. Clearly, the high magnetic field transport properties of HOPG are not fully understood yet and we hope this work will trigger further investigations and dedicated theoretical calculations.

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