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MAGNETIC FIELD GENERATED RESISTIVITY MAXIMUM IN GRAPHITE

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TECHNICAL PAPER presented at the March 1976 Meeting of
the American Physical Society
Atlanta, Georgia, March 29 - April 1, 1976

ABSTRACT

In zero magnetic field, B, the electrical resistivity, $\rho(O, T)$ of highly oriented pyrolytic (polycrystalline) graphite drops smoothly with decreasing T, becoming constant below 4 K. However, in a fixed applied magnetic field B, the resistivity $\rho(B, T)$ goes through a maximum as a function of T, with larger maximum for larger B. The temperature of the maximum increases with B, but saturates to a constant value near 25 K (exact T depends on sample) at high B. In single crystal graphite a maximum in $\rho(B, T)$ as a function of T is also present, but has the effects of Landau level quantization superimposed. Several possible explanations for the $\rho(B, T)$ maximum are proposed, but a complete explanation awaits detailed calculations involving the energy band structure of graphite, and the particular scattering mechanisms involved.

E-8705

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SUMMARY

In zero magnetic field, the electrical resistivity, $\rho(0, T)$, of HOPG (polycrystalline) graphite drops smoothly with decreasing T, becoming constant below 4 K. However, in a fixed applied magnetic field B, $\rho(B,T)$ goes through a maximum as a function of T, with larger maximum for larger B. The position of the maximum increases with B, but saturates to a constant value near 25 K (exact T depends on sample) at high B. In single crystal graphite a maximum in $\rho(B, T)$ as a function of T is also present, but has the effects of Landau level quantization superimposed. Several possible explanations are proposed, but a complete explanation is not yet available. The unexpected B dependence for $\rho(B, T)$ reported in earlier work (refs. 1 to 3) at fixed temperature is probably related to the anomalous $\rho(B, T)$ maximum.

INTRODUCTION

Graphite is a semimetal with narrowly overlapping valence and conduction bands (refs. 4 and 5). The crystal structure is hexagonal, as shown in figure 1(a), with ABAB. . . stacking, and the Brillouin zone is hexagonal. The Fermi surfaces are very narrow cigar-shaped pieces located at the edges of the Brillouin zone boundary and parallel to the c axis (fig. 1(b)). The Fermi surface and many electronic properties are fairly well understood. These were reviewed recently by McClure (ref. 4) and by Spain (ref. 5). The high field galvanomagnetic properties (electrical resistivity and Hall effect) for fields above one or two tesla have not been as well

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studied (refs. 2, 3, and 6). It is the purpose of this paper to report on detailed studies of the temperature and field dependence of the electrical resistivity $\rho(B,T)$ and of the Hall coefficient, and to report on anomalies seen in these properties.

Two types of graphite were studied: highly oriented pyrolytic graphite, called HOPG, and a purified natural single crystal. HOPG is formed by pyrolysis of methane at temperatures near 2000° C, and subsequently annealed under pressure to increase alignment of crystallites (ref. 7). Single crystal graphite has hexagonal structure (fig. 1(a)), and HOPG has the same structure but is polycrystalline, with basal plane grain diameters ranging from 10 to 100 μm in our samples, as measured by electron microscopy. These grains are highly aligned, and the electronic energy band structure of HOPG and SCG are nearly identical (ref. 8). In zero magnetic field the main difference in electronic properties between HOPG and SCG are due to different carrier scattering mechanisms (ref. 5). Below some temperature T* (typically 5 to 10 K), depending on the sample, grain boundary scattering in HOPG, and ionized impurity scattering in SCG become dominant over phonon scattering. For either grain boundary or ionized ionized impurity scattering dominance, the electrical resistivity $\rho(B,T)$ should depend strongly on field B (for high B and low temperature), but not on temperature T, according to the classical Lifshitz, Azbel, Kaganov (LAK) theory (refs. 9 and 10).

In this paper we report a magnetic field generated $\rho(B,T)$ temperature dependence, including a maximum near 25 K for HOPG. This temperature dependence occurs in a region where $\rho(B,T)$ should be independent of temperature according to the LAK theory.

EXPERIMENTAL

HOPG was formed by compression annealing to 3100° C (refs. 7 and 13) and samples were cut by fine grain sand erosion using steel masks to form straight edges and small arms to which leads were attached. Leads were made of copper and were wound around the arms and then covered with conductive epoxy or conductive paint. A crystal of graphite was obtained from rock formations in the New York State mountains, and purified (ref. 14).

Leads were attached as described above.

Standard four-probe measurements of electrical resistance and Hall effect were made using a constant current supply and dc amplifiers, and $\rho(B,T)$ or ρ_{Hall} was plotted versus field B- or temperature T-dependent voltages. A B-dependent voltage was generated from calibrated magnetoresistors built into the magnets, and T-dependent voltages were generated from voltage drops across carbon thermometers (calibrated in magnetic fields) or semiconducting diodes. Sample current was maintained in the basal plane (perpendicular to the c axis) and was perpendicular to the field at all times. The field was parallel to the "c" axis (perpendicular to the basal planes).

Three magnets were used: a 2-tesla conventional iron core, and 11 and 14.5 tesla superconducting solenoids, all with liquid helium insert dewars with variable temperature capability in the range 1.1 to 300° K.

It will be useful to precisely define quantities measured. If $\overline{J}$ is vector current, $\overline{\overline{\sigma}}$ is the tensor conductivity, $\overline{E}$ is the vector electric field, and $\overline{\overline{\rho}}$ is the tensor resistivity, then

$$\overline{J} = \overline{\overline{\sigma}}\,\overline{E} \tag{1}$$

and

$$\overline{E} = \overline{\overline{\rho}}\,\overline{J} \tag{2}$$

Because B is parallel to an axis of sixfold rotational symmetry,

$$\rho_{yy} = \sigma_{yy}/(\sigma_{yy}^2 + \sigma_{yx}^2) \tag{3}$$

and

$$\rho_{yx} = \sigma_{yx}/(\sigma_{yy}^2 + \sigma_{yx}^2) \tag{4}$$

Experimentally it is found in graphite that $\sigma_{yx} \ll \sigma_{yy}$ and $\rho_{yx} \ll \rho_{yy}$, Therefore

$$\rho_{yy} \simeq 1/\sigma_{yy}$$

and

$$\rho_{yx} \simeq \sigma_{xy}/\sigma_{yy}^2$$

at high field, B, in graphite. For simplicity we define $\rho_{yy} \equiv \rho(B,T)$ to indicate that ρ_{yy} is field and temperature dependent, where $\rho(B,T)$ is called the resistivity. ρ_{yx} is the Hall resistivity, due to the transverse electric field generated by current flow perpendicular to the magnetic field. The electrical conductivity σ_{yy} will be denoted $\sigma(B,T)$ and the Hall resistivity by ρ_{Hall}.

RESULTS

Figure 2 shows the resistivity $\rho(B,T)$ for two HOPG samples at two different temperatures plotted as a function of magnetic field. A most interesting feature is that $\rho(B,T)$ is lower for the lower temperatures. We have observed this effect in seven different HOPG samples (see also refs. 3 and 6). Figure 3 more clearly illustrates what is occurring. In figures 3(a) and (b), $\rho(B,T)$ is plotted versus temperature, T, for a series of fixed magnetic fields between zero and 14 tesla for both HOPG and SCG. A maximum in $\rho(B,T)$ as a function of T is clearly evident. The maximum grows in magnitude with increasing B, and the temperature at maximum, T_{max}, is nearly constant above about 4 tesla in HOPG. In SCG, T_{max} is constant above 8 tesla, but is strongly influenced by the SdH effect below 8 tesla. Below 4 tesla in HOPG, T_{max} decreases with decreasing field. This trend to lower T_{max} at lower B is illustrated for HOPG in figure 4. Notice that T_{max} depends on sample. The decrease of T_{max} and the decrease of the magnitude of the maximum are shown for low fields in figure 3(c) for one HOPG sample. In both HOPG and SCG, $\rho(0,T)$ in zero field drops monotonically with decreasing temperature, showing no maximum. This is illustrated for HOPG in figure 3(b).

To aid in the interpretation of results on SCG, we also made plots of $\rho(B,T)$ as a function of field in SCG at 4.8 K and at 28 K, illustrated in figure 5. It is found that the 4.8 K curve is below the 28 K curve for all fields. Finally, it was found desirable to know if any unusual behavior was occurring in the Hall conductivity σ_{yx}. Since at high B, the product $\sigma_{yx}B$ is proportional to the density of hole carriers minus the density of electron carriers, the product $\sigma_{yx}B$ is plotted in figure 6(a) and (b)

versus B, for several HOPG samples and SCG. Also plotted in figure 6 is the net carrier density p - n where n is the density of electron carriers, and p is the density of hole carriers. This figure shows varying field dependencies and even sign changes for $\sigma_{yx}B$ and p - n.

THEORY AND INTERPRETATION

The theory of Lifshitz, Azbel and Kaganov (LAK) predicts a temperature independent $\rho(B, T)$ for low temperatures and high fields (refs. 9 and 10). In the LAK theory it is assumed that the electric field causes carrier energy changes much less than the Fermi energy and much less than kT, where T is the temperature of the carriers. This permits linearization of the Boltzman transport equation with respect to electric field, and results in an equation for the coefficients of the expansion of the distribution function in electric field. This linearized equation is then solved using expansions in a parameter $\gamma \equiv B_0/B$ where B_0 is the field at which carriers complete circular paths before being scattered. This condition is expressed as

$$\omega \tau = 1$$

where $\omega = eB/m^*$, m^* is an effective mass for carriers, and τ is the mean time between collisions. The results of the LAK theory show that $\rho(B, T)$ is independent of the particular scattering mechanism at low temperature and is independent of the particular carrier energy versus momentum relationship. The high field resistance is found to depend only on field strength and Fermi surface topology. In graphite, the number of electrons, n, nearly equals the number of holes, p, and deviations from this state of "compensation" are usually on the order of about 10^{22} per cubic meter. (See below and fig. 6(a).) There are no "open" orbits for B parallel to the c axis and LAK theory would predict $\rho(B, T) \propto B^2$ for perfect compensation, and $\rho(B, T) \propto$ constant for $n \neq p$ at high B. In addition, as long as $\omega \tau >> 1$ (equivalent to $\gamma << 1$, or $B >> B_0$) these dependencies should hold. According to LAK theory, $\rho(B, T)$ at fixed B should be independent of temperature for $T < T^*$, and should decrease as T increases above T^*.

We have calculated $\omega\tau$ for various fields and temperatures in graphite using experimentally measured mobilities $\mu = e\tau/m^*$ to obtain values of $\tau(\sim 10^{-11}$ sec for HOPG). These calculations show that $\omega\tau \sim 5$ at 0.1 tesla at 4.2 K in HOPG, and $\omega\tau \sim 20$ at 1 tesla at 40 K. For the fields and temperatures of interest in our results (1 tesla $< B <$ 20 tesla, and 1 K $< T <$ 40 K) the condition $\omega\tau >> 1$ is easily met. Thus the essential $\omega\tau >> 1$ condition for the LAK theory is met. The strong temperature maximum of $\rho(B, T)$ in HOPG, from 1 K to above 30 K thus appears to be in violation of LAK theoretical predictions. A large number of experimental results on a variety of materials have been explained by the LAK theory (ref. 10), and the apparent violation in graphite is highly unusual.

We wish to discuss four possible reasons for the anomalous $\rho(B, T)$ versus temperature maximum, and disagreement with predictions of the LAK theory. First is the possibility of orbital quantization (refs. 11 and 15). One of the conditions of the LAK theory was that classical equations of motion apply. In a high magnetic field at low temperatures, the orbital motion can be quantized and quantum energy levels called Landau levels result. For classical motion, the spacing between Landau energy levels must be much smaller than the Fermi energy. This condition, plus the condition $\omega\tau >> 1$, is most easily met in metals having high carrier concentration and high Fermi energies. In graphite, the Fermi energy is small and is comparable to the Landau spacing, for fields on the order of 10 tesla. The effect of Landau levels on $\rho(B, T)$ is known as the Shubnikov-de Haas effect (SdH) and this has been observed in many materials including graphite (refs. 5, 6, 8, and 12). The SdH effect causes minima in $\rho(B, T)$ whenever a Landau level is near the Fermi energy for carriers. By comparing figures 2 and 5 it is clear that structure due to the SdH effect is more pronounced in SCG than in HOPG at any given temperature and is stronger at lower temperatures. There are a number of reasons why the SdH effect is probably not the origin of the $\rho(B, T)$ maximum in either HOPG or SCG, and these are discussed below.

Before discussing why we feel that the SdH effect is probably not the origin of the $\rho(B, T)$ maximum, there is a reason why the SdH could be the origin in SCG. There is a predicted crossing of the Fermi energy across the $n = 0$ Landau level at 40 tesla (ref. 16). Thus the lower $\rho(B, T)$ for 4.8 K than for 28 K, $B > 10$ tesla could be due to the SdH

effect at 40 tesla. Against this possibility is that: (a) Brandt, et. al. (ref. 17) saw no SdH minimum for B to 50 tesla and (b) the value of the "Δ" energy band parameter (refs. 4 and 5) would conflict with the Δ value obtained from other experiments (ref. 16).

Another reason why the SdH is probably not the origin in SCG is that the 4.8 K curve is lower than the 28 K curve over the entire field range from 0 to 15 tesla. (The point of near contact at 8.3 tesla is probably due to a SdH increased $\rho(B, T)$ in a narrow field range. A small increase is predicted by Adams and Holstein (ref. 11) theory, even at absolute zero.) If the SdH effect were the origin, then the resistivity would be lower only near Landau level crossings, which it is not.

For HOPG the $\rho(B, T)$ maximum seen in figure 3(b) is much too large to be accounted for by the SdH effect. Furthermore, $\rho(B, T)$ continues to decrease, in high B, for decreasing temperatures below 4 K. The effects of the SdH effect are only weakly temperature dependent below 4 K. Thus, the maximum is not due to the SdH effect in either SCG or HOPG.

A second possible explanation for the $\rho(B, T)$ versus T maximum, especially for HOPG, is a negative component of magnetoresistance. Negative magnetoresistance has been found in low fields in more disordered carbons (refs. 18, 19, and 20). The more the disorder the stronger the negative component of magnetoresistance. The effect of a negative component of magnetoresistance is to lower $\rho(B, T)$ in high fields over that expected otherwise. One mechanism which could be possible in HOPG is the presence of localized magnetic moments (ref. 21). The moments would tend to align, and alignment would be proportional to B/T. Aligned moments interacting with the conduction electron moments would present a lower magnetoresistance than unaligned moments. Other mechanisms for a negative component of magnetoresistance in carbon have been proposed. Specifically, attention should be paid to the calculations of MacDonald and Sarginson (ref. 22), and by Fujita (ref. 23) which consider the effects of crystallite boundary scattering in an applied field. Scattering in HOPG is known to be limited by crystallite boundary scattering at low temperatures. There are no grain boundaries in SCG so the anomalous $\rho(B, T)$ maximum is unlikely to be due to negative magnetoresistance. Because of the similarity of the $\rho(B, T)$ maximum effect in SCG and HOPG, the maximum is also not likely to be due to negative magnetoresistance

in HOPG. This conclusion is in contrast to what we concluded at the 12th Biennial Conference on Carbon (ref. 24). At that time we did not have results on SCG.

A third possibility for the origin of the anomalous maximum in $\rho(B,T)$ is a change in carrier concentration. A change from perfect compensation (density of electrons, n, equal to the density of holes, p) to an uncompensated state would change the high field $\rho(B,T)$ behavior according to the LAK theory. Most samples do not have $n = p$ identically and changes in $p - n$ should be considered. Brandt, et al. (ref. 17) mention possible origins for a change in concentration, such as partial magnetic freeze out of carriers.

The variety of field dependencies of $\sigma_{xy}B$ (and $p - n$) shown in figure 6 indicate that the state of compensation has no influence on the presence of the $\rho(B,T)$ maximum. That is. $\rho(B,T)$ has qualitatively the same behavior, independent of the B dependence of $\sigma_{xy}B$.

As a final consideration, McClure (ref. 16) has suggested making detailed calculations, for graphite, of the effect of B on how various scattering mechanisms (phonons, ionized impurities, grain boundaries) influence $\rho(B,T)$. The electronic structure of graphite, especially in high fields, is unusual enough to result in significant differences in transport properties from more conventional metals. Above 8 tesla graphite is in the "quantum limit" and this adds to the complexity of the theoretical problem (refs. 25 and 26).

CONCLUSIONS

Much emphasis in the past has been on the unusual field dependence of $\rho(B,T)$ at fixed temperature (e.g. $\rho(B,T)$ is quadratic in B over only a very limited field region). We want to point out that problems in explaining the $\rho(B,T)$ dependence on B are probably related to the temperature dependent effects on $\rho(B,T)$ in high B. Thus $\rho(B,T)$ exhibits both B and T dependent anomalies and any theory concerned with the B dependence should involve the T dependence also.

The $\rho(B,T)$ maximum is definitely not due to the Shubnikov de Haas effect in HOPG. The same is true in SCG, but studies of $\rho(B,T)$ in SCG should be done in fields above 20 tesla to be absolutely certain of the

behavior. It would also be very helpful to have detailed Hall coefficient dat· .s a function of temperature in fields above 8 tesla. We can also say that the $\rho(B,T)$ maximum is not due to a component of negative magnetoresistance. We find that the anomaly is not exclusively a quantum limit phenomena, but the Landau level structure for graphite must be considered for all magnetic field strengths. Our major conclusion is that the $\rho(B,T)$ maximum probably has the same origin for both single crystal graphite (SCG) and highly oriented pyrolytic graphite (HOPG). Because the scattering mechanisms are so different for SCG and HOPG, the anomaly must be closely associated with the unique energy band structure of graphite in high magnetic fields.

SYMBOLS

B_0	magnetic field at which $\omega\tau = 1$ or $\gamma = 1$
B	magnetic field strength, tesla
$\overline{c}$	direction perpendicular to planes (see fig. 1)
C	temperature, degrees Centigrade
e	charge on electron
$\overline{E}$	electric field
HOPG	Highly Oriented Pyrolytic Graphite
$\overline{J}$	electric current
LAK	Lifshitz, Azbel, Kaganov (ref. 9)
K	temperature, degrees K
m^*	effective mass
n/p	electron carrier density/hole carrier density
SCG	Single Crystal Graphite
SdH	Shubnikov-de Haas
T	temperature
T^*	temperature above which phonon scattering dominates

T_{max}	temperature of maximum in $\rho(B,T)$
γ	B_0/B
$\rho(B,T)$	resistivity in a field $\equiv \rho_{yy}$
$\rho(O,T)$	resistivity in zero field
ρ_{yx}	Hall resistivity
ρ_{yy}	resistivity $\equiv \rho(B,T)$
$\overline{\rho}$	resistivity tensor
ρ_{Hall}	Hall resistivity
$\sigma(B,T)$	conductivity in a field $\equiv \sigma_{yy}$
σ_{yx}	Hall conductivity
σ_{yy}	conductivity $\equiv \sigma(B,T)$
$\overline{\overline{\sigma}}$	conductivity tensor
ω	cyclotron frequency $\equiv eB/m^*$
τ	relaxation time, mean time between collisions

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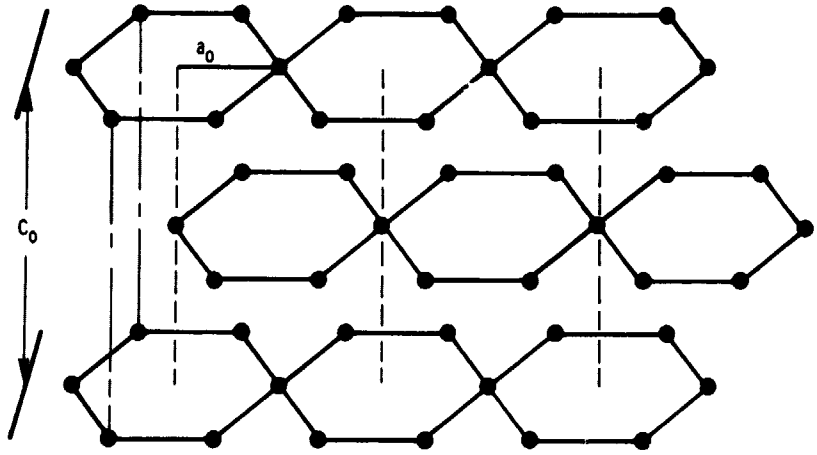
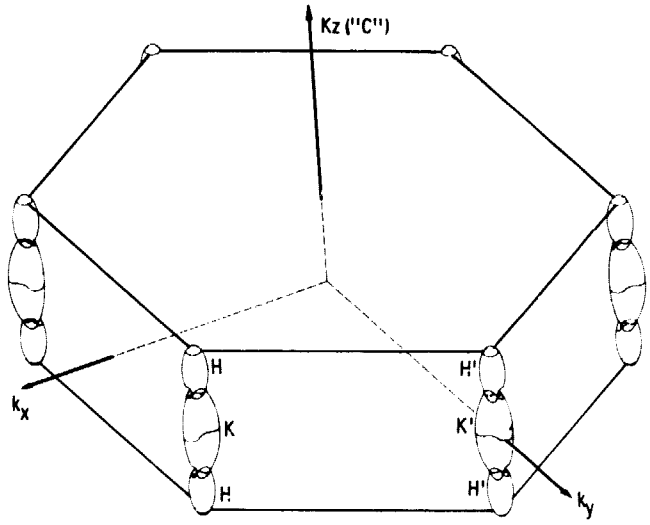


(a) CRYSTAL STRUCTURE OF GRAPHITE.



(b) BRILLOUIN ZONE AND FERMI SURFACES OF GRAPHITE.

Figure 1. - Structure of graphite.

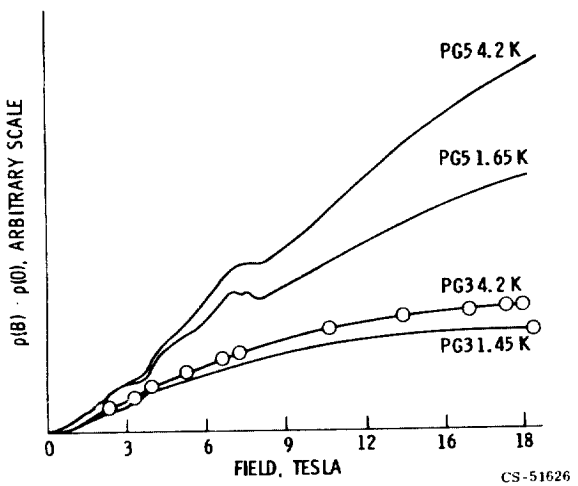
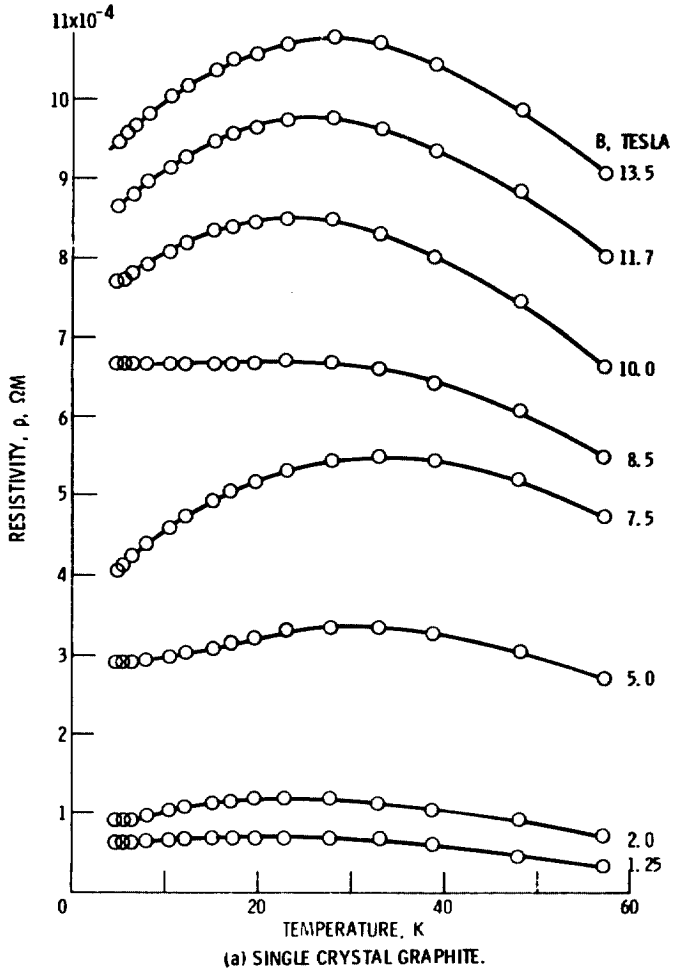
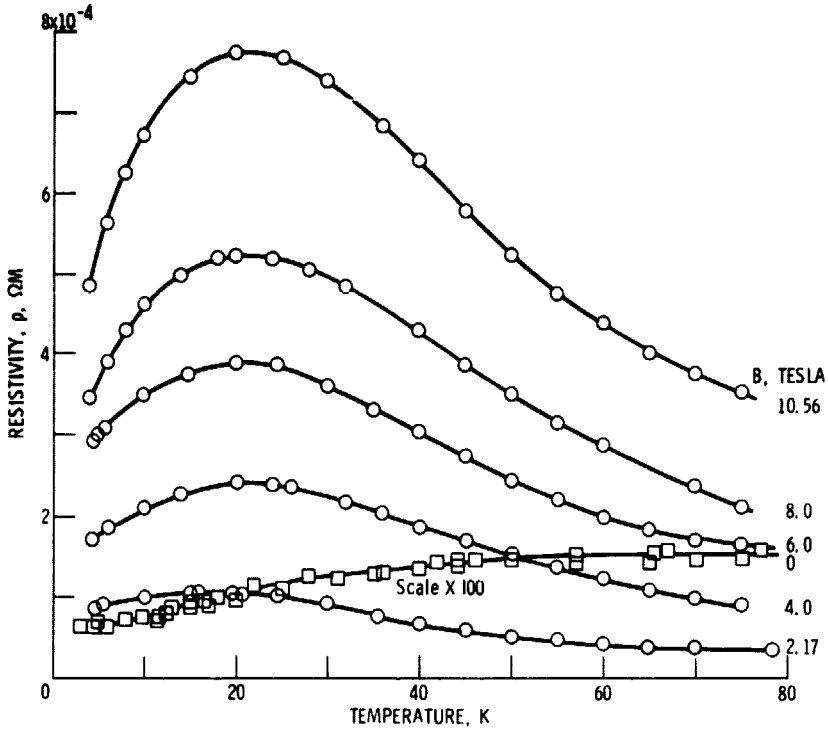


Figure 2. - Change in resistivity, ρ(B) - ρ(0) with magnetic field for two HOPG samples at two temperatures.



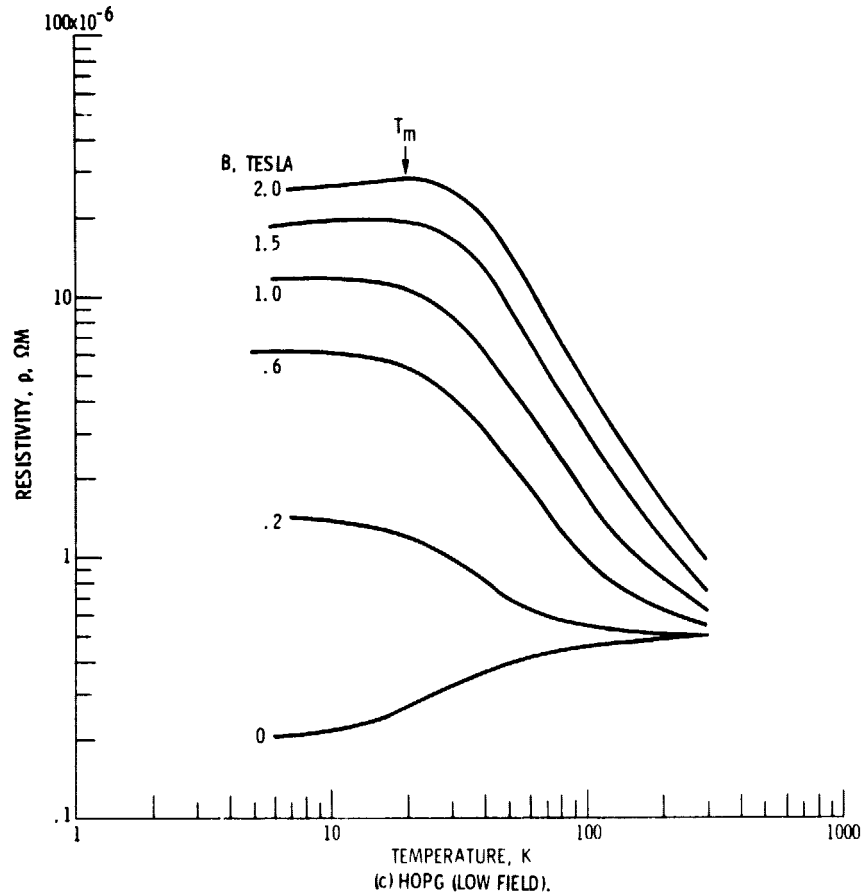
(a) SINGLE CRYSTAL GRAPHITE.

Figure 3. - Resistivity, ρ, vs. temperature for a series of field strengths.



(b) HOPG.

Figure 3. - Continued.



(c) HOPG (LOW FIELD).

Figure 3. - Concluded.

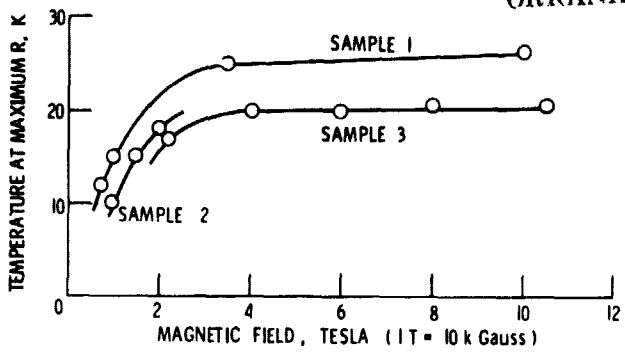


Figure 4. - Temperature at maximum in ρ (see Fig. 3(b)) vs. magnetic field for three HOPG samples.

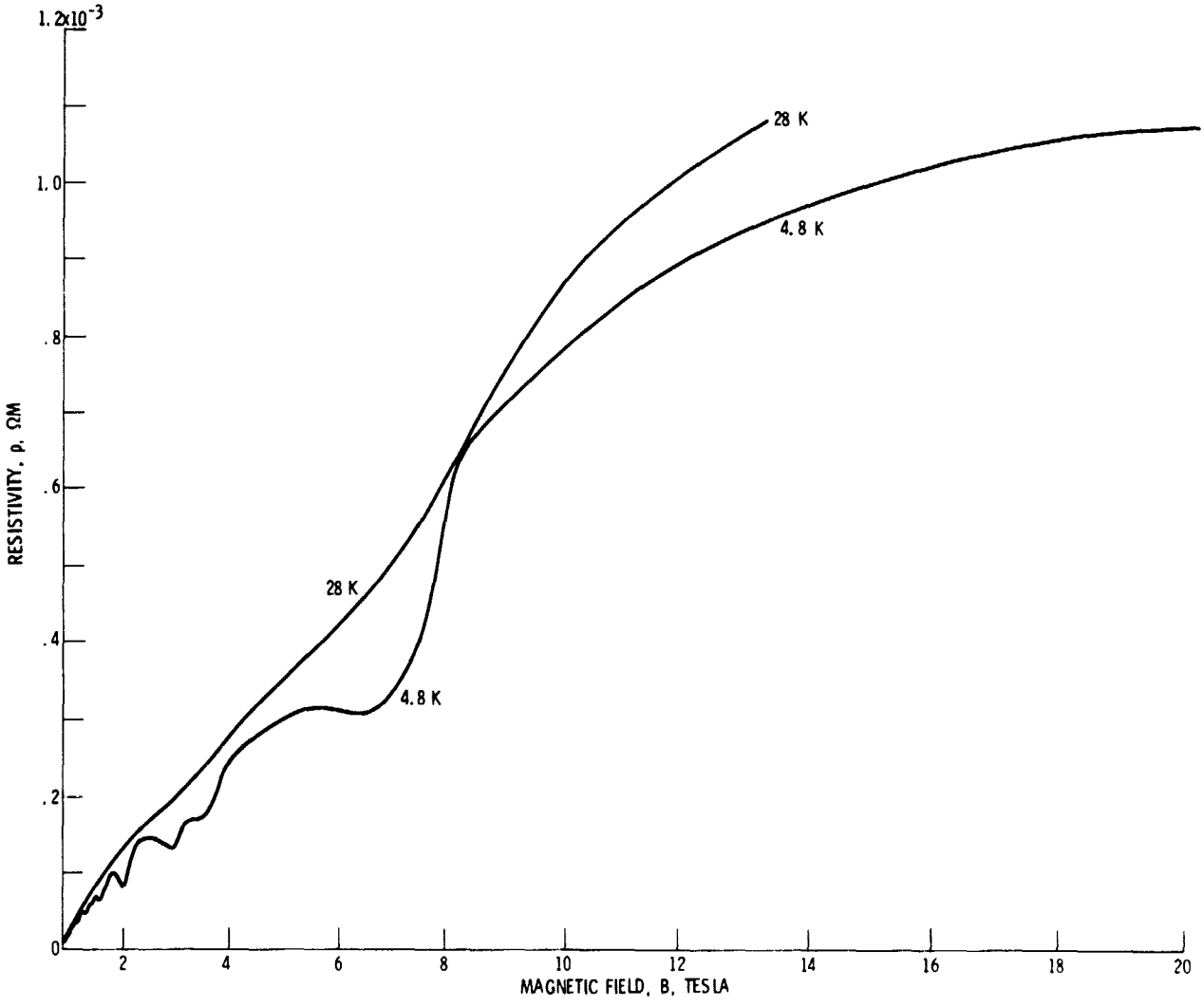
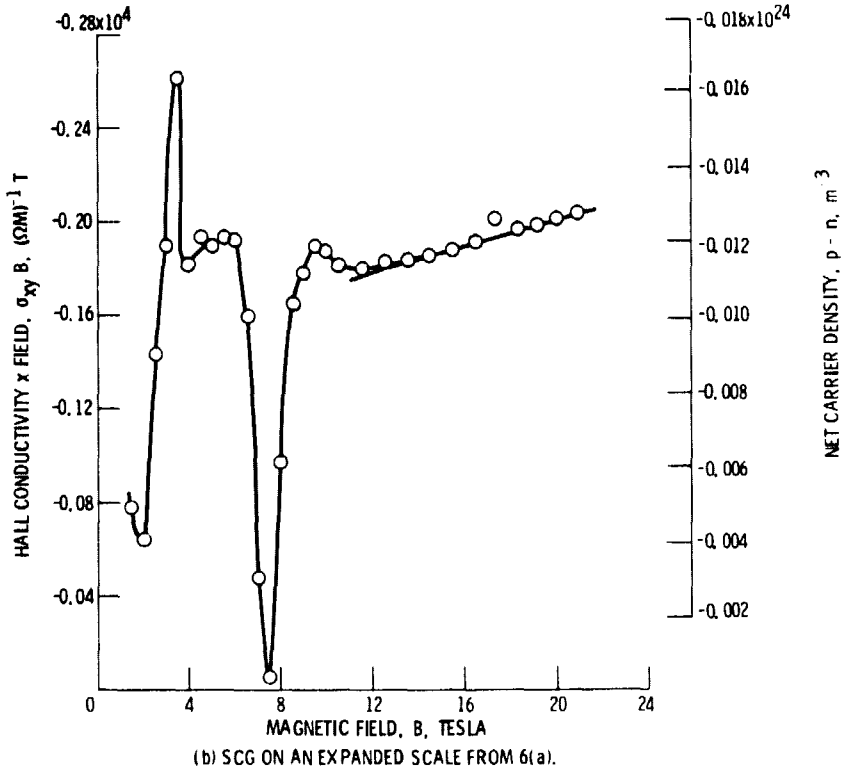


Figure 5. - SCG: Resistivity, ρ, vs. magnetic field for 4.8 and 28 K.



(b) SCG ON AN EXPANDED SCALE FROM 6(a).

Figure 6. - Concluded.