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T^2 dependence of the in-plane resistivity of graphite at very low temperatures

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High-precision measurements of the in-plane resistivity of graphite have been made in a dilution refrigerator down to 20 mK. Below 5 K, the resistivity varies as a quadratic function of temperature, behavior consistent with the electron-hole scattering mechanism. The strength of the interaction is in good agreement with a model based on the cylindrical Fermi surfaces of graphite.

The electrical resistivity of graphite has been a subject of interest for many years. Measurements of the in-plane resistivity have been performed by several groups,[1-4] and, as a result, a picture has emerged of the basic scattering mechanisms governing the conductivity in various temperature regimes. At liquid-helium temperatures, the resistivity appears to be essentially constant, as a result of the strong scattering of carriers by impurities and defects. On the other hand, at higher temperatures the conductivity is limited by phonon scattering.

The recent upsurge of interest in the properties of graphite intercalation compounds (GIC's) has precipitated a need to reexamine the transport behavior of graphite in more detail. In particular, attempts are frequently made[5,6] to fit the temperature dependence of the resistivity of GIC's to a power law of the form $\rho(T)=\rho_0+AT+BT^2$, where the quadratic term is interpreted as a sign of significant carrier-carrier scattering. Since the available measurements on pure graphite are limited to a 1%–2% precision level, and the residual resistance ratio (RRR) normally is less than 20, it is not possible on the basis of existing experimental evidence to ascertain whether or not the carrier-carrier scattering is present already in the pristine material. In fact, the possible role of this interaction in graphite has not yet been considered even theoretically.

In this Rapid Communication we report on our high-precision, very-low-temperature, investigations of the in-plane resistivity of highly oriented pyrolytic graphite (HOPG) and we show that carrier-carrier scattering represents an important and dominant temperature-dependent resistive mechanism below 5 K.

The measurements were made in a dilution refrigerator down to 20 mK and we used a SQUID as a sensitive null detector. Sample currents were kept below 200 μA to prevent Joule heating of the samples. Precision achieved in the measurements was about three parts in 10^5. The Peltier contribution to the signal was calculated from the measured values of the thermopower and thermal conductivity and found to be negligible on the stated scale of precision at all temperatures. Several relevant parameters concerning the samples are given in Table I.

In the inset of Fig. 1 is shown the temperature dependence of the resistivity ρ of sample 1 up to 300 K; the data are typical of the results found for sample 2 and of previous measurements.[1-4] We note the rapid decline of the resistivity below 100 K and the onset of the impurity-limited regime below about 10 K. It is this latter regime which is of primary interest here. The results of our resistivity measurements on two samples of HOPG are presented in Fig. 1. Both samples show significant temperature dependence down to the lowest attainable temperature. Assuming that Matthiessen's rule applies, we determine ρ_0 by extrapolating the curves to $T=0$ and obtain the temperature-dependent resistivity from $\rho_T=\rho-\rho_0$. The latter is plotted on a log-log scale in Fig. 2. We find that ρ_T is proportional to T^2 below 5 K, then increases faster $\sim T^3$ to about 15 K, and finally becomes more weakly temperature dependent at higher temperatures. The quadratic dependence is clearly resolved for at least a decade in T down to about 0.5 K. The scatter of the points below 0.5 K becomes too large even for our high-resolution measurements and it is not possible to extract the temperature dependence accurately enough below this temperature.

We now discuss the implications of the temperature variation of the resistivity based on theoretical models of conduction in semimetals. Specifically, we wish to show that the observed T^2 dependence is not compatible with carrier-phonon scattering but, rather, has its origin in the carrier-carrier interaction.

Regardless of the details of the Fermi surface and phonon distribution, the effect of carrier-phonon scattering on the temperature-dependent resistivity has the following general features: for $T > T_{\text{cutoff}}$, $\rho_T \sim T$ and, as the temperature decreases, ρ_t becomes proportional to higher powers of T. In the case of semimetals where the Fermi surfaces occupy only a tiny fraction of the Brillouin zone, the cutoff is not imposed by the Debye "sphere," but by a maximal caliper of the Fermi surface $2k_F^{\max}$. On the other hand, the exact shape of the ρ_T vs T curves depends on the character of the Fermi surface and phonon distribution. This may be represented by the familiar Bloch-Grüneisen integral as in the case of spherical Fermi surfaces or, as shown by Kuk-

TABLE I. Relevant parameters of samples.

Sample designation	Dimensions (mm^3)	RRR	ρ_0 (Ω cm)	Coefficient B (Ω cm K^{-2})
1	$2.3\times3.3\times15.5$	11.1	0.4068×10^{-5}	3.7×10^{-9}
2	$2.7\times5.1\times11.4$	6.5	0.8376×10^{-5}	6.4×10^{-9}

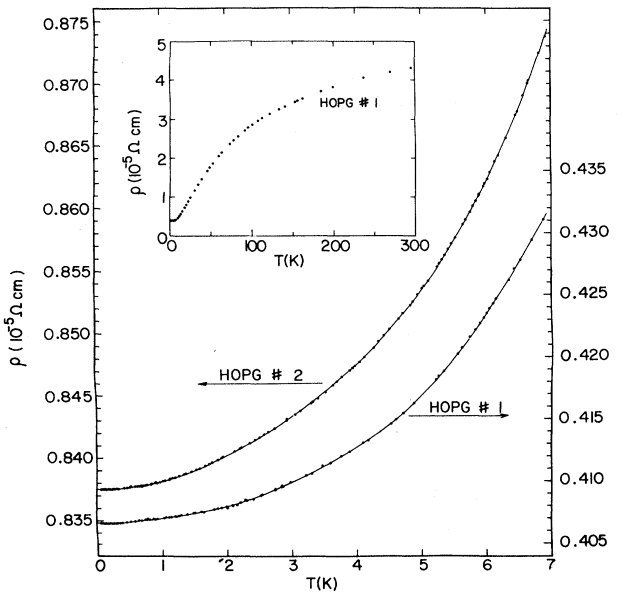

FIG. 1. Temperature dependence of the resistivity of two different HOPG samples.

konen[7] for cylindrical surfaces (which are a more reasonable representation of the highly elongated ellipsoidal carrier pockets of graphite), by a linear dependence of ρ_T for $T > T_k$, changing into an extended "window" of quadratic dependence for $T_p < T < T_k$, followed by higher power dependence for $T < T_p$. The bounds of the expected quadratic dependence are given by[8] $T_p = 2\hbar s p_F / k_B$ and $T_k = 2\hbar s k_F / k_B$ where s is the speed of sound and $2k_F$ and $2p_F$ are the height and diameter of the cylinder, respectively. Using appropriate values for graphite,[9] they are $T_p = 43$ K and $T_k = 731$ K for electrons and $T_p = 37$ K and $T_k = 444$ K for holes—much too high a temperature regime to explain the observed T^2 dependence. Thus, neither the observed crossover in ρ_T from T^3 to T^2 variation nor the temperature regime where the T^2 dependence is actually observed are compatible with any reasonable predictions based on the carrier-phonon interaction in graphite. Consequently, the carrier-phonon scattering, which certainly dominates the transport at high temperatures, cannot explain the temperature-dependent resistivity of graphite below 5 K.

We now turn to an alternative mechanism: carrier-carrier scattering. It is a long-established fact[10] that such a scattering mechanism leads invariably to a T^2 term in the resistivity. Since this contribution is, in general, most easily resolved at low temperatures, we assume that the carrier-carrier interaction is limited to intrapocket processes only. Out of these, the electron-hole scattering is the sole resistive mechanism as both electron-electron and hole-hole processes conserve momentum. As shown by Kukkonen and Maldague[11] this is true not only for a simple spherically symmetrical surface but also for any ellipsoidal Fermi surface. A general theory of the electron-hole scattering in a semimetal has been developed by Kukkonen and Maldague.[12,13] Application of this theory to graphite yields the temperature-dependent resistivity

$$\rho_T = \frac{1.06 m_e^2 m_h^2 (k_B T)^2 W}{\pi^2 n e^2 h^6} , \tag{1}$$

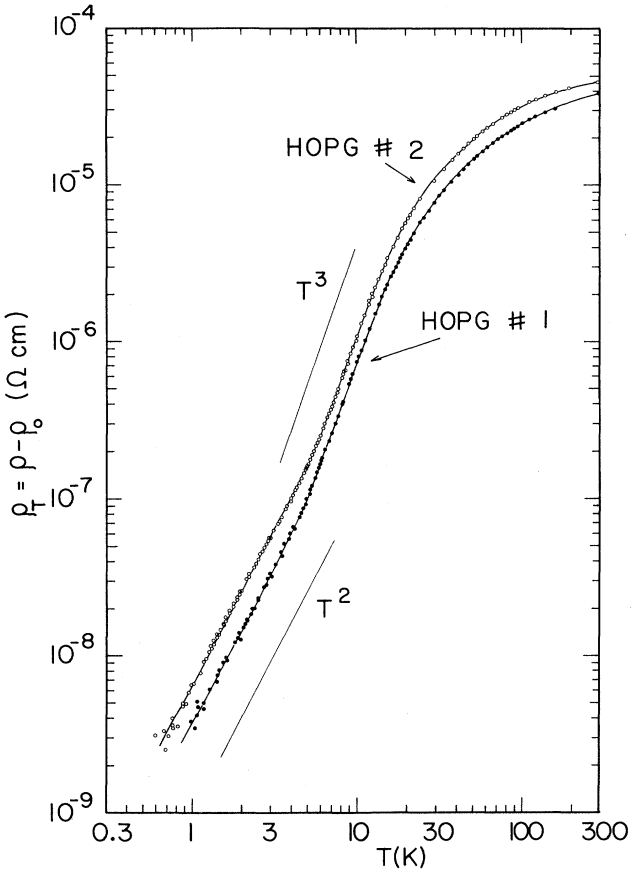

FIG. 2. Temperature-dependent part of the resistivity of HOPG plotted on a log-log scale.

where W is the electron-hole scattering rate.

In the Born approximation and for spherical Fermi surfaces, the theory of Kukkonen and Maldague predicts the scattering rate in graphite as

$$W = \frac{2\pi}{h} \int_0^{2p_F^e} \frac{dq}{2p_F^e} V^2(q) 4 \left(\frac{q}{2p_F^e} \right)^2 , \tag{2}$$

where $V(q)$ is the electron-hole interaction potential. In the Thomas-Fermi approximation $V(q)$ is given by

$$V(q) = \frac{4\pi e^2}{\epsilon q^2 + (q_{\mathrm{TF}}^e)^2 + (q_{\mathrm{TF}}^h)^2} . \tag{3}$$

Substituting values appropriate for graphite, $\epsilon = 2.8$,[14] $n = 3 \times 10^{18}\ \mathrm{cm}^{-3}$, $m_e = 0.057 m_0$, and $m_h = 0.039 m_0$,[15] we find $\rho_T / T^2 = 3.53 \times 10^{-8}\ \Omega\,\mathrm{cm\,K}^{-2}$. This value is about 5–10 times larger than the experimental values. The discrepancy is not surprising, however, since the calculation [Eqs. (1) and (2)] assumes spherical carrier pockets which is clearly an inappropriate description of graphite. We, therefore, attempt to rescale the results for the spherical Fermi surface into the cylindrical geometry which is a more reasonable representation of highly anisotropic Fermi surfaces of graphite (Fig. 3). A change in the shape of the Fermi surface will affect both the effective mass and the scattering time. Conservation of the total carrier density requires that the Fermi surfaces occupy the same volume in k

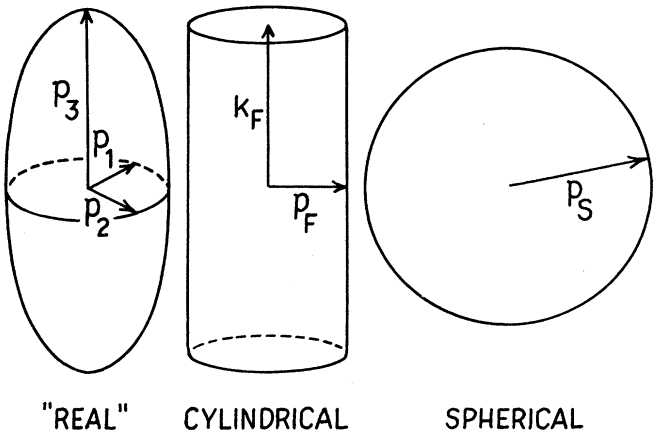

FIG. 3. Models of the Fermi surface of graphite.

space. In terms of effective masses this becomes

$$(m_1 m_2 m_3)^{1/2} = \tfrac{3}{2} m_p m_k^{1/2} = m_s^{3/2} \ , \tag{4}$$

where m_k and m_p are masses parallel and perpendicular to the cylindrical axis, and m_s corresponds to the spherical surface. Equating the diameter of the cylinder to the diameter of the p_2-p_3 section of the ellipsoid determines the ratio $\sqrt{m_k/m_p} = 17$. Substituting into (4) we get $m_p = 0.115 m_s$. The ratio of resistivities in the cylindrical and spherical Fermi surface geometries is then

$$\rho_c/\rho_s = (m_p/m_s)(\tau_s/\tau_c) = 0.115 \tau_s/\tau_c \ . \tag{5}$$

The ratio of the scattering times in the electron-hole interaction is estimated by Maldague[16] as $\tau_s/\tau_c \simeq 2$. Thus, the scattering on the cylindrical surfaces is considerably weaker than on the spherical surface by a factor $\rho_c \simeq 0.053 \rho_s$. In the case of graphite such a rescaling leads to $\rho_T/T^2 \simeq 1.87 \times 10^{-9}\ \Omega\ \mathrm{cm\,K^{-2}}$ which is somewhat lower than the experimental T^2 coefficients, in fact, differing by less than a factor of 2 with respect to the higher-quality specimen. The T^2 variation of the resistivity of graphite at low temperatures is thus not only in a good qualitative agreement with the predictions of the carrier-carrier scattering but the strength of the interaction is also in a reasonable quantitative accord with the estimate based on the simple cylindrical model of the Fermi surfaces of graphite. While the cylindrical model is certainly a good first approximation, it is not a perfect one. It neglects several detailed features of the carrier spectrum, notably the trigonal warping of the Fermi surfaces.[17] These features will have to be included in any future more refined theoretical calculations.

ACKNOWLEDGMENTS

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[17] As a result of trigonal warping, the Fermi surfaces of graphite deviate somewhat from perfect ellipsoids. This deviation could make the normal electron-electron and hole-hole processes resistive. However, the contribution of these processes to the resistivity is not expected to be large. In fact, Kukkonen and Maldague (Ref. 11) show that a deviation from ellipsoidicity as large as 14% produces only about 4% correction in the T^2 term of the resistivity.