INTRODUCTION

Over the last 60 years the literature contains a substantial number of measurements and theoretical work on the electrical and thermal transport properties of the semimetal graphite. In contrast to the common believe, however, several transport properties of graphite are not understood and some theoretical assumptions done in the past seem now less plausible. These doubts have their origin in the relatively new and controversial physics of a two-dimensional (2D) electron gas. Graphite has been tacitly assumed to be a 2D material, but the relatively low quality of the samples prevented clear measurements of its true 2D transport properties. The number of open questions regarding the transport properties of graphite is significant. Already early work noted that the magnetic field dependence of the electrical longitudinal resistivity \( \rho_{xx} \) and Hall resistance \( R_H \), even including ad-hoc dispersion relation and trigonal warping of the constant energy surfaces, was (and still remains) basically unexplained.

Recent measurements of the longitudinal resistivity of highly oriented pyrolytic graphite (HOPG) samples show a clear magnetic field driven metal-insulator transition (MIT) with a giant magnetoresistance at low fields and at low temperatures. For example, the longitudinal resistivity at 4.2 K can increase by more than one order of magnitude with a field \( B \simeq 0.2 \) T. This MIT shows a scaling as found for 2D electron systems with similar scaling exponent but with a critical field \( \sim 0.1 \) T applied perpendicular to the graphene layers and trigonal warping of the constant energy surfaces, was (and still remains) basically unexplained.

The better the sample quality - characterized by the full width at half maximum (FWHM) of the rocking curve - and suggests that the coupling between planes is much less than the commonly assumed 0.3 eV. In the quantum limit (QL) when only the lowest Landau levels of graphite are occupied \( (B > 2 \) T), the longitudinal electrical resistivity shows a reentrance to a metallic-like state below a field-dependent temperature \( T_m(B) \). The function \( T_m(B) \) depends on the dimensionality of the graphite sample and it oscillates as a function of field for quasi 2D samples. This behavior might be an evidence for field-induced superconductivity at the QL in graphite, discussed in Refs. In the QL the Hall resistance \( R_H \) shows clear signs of the quantum Hall effect for samples with small FWHM.

For ideal graphite the conduction electrons are expected to follow a Dirac dispersion relation. These quasi-particles (QP) should have some similarities with the nodal QP of the \( d \)-density wave (DDW) state, which is expected to follow a Dirac dispersion relation. These quasi-particles should have some similarities with the nodal QP of the DDW state, which is expected to follow a Dirac dispersion relation. These quasi-particles should have some similarities with the nodal QP of the DDW state, which is expected to follow a Dirac dispersion relation.
regime.

The magnetic field dependence of the thermal conductivity of strongly anisotropic HOPG samples was already measured in the past but one does not find curves in the published literature with the necessary resolution in the QL regime. There are at least two unpublished studies which deserve our attention. In his Ph.D. thesis, Ayache [17] measured \( \kappa(T, B) \) and observed well defined oscillations of \( \kappa(B) \) at fields above 2 T and at constant temperatures below 10 K. This behavior was apparently also observed by Woollam [18] but the curves were not included in the corresponding paper. Interestingly, both authors emphasized that the oscillations in \( \kappa(B > 2 \, \text{T}) \) as a function of field were apparently in phase with the electrical resistivity oscillations, although the electronic contribution to \( \kappa \) at high fields freezes out according to the Wiedemann-Franz law. In spite of this striking result neither the curves nor any analysis of the data was published to our knowledge.

High-resolution measurements of the field dependence of the thermal conductivity of quasi 2D HOPG samples have nowadays special relevance. In particular because evidence for a quantum-Hall behavior in 2D samples in the QL has been recently reported [11]. The behavior of \( \kappa(T, B) \) in graphite is not only important to understand the nature of the QP in this material at the QL but also gives us the chance to study the thermal transport in the quantum-Hall effect (QHE) regime. We note that the thermal transport in the QHE regime still remains an unclear problem since the discovery of this effect. In this work we have measured the longitudinal thermal conductivity \( \kappa \) of a well characterized HOPG sample as a function of magnetic field applied parallel to the \( c \)-axis of the graphite structure. These measurements were accompanied by measurements of the longitudinal and Hall resistances. The results clearly show that the WF-law is violated in the QL, whereas deviations are observed at lower fields.

**EXPERIMENTAL DETAILS**

The HOPG sample from the Union Carbide company measured in this work was selected because of its clear quasi-2D properties observed in the electrical and Hall resistivity. This behavior is correlated with the small FWHM = 0.26° of the rocking curve, which is a measure of the misorientation relative to the \( c \)-axis of the crystallites in the sample. The measured FWHM is one of the smallest we have obtained for HOPG samples. We note that most of the graphite samples studied in the literature of the 70’s and 80’s had much larger FWHM. Our experimental evidence indicates that in samples with FWHM values larger than \( \sim 0.5° \) the transport properties show clear sign of 3D behavior and coherent transport in the \( c \)-direction [2, 13] and therefore they do not reflect true 2D behavior of ideal graphite. The dimension of our sample was: length = 1.6 mm, width = 1.2 mm and thickness \( \sim 60 \, \mu\text{m} \). The room temperature out-of-plane/basal-plane resistivity ratio at \( B = 0 \) of the sample was \( \rho_c/\rho_b \sim 5 \times 10^4 \). Furthermore, this sample does not show any maximum in the \( c \)-axis resistivity as a function of angle for fields parallel to the graphene planes [3]. This indicates incoherent electrical transport expected for weak-coupled conducting planes and for samples with a low density of defects.

The Hall resistance was measured using the van der Pauw configuration with a cyclic transposition of current and voltage leads [11, 20] 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 an uniform current distribution through the sample cross section. All resistance measurements were performed in the Ohmic regime. The absolute value of the longitudinal (basal-plane) resistivity at zero field was \( \rho_b(6 \, \text{K}, 0) \approx 2.4 \mu\text{Omega}\text{cm} \) and 2.6 \( \mu\text{Omega}\text{cm} \) at 10 K. The error in the absolute value is estimated to be \( \sim 30\% \) due to geometrical errors. At 10 K \( \rho_b \) reaches its low-temperature rest value within 10%. The resistivity increases by two orders of magnitude for an applied field of 1 T at \( T < 10 \, \text{K} \).

For the longitudinal thermal conductivity measurement the temperature gradient (of the order of 200 to 300 mK) was measured using a previously field- and temperature-calibrated type E thermocouples with a decameter [21]. The thermocouple ends were positioned one at the top and the other at the bottom of the main surface of the sample. A detailed calibration below 8 K was performed because in this temperature region the thermapower of our thermocouple is specially sensitive on the magnetic field with a non-monotonous dependence [21]. The experimental arrangement was recently used to study the longitudinal and Hall thermal conductivities of high-temperature superconducting crystals [22, 23]. We note that in general the measured thermal conductivity is \( \kappa = \kappa_i - T S^2 \sigma_i \), where \( \kappa_i \) is the “real” thermal conductivity of the sample, \( S \) the thermapower and \( \sigma_i \) the electrical conductivity. In the case of our graphite sample the correction term to \( \kappa \) is four orders of magnitude smaller than \( \kappa_i \) at 10 K.

Our system enables us to measure \( \kappa(B) \) with a relative resolution better than 0.1% above 5 K. The thermal stability was better than 10 mK in the whole temperature range 5 K \( \leq T \leq 20 \, \text{K} \) and magnetic field 0 \( \leq B \leq \text{9 T} \). The absolute error in the thermal conductivity was estimated to be \( \leq 30\% \). The obtained absolute value of \( \kappa \) and its temperature dependence are similar to those from previous studies [2, 17, 18, 22, 23]. For example, at 10 K we obtain \( \kappa(0) \approx 130 \, \text{W/mK} \) and \( \kappa(0) \approx 33 \, \text{W/mK} \) at 5 K and zero fields. In all magnetic-field runs \( \kappa(B) \) showed
results and discussion

Figure 1(b) shows the reduced longitudinal thermal conductivity \(\kappa(T, B)/\kappa(T, 0)\) as a function of the field applied parallel to the \(c\)-axis at different constant temperatures between 5 K to 20 K. In Fig. 1(b) we show the Hall resistance of the same sample. The decrease of \(\kappa\) with field can be related to the decrease of the electronic contribution. The clear oscillations in \(\kappa(B)\) observed at \(B > 1 \text{T}\) are apparently due to the quantization of the Landau levels and the crossing of the Fermi energy as the oscillations in the Hall effect indicate, see Fig. 1(b). Figure 2 shows the same data as Fig. 1 but in a linear field scale.

It is noticeable the appearance of the plateau-like features at \(B \sim 2 \text{T}\) and \(4 \text{T}\) in the Hall resistivity that clearly suggests the occurrence of the Quantum Hall effect (QHE) in graphite. In fact, the temperature dependence of the maximum slope \((d|R_H|/dB)_{\max}\) vs. \(T^{-1}\) between two plateaus at 3.5 \(\text{T}\), and measured to 70 mK shows a temperature dependence \(T^{-k}\) with an exponent \(k = 0.42\) similar to that found in QHE systems [1]. This result is not unexpected taking into account the quasi 2D structure of the sample. We note that the occurrence of the integral QHE in graphite has been predicted recently [20]. The reason why it was not found before is related to the sample quality which affects the 2D behavior of the transport properties. Our studies show that the dimensionality is strongly affected by internal lattice defects, some of them appear to short circuit the graphene planes.

The fact that we want to stress is the good correspondence between the features measured in \(\kappa\) and \(R_H\) at the QL. To recognize this we show in the inset of Fig. 1(b) the temperature dependence of the field at the onset of the plateau in \(R_H\) at \(\sim 3.7 \text{T}\) (○) and the position of the minimum in \(\kappa\) (■).

Figure 3 shows in more detail the field dependence of the basal-plane and Hall resistances, taken at 4.2 K, as well as of the thermal conductivity at 5 K. The thermal conductivity data shown in this figure were taken increasing and decreasing field. As seen in the figure, no significant hysteresis is observed. This result is in contrast to the hysteresis observed by Ayache in his Ph.D. work [17]. We speculate that a small temperature drift might have been the reason for the observed hysteresis.

Can we understand the decrease with field and the oscillations observed in \(\kappa(B)\) within the Wiedemann-Franz relation? To answer this question we proceed as follows. We assume that the thermal transport of graphite is given by two contributions [11]:

\[
\kappa = \kappa_p(T) + \kappa_e(T, B),
\]

where \(\kappa_p\) is due to the phonons, the contribution of the atomic lattice with the appropriate lattice anisotropy, and \(\kappa_e\) due to conduction electrons. Usually one assumes that the field dependence of the thermal conductivity is given only by the electronic part \(\kappa_e(T, B)\), which can be estimated with the WF relation. This universal relation relates the electrical resistivity \(\rho(T, B)\) with the thermal conductivity due to electrons by

\[
\frac{\kappa_e \rho}{T} = L_0,
\]
through the universal constant $L_0 = 2.45 \times 10^{-8} \text{W} \Omega \text{K}^{-2}$ at low enough temperatures. One can recognize easily the difficulty to measure accurately the field dependence of the electronic contribution to the thermal transport above $\sim 4$ K due to the small electronic contribution. From Eq. (4) we expect for well ordered HOPG samples at zero field a ratio between the electronic and total thermal conductivity $\kappa_e/\kappa < 0.15$ at 5 K, and $< 0.05$ at 10 K. Literature data are in general in good agreement with these estimates [17, 24].

The relation (2) holds strictly for elastic or quasielastic electron scattering and therefore the range of validity is usually set, either at low enough temperatures where the resistivity is temperature independent (impurity scattering dominates), or at high enough temperatures where the electron-phonon scattering is large [27]. For the sample measured in this work, the temperature dependence of the electrical resistivity indicates a saturation below 10 K (curves for a similar sample can be seen in Refs. [6, 28]) and therefore at $T \leq 10$ K we expect to be roughly in the validity range of the WF-law. From the measured field dependence of the electrical resistivity we can calculate the relative change of the total thermal conductivity at a fixed temperature as:

$$\frac{\kappa(B)}{\kappa(0)} = \frac{\kappa_e(B) - \kappa_e(0)}{\kappa(0)} + 1,$$

assuming that the phonon conductivity does not depend on magnetic field. In Fig. 1(a) we show three curves calculated with Eqs. (3) and (2) using the measured $\rho(B)$ at 10 K (curves (1) and (2)) and 6 K (3). Curve (1) was obtained with the same parameters as (2) but with $L_0 = 2.0 \times 10^{-8} \text{W} \Omega \text{K}^{-2}$, assuming a decrease of $L_0$ due to the possible influence of the inelastic scattering.

From the comparison between the computed curves and the experimental ones one would tend to conclude that Eqs. (2) and (3) provide reasonably well the overall decrease of $\kappa$ with field, within the geometrical errors in the measurement of both conductivities. Nevertheless we should note that the WF law and Eq. (3) do not reproduce accurately the measured field dependence, see Fig. 1(a). Due to the electrical resistivity increase (a factor $\sim 100$ from zero field to 1 T at $T \leq 10$ K) the electronic contribution, according to the WF law, becomes negligible. Therefore the electronic contribution to $\kappa$ should be negligible, e.g. at $B > 0.4$ T and $T = 10$ K, and a saturation of $\kappa$ at larger fields is expected. This is not observed experimentally. This means also that the relatively small oscillations observed in the longitudinal resistivity above 1 T that accompany the features in the Hall effect (see Fig. 2) should not affect $\kappa$ according to Eq. (2) in contrast to the experimental results, see Fig.1(a). These results clearly indicate that the WF law in its original form fails to explain the field dependence of the thermal conductivity in the QL of graphite and in the measured temperature range.
decreases in this field region whereas we naively expect a decrease of $\kappa_e$ in the plateau region and reaches a maximum at the end of the plateau region between two neighboring maxima in the field region. A similar result has been obtained in previous theoretical work \[30, 31\]. In our case, however, we obtain the striking result that $\kappa_e(B)$ decreases in this field region whereas increases with field in the plateau region and reaches a maximum at the end of the corresponding plateau, see Fig. 1(a). If we would have localized QP in the field region of the plateau we would naively expect a decrease of $\kappa_e$. On the other hand, the opposite behavior may be also possible, i.e. an increase of $\kappa_e$ with field, if the density of interacting QP would decrease in this field region and the main scattering mechanism is given by QP-QP scattering, as in the case of high-temperature superconductors \[32\]. In this case the theoretical description of the thermal conductivity may become more complicated to handle.

According to recently published theory \[7, 33\], a magnetic field applied perpendicular to the graphene planes opens an insulating gap in the spectrum of Dirac fermions, associated with an electron-hole pairing, leading to the excitonic insulator state below a field dependent transition temperature. The experimental value of the critical field of the field-driven metal-insulator transition in graphite is $\sim$50 times smaller than the predicted in Refs. \[34\]. The discrepancy can be understood, however, assuming that the Coulomb coupling, given by the dimensionless parameter $g = 2\pi e^2/\epsilon_0 \epsilon (\epsilon_0$ is the dielectric constant) \[7, 33\], drives the system very close to the excitonic instability. In this case, the threshold field $B_c$ can be well below the estimated value of 2.5 T. The above analysis, together with the experimental evidence that only the perpendicular component of the applied field drives the MIT \[9\], appear to support the theoretical expectations of a field-induced excitonic insulator state in graphite. In this case and according to Ref. \[31\] we would expect a monotonic decrease of $\kappa_e(B)$ with field and a kink at $B \sim B_c$ with a plateau region in the insulating-like state of the QP at $B > B_c$. In the temperature range of our experiments the results do not show a clear kink at $B \sim 0.1$ T nor a plateau at higher fields and $T \geq 6$ K, see Fig. 1(a), although one may tend to recognize it at $T = 6$ K and $B \sim 0.5$ T when the data are plotted in a linear field scale, see Fig. 2(a). At the temperature limit of our system (5 K) the density of points at $B < 1$ T is too low to assure the existence or non-existence of a kink. Measurements at lower temperatures are needed to enhance the relative contribution of the QP to $\kappa$ and check whether the predicted feature is observable. This issue will be studied in the future.

Can the oscillations in $\kappa(B > 1$ T) be due to the lattice contribution $\kappa_p(B)$ via electron-phonon interaction as, for example, in antimony \[35\]? The temperature dependence of $\kappa \propto T^2.4$ at $5$ K $< T < 30$ K speaks for phonon scattering by grain boundaries and not by electrons \[1\]. The inelasticity parameter $\eta = v/\lambda \omega_c$ (here $v$ is the sound velocity, $\lambda$ the magnetic length and $\omega_c$ the cyclotron frequency), that provides an estimate of the efficiency of the electron-phonon scattering, is $\sim 0.01$ at 4 T for graphite. Therefore, unless there is an intersection of Landau levels that favors acoustic phonon transitions \[36\], it does not seem that the phonon-electron scattering can be significantly enhanced at high fields in graphite. The overall correlation of $\kappa(T, B)$ with the Hall resistivity indicates that the origin of the oscillations in $\kappa(B)$ should be related to a pure QP phenomenon.

FIG. 4: The thermal conductivity difference between the minimum (at $B \simeq 3.7$ T) and maximum (at $B \simeq 5.5$ T) $\Delta \kappa$ (see Fig. 1) as a function of temperature. The right scale provides the estimate values per graphene layer (within a geometrical error of $\sim 30\%$).
In summary, high-resolution measurements of the magnetic field dependence of the thermal conductivity in a quasi 2D sample of graphite show clear oscillations in the quantum limit. The Hall effect for the same sample shows quantum Hall effect features which are correlated to the features observed in $\kappa$. With the measured longitudinal electrical resistivity we show that the observed oscillations in $\kappa$ cannot be explained with the original WF law. Lower temperature measurements as well as an appropriate theoretical framework for graphite are highly desirable.

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