

Reentrant Metallic Behavior of Graphite in the Quantum Limit

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Magnetotransport measurements performed on several well-characterized highly oriented pyrolytic graphite and single crystalline Kish graphite samples reveal a reentrant metallic behavior in the basal-plane resistance at high magnetic fields, when only the lowest Landau levels are occupied. The results suggest that the quantum Hall effect and Landau-level-quantization-induced superconducting correlations are relevant to understand the metalliclike state(s) in graphite in the quantum limit.

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Conduction processes in two-dimensional (2D) electron (hole) systems, in particular, the apparent metal-insulator transition (MIT) which takes place either varying the carrier concentration or applying a magnetic field H , have attracted a broad research interest [1]. Recently, a similar MIT driven by a magnetic field applied perpendicular to basal planes has been reported for graphite [2–5]. The quasiparticles (QP) in graphite behave as massless Dirac fermions (DF) with a linear dispersion relation, similar to the QP near the gap nodes in high-temperature superconductors. Theoretical analysis [6–8] suggests that the MIT in graphite is the condensed-matter realization of the magnetic catalysis (MC) phenomenon [9] known in relativistic theories of $(2 + 1)$ -dimensional DF. According to this theory [6–8], the magnetic field H opens an insulating gap in the spectrum of DF of graphene, associated with the electron-hole (e-h) pairing, below a transition temperature $T_{ce}(H)$ which is an increasing function of field. However, at higher fields and at temperatures $T < T_{\max}(H)$ an insulator-metal transition (IMT) occurs [2] indicating that additional physical processes may operate approaching the field H_{QL} that pulls carriers into the lowest Landau level. The occurrence of superconducting correlations in the quantum limit (QL) [10,11] and below the temperature $T_{\max}(H)$ has been proposed for graphite in Ref. [2]. On the other hand, authors of Ref. [8] argued that at high enough carrier concentration, the basal-plane resistance $R_b(H, T)$ can decrease decreasing temperature below the e-h pairing temperature, and identified $T_{\max}(H)$ with $T_{ce}(H)$. Other theoretical works predict the occurrence of the field-induced Luttinger liquid [12] and the integral quantum Hall effect (IQHE) [13] in graphite. All these indicate that understanding of the magnetic-field-induced insulating and metallic states in graphite is of importance and has an interdisciplinary interest. The aim of this Letter is to provide a fresh insight on the magnetotransport properties of graphite in the QL. We show that the IMT is generic

to graphite with a sample-dependent $T_{\max}(H)$. Our results of the Hall resistance $R_h(H, T)$ measurements performed on strongly anisotropic samples reveal characteristics related to the QHE.

We have performed measurements of both $R_b(H, T)$ and $R_h(H, T)$ resistances on several well-characterized [2–5,14,15] quasi-2D highly oriented pyrolytic graphite (HOPG) and, less anisotropic, flakes of single crystalline Kish graphite [16]. Three HOPG samples with the room temperature and $H = 0$ out-of-plane/basal-plane resistivity ratio $\rho_c/\rho_b = 8.6 \times 10^3$ (HOPG-1) and $\sim 5 \times 10^4$ (HOPG-3 and HOPG-UC), and the Kish single crystal (K-1) with a ratio of ~ 100 have been studied. HOPG samples were obtained from the Research Institute “Graphite,” Moscow (HOPG-1, HOPG-3) and the Union Carbide Co. (HOPG-UC). ρ_b values at $T = 300$ K ($H = 0$) are $\sim 3 \mu\Omega$ cm (HOPG-UC), $\sim 5 \mu\Omega$ cm (HOPG-3, K-1), and $\sim 45 \mu\Omega$ cm (HOPG-1). Low-frequency ($f = 1$ Hz) and dc standard four-probe magnetoresistance measurements were performed on samples with dimensions $4.9 \times 4.3 \times 2.5$ mm³ (HOPG-1), $4 \times 4 \times 1.2$ mm³ (HOPG-3), $5 \times 5 \times 1$ mm³ (HOPG-UC), and $2.7 \times 2.4 \times 0.15$ mm³ (K-1) in fields applied parallel to the sample hexagonal c axis in the temperature interval 70 mK $\leq T \leq 300$ K using different 9 T-magnet He cryostats and a dilution refrigerator. The Hall resistance was measured using the van der Pauw configuration with a cyclic transposition of current and voltage leads [17,18] at fixed applied field polarity, as well as magnetic field reversal; no difference in $R_h(H, T)$ obtained with these two methods was found. For the measurements, silver past electrodes were placed on the sample surface, while the resistivity values were obtained in a geometry with a uniform current distribution through the sample cross section. All resistance measurements were performed in the Ohmic regime. Complementary magnetization measurements $M(H, T)$ were carried out with $H \parallel c$ axis using a SQUID magnetometer.

Figure 1(a) illustrates the field-induced suppression of the metallic state measured in the Kish graphite sample (K-1) at low fields, and Fig. 1(b) shows the reappearance of the metallic state at the $T < T_{\max}(H)$ increasing field. We note that the reentrant metallic state takes place in the Landau level quantization regime, verified through measurements of the oscillation in both $R_b(H)$ and $R_h(H)$ associated with the Shubnikov–de Haas effect [19,20].

The noticeable difference in the high-field behavior between HOPG and Kish graphite samples is a multiple crossing in both $R_b(H, T)$ and $R_h(H, T)$ isotherms measured in HOPG (see Figs. 2 and 3) and its absence in the case of Kish graphite [20]. The appearance of plateau-like features in the Hall resistance $R_h(H)$ measured in HOPG can be seen in Fig. 3. The results in Fig. 3 suggest the QHE occurrence in HOPG. This new result is not unexpected taking into account the quasi-2D nature of HOPG. The QHE has previously been reported for various multilayered systems [21–23], and the occurrence of IQHE in graphene has been predicted in Ref. [13].

Following the analysis of transitions between adjacent quantum Hall plateaus [24], in the inset of Fig. 3 we plot the temperature dependence of the maximum slope $(d|R_h|/dH)_{\max}$ vs T^{-1} associated with the largest step in $R_h(H, T)$ measured at ~ 3.5 T. At $T \geq 1.5$ K this slope is $\propto T^{-\kappa}$ with an exponent $\kappa = 0.42(0.45)$ for the HOPG-UC (HOPG-3) sample. Numerous experiments performed

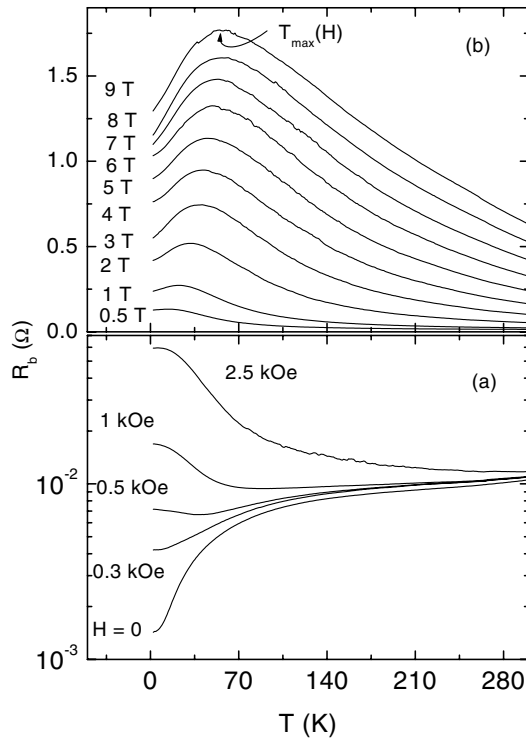


FIG. 1. Basal-plane resistance measured in single-crystalline Kish graphite sample (K-1) in the low- (a) and high-field (b) regimes. Arrow indicates $T_{\max}(H)$ below which reentrant metallic phase appears.

on QHE systems showed that κ varies from sample to sample and can even depend on whether it is determined from Hall or longitudinal resistance measurements [25,26]. Nevertheless, it is interesting to note that the here obtained exponent κ agrees with that predicted for transitions between both IQHE and fractional QHE plateaus [27,28]. The observed saturation in $(d|R_h|/dH)_{\max}$ vs T^{-1} at $T < 1.5$ K (see inset in Fig. 3) is similar to that found in QHE systems but its origin is still unclear [29–31]. The analogous behavior has also been reported for other quasi-2D bulk QHE systems as, e.g., $(\text{TMTSF})_2\text{AsF}_6$ [22]. We stress that $R_h(H, T)$ is the Hall resistance measured for the bulk sample which translates, e.g., to $\rho_h = 3.5$ m Ω cm at the main plateau for HOPG-UC sample. This gives $R_h/\square = \rho_h/d \sim 10$ k Ω ($d = 3.35$ Å is the interlayer distance), i.e., only a factor ~ 2.5 less than the Hall resistance quanta h/e^2 . The upper inset in Fig. 2 shows $R_b(T)$ measured at $H = 0, 2,$ and 8 T down to 70 mK, the lowest available temperature. As can be seen, at high fields and $T < 1$ K the resistance drop is followed by a logarithmic increase which can be accounted for by a possible formation of the Wigner crystal or charge density wave of Cooper pairs (see below) in quasi-2D systems [32,33] in the presence of quenched disorder.

We note further that if the QHE-like behavior of HOPG samples is related to their quasi-2D nature, the lack of any signature for the QHE in Kish graphite provides an additional evidence for its 3D character. On the other hand, the reentrant metallic state takes place for

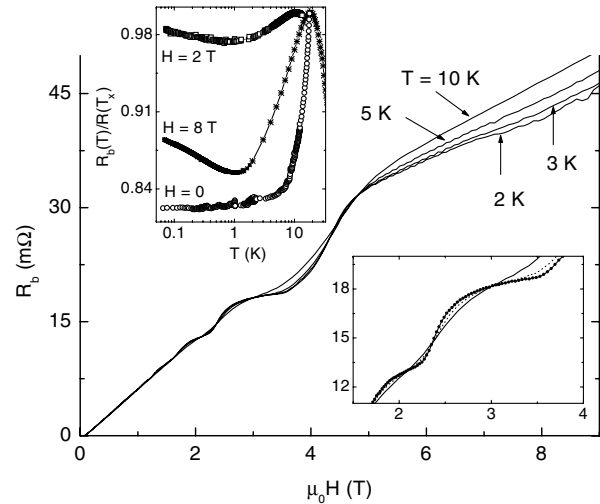


FIG. 2. Basal-plane resistance measured in HOPG-3 sample at four temperatures, demonstrating crossings of the $R_b(H)$ isotherms, i.e., the sequence of the field-driven metal-insulator-metal transitions. The lower inset gives a detailed view of the crossing in $R_b(H)$ isotherms; $T = 2$ K (●), 5 K (dotted line), 10 K (solid line). The upper inset shows normalized resistance $r = R_b(T)/R(T_x)$ where $T_x = 18$ K ($H = 0$, $H = 8$ T), and $T_x = 11$ K ($H = 2$ T).

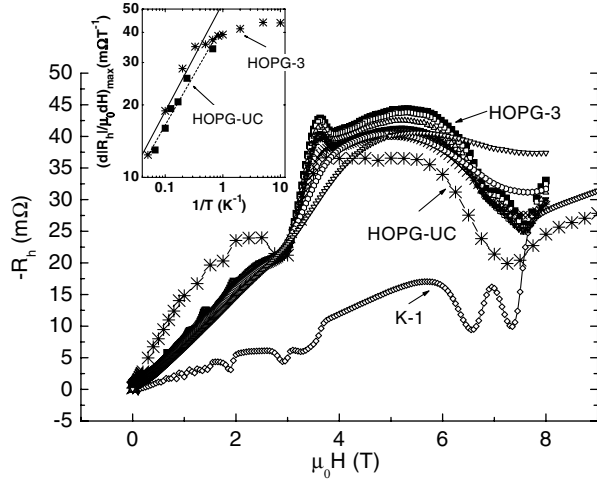


FIG. 3. Hall resistance $R_h(H, T)$ measured for HOPG-3 sample between 100 mK (■) to 20 K (▽), for HOPG-UC at $T = 4.2$ K, and for K-1 ($R_h/10$) at $T = 1.5$ K. Inset shows $(dR_h/dH)_{\max}$ vs $1/T$ for the HOPG samples; dashed and solid lines are linear fits to the function $\sim T^{-\kappa}$ with $\kappa = 0.42$ and 0.45 for the HOPG samples.

all filling factors or magnetic fields $H > H_{\text{QL}} \sim 4$ T for HOPG samples, and $\mu_0 H > 0.2$ T for the K-1 sample, indicating that the QHE alone cannot account for this effect.

Figure 4 presents $T_{\max}(H)$ obtained for all measured samples. It demonstrates that $T_{\max}(H)$ for the K-1 sample can be surprisingly well approximated by the equation

$$T_{\max}(H) = C[1 - (H_c/H)^2]H^{1/2}, \quad (1)$$

with H_c and C being fitting parameters. Equation (1) is similar to expression (64) of Ref. [8], $T_{ce} \sim (1 - \nu_b^2)H^{1/2}$, obtained within the MC theory, where $\nu_b = 2\pi c n_{2D}/N_f |eH| \equiv H_c/H$ is the filling factor, N_f is the number of fermion species ($N_f = 2$ for graphite), and n_{2D} is the 2D carrier density. We note, however, the order of

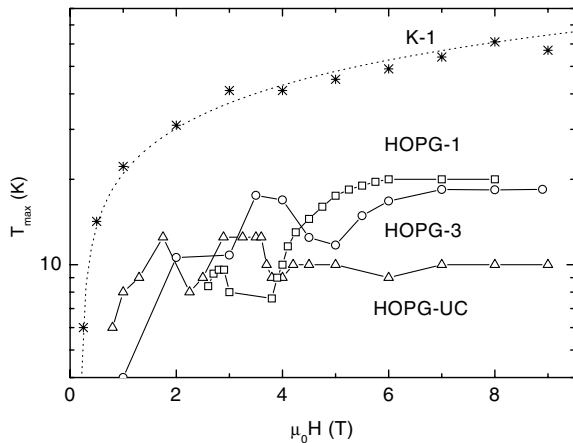


FIG. 4. T_{\max} vs H for all studied samples. Dotted line corresponds to Eq. (1) with $C = 21.5$ K/ $T^{0.5}$ and $\mu_0 H_c = 0.16$ T.

magnitude difference between the predicted value for $\mu_0 H_c \approx 2.5$ T (using $n_{2D} = n_{3D}d \sim 10^{11}$ cm $^{-2}$ taking $n_{3D} \sim 3 \times 10^{18}$ cm $^{-3}$) [8] and the fitting value $\mu_0 H_c = 0.16$ T; see Fig. 4.

Alternatively, the reentrant metallic state in both HOPG and Kish graphite samples can be caused by a common mechanism associated with the Cooper-pair formation. The appearance or reappearance of superconducting correlations in the regime of Landau level quantization has been predicted by several theoretical groups (for review articles see Refs. [10,11]). According to the theory, superconducting correlations in quantizing field result from the increase of the 1D density of states $N_1(0)$ at the Fermi level. In the quantum limit ($H > H_{\text{QL}}$) the superconducting critical temperature $T_{\text{SC}}(H)$ for a 3D system is given by the equation [10]

$$T_{\text{SC}}(H) = 1.14\Omega \exp[-2\pi l^2/N_1(0)V], \quad (2)$$

where $2\pi l^2/N_1(0) \sim 1/H^2$, $l = (\hbar c/eH)^{1/2}$, V is the BCS attractive interaction, and Ω is the energy cutoff on V (in 2D case, T_{SC} increases linearly with field [11,34,35]). The increase of T_{\max} with field (see Fig. 4) is in qualitative agreement with Eq. (2) and the 2D predictions [11,34,35]. Above a certain field $H > H_{\text{QL}}$ a reentrant decrease of T_{SC} is also expected [10], being consistent with the saturation in $T_{\max}(H)$; see Fig. 4. The occurrence of either spin-singlet or spin-triplet [36] superconductivity in graphite may be possible in the QL. Theory predicts an oscillatory behavior of $T_{\text{SC}}(H)$ at $H < H_{\text{QL}}$, i.e., with an increasing number of occupied Landau levels; indeed, a nonmonotonic $T_{\max}(H)$ is observed for all HOPG samples at $\mu_0 H < 4$ T (see Fig. 4). The absence of pronounced T_{\max} vs H oscillations in Kish graphite can naturally be understood taking into account its lower anisotropy. In a (quasi-)2D case the density of states $N(0)$ is a set of delta functions (broadened, however, by quenched and thermal disorder) corresponding to different Landau levels, and hence T_{\max} should oscillate stronger with field in HOPG, as observed. A $T_{\max}(9 \text{ T}) = 62$ K obtained for Kish graphite is much higher than $T_{\max}(9 \text{ T}) = 11$ K measured for strongly anisotropic HOPG-UC sample. This fact can be understood taking into account quantum and/or thermal fluctuations [10,11], which are stronger in quasi-2D HOPG and hence can effectively reduce T_{\max} (i.e., T_{SC}). It is expected that below $T_{\text{SC}}(H)$ and for 3D samples, the resistance along the applied field vanishes and the resistance perpendicular to the field direction shows a drop [10,11]. However, in graphite both the c -axis and basal-plane resistances remain finite due to the layer crystal structure, implying the occurrence of superconducting correlations without macroscopic phase coherence.

In Fig. 5 we compare $R_b(T)$ and the magnetization $M(T)$ measured for the HOPG-UC sample at $\mu_0 H = 1$ and 5 T (inset), viz., in the QL, illustrating that the

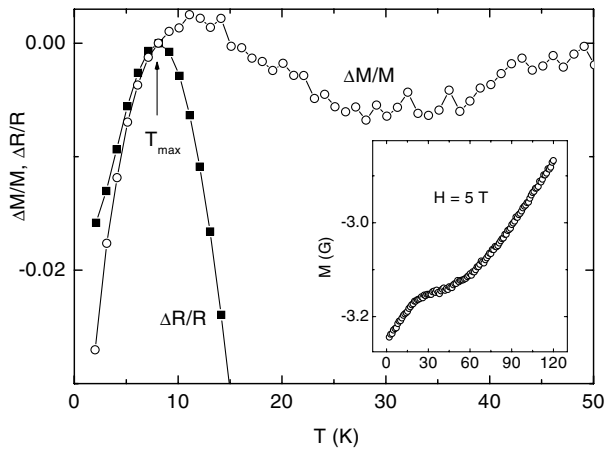


FIG. 5. $\Delta M/M = [M(T) - M(T_{\max})]/M(T_{\max})$ and $\Delta R/R = [R_b(T) - R_b(T_{\max})]/R_b(T_{\max})$ measured for the HOPG-UC sample at $\mu_0 H = 1$ T. The inset presents the magnetization $M(T)$ measured at $\mu_0 H = 5$ T.

reentrant metallic state(s) is (are) accompanied by the enhanced diamagnetic response, supporting both the superconductivity- and QHE-based scenarios for the field-induced metallic state(s).

In summary, the results of the present work provide an unambiguous evidence for the reentrant metallic state(s) in graphite induced by a magnetic field in the quantum limit. The observed sequence of the field-driven insulator-metal-insulator transitions as well as a signature for the QHE in HOPG samples rule out any trivial explanation for the phenomenon. On the other hand, the overall results can consistently be understood assuming the occurrence of superconducting correlations in the regime of Landau level quantization, providing thus a possible solution of the longstanding problem of the metallic resistance behavior ($dR_b/dT > 0$) in graphite in the QL even below 1 K [37].

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