

Electrical resistivity of single-crystal graphite under pressure: An anisotropic three-dimensional semimetal

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The in-plane (ρ_a) and c -axis (ρ_c) resistivities of natural single-crystal graphite have been measured from 4 to 450 K at zero pressure and from 77 to 450 K under pressures up to 500 MPa. Data for ρ_c differ strongly from earlier results obtained on synthetic graphite in showing a strong T dependence of the pressure coefficient, while data for ρ_a agree well with those from previous studies. Our results can be analyzed *quantitatively* in a simple free-electron model, and we conclude that in contrast to quasi-two-dimensional synthetic graphite, natural single-crystal graphite is an anisotropic three-dimensional semimetal. [S0163-1829(98)01208-9]

During the last decade the interest in layered materials, such as oxide high-transition-temperature superconductors (HTS's), intercalation compounds, and multilayer structures, has increased enormously because of their interesting physical properties, but although large advances have been made, many questions still remain unanswered. One area that is currently under intense investigation is electrical transport along the c axis in these materials that often show an apparent inconsistency between the observed magnitudes of the c -axis resistivity ρ_c and a "metallic" $d\rho_c/dT$ (>0), which are incompatible with the concepts of Mott's minimum metallic conductivity or the Ioffe-Regel criterion. In spite of extensive studies there is still no theory that can predict either the magnitude or the temperature (T) or pressure (p) dependence of ρ_c for HTS's (Ref. 1) or graphite intercalation compounds² (GIC's) given, say, the structure and chemical composition. In the case of GIC's this lack of understanding even extends to the host, whether natural graphite or synthetic [highly oriented pyrographite (HOPG)].^{3,4} Typical room-temperature (RT) values of the resistivity anisotropy of layered materials cover a vast range from near unity in metallic multilayer materials and about 20 in some rich donor GIC's, over 10^2 for single-crystal graphite and $\text{YBa}_2\text{Cu}_3\text{O}_x$, $\geq 10^3$ for HOPG, 10^5 for the most anisotropic HTS's, to reach almost 10^7 for the most highly anisotropic GIC's.¹⁻⁵ Although the in-plane resistivities ρ_a of these materials are all "metallic" in the sense that $d\rho_a/dT > 0$, the c -axis resistivity can have either sign of the slope, and in general there is little correlation between the magnitude of ρ_c , its slope, and the anisotropy. While collecting literature data in an attempt to improve our understanding of c -axis transport in GIC's and HTS's we recently noted that very little data were available on the combined effects of T and p on the properties of high-quality single-crystal graphite, since almost all studies have been carried out on HOPG because of the easy avail-

ability and large size of samples. Graphite is, of course, the archetypical natural layered material, and although its properties were well studied and partly understood in the 1960s there has recently been a renewal of interest in graphite.^{6,7} For these reasons we felt that a further investigation was needed, and we have now measured both ρ_a and ρ_c on several natural single crystals over wide ranges of both T and p . Our results show that, in contrast to HOPG, the c -axis resistivity of single-crystal graphite can be described very well by simple theory as that of an anisotropic and highly resistive but *normal* semimetal.

The data presented below were obtained by measurements on four graphite single crystals from Madagascar and on one HOPG sample from Union Carbide. All samples had been cut to a circular shape, 4 mm in diameter, with the c axis along the cylinder axis. The ($hk0$) diffraction patterns of the Madagascar samples showed only intense spots, not rings, confirming that the samples were indeed single crystals. The RT in-plane resistivities were in the range 55–65 $\mu\Omega$ cm for the single crystals and 40 $\mu\Omega$ cm for the HOPG sample, in excellent agreement with literature data. Because the contactless technique used is very sensitive to mechanical imperfections (cracks, etc.), this further verifies the structural quality of our samples. The thickness of the single crystals was about 0.11 mm and that of the HOPG sample 0.38 mm. The resistances were measured by a dc four-probe technique using current switching because of the very small resistances involved (about 60 $\mu\Omega$ at low T). Several contacting techniques were tried, but in all cases two contacts were formed on each of the two flat faces of the samples. For the measurements of ρ_c one of these was used for current and the other for the voltage measurements, while for the in-plane studies the two current leads were attached on the same side. Attaching the samples with silver paint to copper strips on a ceramic base (Macor® glass ceramic) and with silver paint contacts to thin copper wires on the top surface worked well

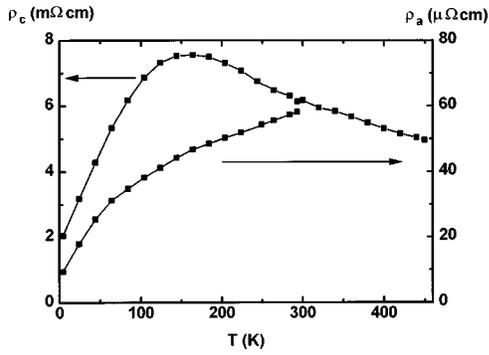


FIG. 1. Electrical resistivity vs T for a graphite single crystal, both in the plane (right-hand scale) and along the c axis (left-hand scale).

at zero pressure but often gave strongly nonlinear readings versus pressure, probably because of strains set up by the difference in compressibility between the base and the sample, which has an in-plane bulk modulus similar to that of diamond. The best results were obtained by simply attaching thin copper wires to both sides of the crystal using silver paint and most of the results shown were obtained in this way. All high- p data presented were measured under hydrostatic conditions. Most were obtained in a piston-and-cylinder device, either cooled by a closed-cycle helium refrigerator or heated by an external heater, using as pressure medium a 50/50 mixture of n -iso-pentane at low T and silicone oil at high T . The pentane mixture solidifies near 150 K (Ref. 8) and in order to obtain accurate data below this, measurements were also carried out on one sample in a helium gas device at UNIPRESS, Poland, at RT, and at 77 K. Because of previous reports of nonrepeatable results on graphite at high p we have limited the maximum pressure in our experiments to 500 MPa, but even below this pressure we found that in order to obtain repeatable results it was necessary to change p extremely slowly, by less than 300 kPa/min.

There is a general consensus^{4,10–12} that for both single-crystal graphite and HOPG the T dependence of ρ_a can be understood in terms of normal metallic conductivity limited by impurity and defect (“residual”) scattering at low T and phonon scattering at high T . This is not immediately obvious from the measured data (Fig. 1), but calculations^{11,13} show that because of the very low Fermi energy of graphite there is a rapid increase in the effective number of carriers n above 100 K resulting in the sharp reduction of the slope $d\rho_a/dT$. For ρ_c the situation is less clear. In HOPG ρ_c is not well understood,^{3,4,12,14} since at RT, $d\rho_c/dT < 0$ and only the highest quality of HOPG has a maximum in ρ_c situated between 40 and 60 K.^{3,4,14} For single-crystal graphite, on the other hand, the nearly constant $\rho_c(T)/\rho_a(T)$ for $T < 100$ K and the excellent agreement between the experimental anisotropy and that calculated from the anisotropy of the Fermi surface⁴ indicate that for single crystals, ρ_c can probably be described in a band model. In this model, samples with a very low “residual” resistivity should have a very small or nonexistent maximum at intermediate T , and with increasing magnitude of the “residual” resistivity the slope $d\rho_c/dT$ should become increasingly negative at RT because of the increase in n with T . This model agrees well with the observation of a positive $d\rho_c/dT$ at all T in the single-crystal samples of Uher, Hockey, and Ben-Jacob¹⁴ which had RT

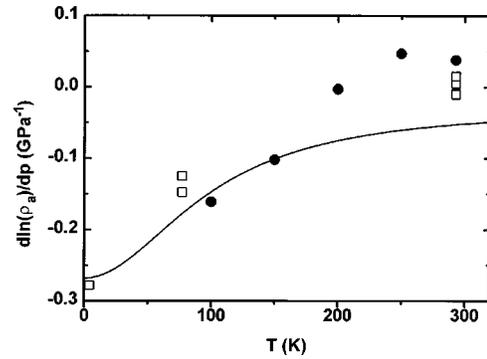


FIG. 2. Pressure coefficient $d \ln \rho_a / dp$ of the in-plane resistivity of graphite vs T . (●) our results (natural graphite), (□) data from Ref. 15 (synthetic graphite). The curve is the result of a simple theoretical calculation (see text).

resistivities > 20 times higher than the low- T limiting values.

The in-plane resistivity of graphite has been well studied as a function of both T and p and it is well known that $d \ln \rho_a / dp$ depends rather strongly on T below RT.^{12,15} As a check of our experimental methods and the structural order in our crystals, and in order to verify previous data, we therefore first measured $d \ln \rho_a / dp$ as a function of T at and below RT on one of our crystals. The accuracy of this study was probably reduced because first, the crystal was glued by silver paint on a ceramic base giving a pressure-induced strain in the crystal, and second, the geometrical arrangement with current leads on one side only of a short sample gives a pressure-dependent error because of changes in the resistance anisotropy. Still, it is obvious from Fig. 2 that our data for $d \ln \rho_a / dp$ are in reasonable agreement with previous ones^{15,16} regarding both magnitude and T dependence. (All data shown have been corrected for sample compression using compressibility data from Ref. 17.) Surprisingly, even recent reviews^{4,12} fail to present convincing explanations for either the observed magnitude of $d \ln \rho_a / dp$ or its T dependence, and before we turn to the c -axis resistivity we therefore analyze briefly the data for ρ_a versus T and p .

Graphite is a semimetal with a small band overlap of about 30 meV and a low carrier density of only 10^{-4} carriers per atom. Because of the low in-plane resistivity, $\rho_a < 70 \mu\Omega \text{ cm}$ at RT, we use a simple quasi-free-electron model for the analysis. The in-plane bonds of graphite are extremely strong giving a linear in-plane compressibility $\kappa_a = -d \ln a / dp$ of only $8 \times 10^{-4} \text{ GPa}^{-1}$ (Ref. 17) and the in-plane phonon frequencies ω_a should thus shift very little with pressure, an assumption that is verified by recent high-pressure neutron-scattering data for the in-plane transverse-acoustic phonons.¹⁸ The electron band structure, on the other hand, is very sensitive to pressure^{4,7,12,13,19,20} because a reduction in the c -axis lattice spacing rapidly increases the overlap of the interplanar π orbitals. The band structure and its pressure dependence have been calculated in detail by many authors, but for simplicity we discuss here the pressure effects in terms of the simple Slonczewski-Weiss-McClure (SWMC) model²¹ in which the various interatomic interactions are described in terms of a set of overlap parameters γ_i . To bring out the essentials of our model we write the electrical resistivity as²²

$$\rho = \rho_{\text{imp}} + \rho_{\text{ep}} = m^*/ne^2\tau_0 + (4\pi)^2\omega_{\text{pl}}^{-2}f(\alpha_{\text{tr}}^2, T), \quad (1)$$

where subscripts imp denotes the impurity and ep the electron-phonon resistivity, ω_{pl} is the plasma frequency, and $\alpha_{\text{tr}}(\omega)$ is the transport electron-phonon coupling function. Although Eq. (1) resembles Mathiessen's rule for ordinary metals we must remember that the magnitude of the impurity term here decreases with increasing T because the carrier density n rises, unlike the case for simple metals. In the quasi-free-electron model $\omega_{\text{pl}}^2 = 4\pi ne^2/m^*$ (Ref. 22) and Eq. (1) can be rewritten

$$\rho = (m^*/ne^2)[1/\tau_0 + 4\pi f(\alpha_{\text{tr}}^2, T)]. \quad (2)$$

Applying the latter expression to ρ_a we can estimate $d \ln \rho_a / dp$ in different ranges of T . First, τ_0 should be proportional to the in-plane lattice constant a , and $d \ln \tau_0 / dp$ should thus be similar in magnitude to $d \ln a / dp$. Second, the pressure dependence of the phonon-dependent term can be estimated from the known pressure dependence of the Bloch-Grüneisen (BG) expression for phonon limited resistivity. The latter is²³ $d \ln f_{\text{BG}} / dp = -2\gamma_a \kappa_a$ [$= -2d \ln \omega_a / dp \approx 0$ (Ref. 18)] above the Debye temperature Θ_D and $-6\gamma_a \kappa_a$ at very low T , with γ_a an effective Grüneisen parameter defined here as $-(d \ln \omega_a) / (d \ln a)$. The term in brackets in Eq. (2) should thus have a small pressure dependence (of order κ_a) at all T . The pressure dependence of the band structure can be found from the SWMC model. We write the effective mass $m^* = C_0 \gamma_1 / (\gamma_0^2 a^2)$,¹³ but for the effective carrier density the situation is more complicated. According to Arkhipov *et al.*¹³ the total carrier density n ($= n_e + n_h$) can be written $n = C_1 \gamma_1 |\gamma_2| / (\gamma_0^2 a^2 c)$ at low T , while above about 100 K, $k_B T > \gamma_2$, the carriers are degenerate and $n = C_2 \gamma_1 k_B T / (\gamma_0^2 a^2 c)$. Here C_1 and C_2 are numerical constants and a and c the lattice parameters. m^*/n is thus proportional to $c/|\gamma_2|$ at low T and to c at high T , and from Eq. (2) we predict a high- T limit $d \ln \rho_a / dp \approx d \ln c / dp = -0.028 \text{ GPa}^{-1}$ (Ref. 17) in good agreement with experiment (Fig. 2). At low T , $d \ln \rho_a / dp \approx d \ln c / dp - d \ln |\gamma_2| / dp$. (Apart from the terms $d \ln c / dp$, the same high- and low- T limits were found by Noto and Tsuzuku.¹⁶) There is still some controversy about the magnitudes of the pressure coefficients of γ_i , but inserting $d \ln |\gamma_2| / dp = 0.24 \text{ GPa}^{-1}$ as obtained by Anderson *et al.*¹⁹ brings experiment and theory into good agreement also at low T . Finally, we parametrize the data for $n(T)$ given by Arkhipov *et al.* to interpolate $d \ln(n) / dp$ as a function of T and use these data to calculate $d \ln \rho_a / dp$ as a function of T . The result is shown as the solid curve in Fig. 2, which indicates that quasi-free-electron theory is able to describe surprisingly well the dependence of ρ_a on both T and p .

Turning now to the more interesting case of ρ_c , our experimental results for $d \ln \rho_c / dp$ are shown in Fig. 3. The results for single-crystal graphite (filled symbols) are strikingly different from the data for synthetic graphite,^{14,15} which are almost T independent (dashed line, open symbols). One group has previously measured ρ_c (Ref. 24) under pressure for both natural and synthetic graphite but their results, $d \ln \rho_c / dp = -0.11 \text{ GPa}^{-1}$ for both materials, do not agree with any other data set and fall outside the range of the figure. Most of the data shown for the single-crystal material

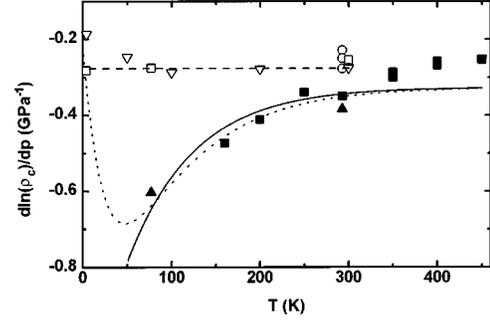


FIG. 3. Pressure coefficient $d \ln \rho_c / dp$ of the c -axis resistivity of graphite vs T . Full symbols: data for single crystals from the present investigation; (■) free-standing sample, (▲) sample on ceramic base under gas pressure. Open symbols: data for synthetic graphite; (○) present results, (□) Ref. 15, and (▽) Ref. 14. The dashed line is a guide for the eye only. Dotted curve is the result of a calculation of $d \ln \rho_c / dp$ vs T (see text) while the full curve shows the pressure dependence of the phonon-scattering term only.

(squares) were obtained on one single sample with painted-on contacts, but we also show (triangles) results for another sample mounted on a ceramic base and studied under high-pressure helium gas at 293 and 77 K. Results for other samples all agreed with the general trend shown, although samples mounted on ceramic bases tended to show more scatter and on average a slightly stronger dependence on pressure. The results shown were all obtained in slow isothermal pressure runs, but similar results were also calculated from the results of isobaric temperature runs at several different pressures.

For the analysis we assume, as indicated above, that the T dependence of ρ_c can also be described by standard electron-phonon models and again we use Eq. (2), now with $\rho = \rho_c$, to analyze the pressure dependence. It has previously been suggested that the effect of pressure on the phonon frequencies is of the order of $d \ln c / dp = -\kappa_c$ and thus of little significance for the very large pressure coefficients observed.¹² However, recent experimental data^{18,25} show that this is not true, especially for the very important longitudinal c -axis acoustic phonons that have a very large effective Grüneisen parameter $\gamma_c = -(d \ln \omega_c) / (d \ln c) \approx 7$.²⁶ This value is very similar to values recently found for C_{60} ,²⁷ which has an intermolecular interaction quite similar to the interplanar interaction in graphite. In the SWMC model the Fermi surfaces are prolate ellipsoids that do not change shape with pressure. Although the expressions for m^* and n given above should basically be good approximations for the in-plane carriers, in this model they should also be valid for electrons traveling in the c -axis direction although the effective number of carriers should be reduced by a factor of the order of 10 and m^* is much larger than in the plane. The pressure coefficient of the electron band parameter (m^*/n) should be the same as above, -0.27 GPa^{-1} as $T \rightarrow 0 \text{ K}$ and -0.03 GPa^{-1} at RT and above, but at intermediate and high T we must now add the very strong pressure dependence of the phonon-scattering term. Using the average value $d \ln \omega_c / dp = 0.16 \text{ GPa}^{-1}$ from the results by Ivanov *et al.*¹⁸ and Alzyab *et al.*²⁵ we find the high- and low- T limits $d \ln f_{\text{BG}} / dp = -0.32$ and -0.96 GPa^{-1} , respectively (see above). The T dependence of this term scales with the Debye temperature Θ_D and we make the standard choice $\Theta_D = 400 \text{ K}$ corresponding to the low- T limit found from specific heat data.²⁸ In order to find

the true relative magnitudes of ρ_{imp} and ρ_{ep} we multiply our data for $\rho_c(T)$ (Fig. 1) by the theoretical carrier density $n(T)$ given by Arkhipov *et al.*¹³ The analysis shows that the p dependence of ρ_c is dominated by the electron-phonon term ρ_{ep} [second term in Eq. (1)] above about 50 K. The pressure coefficient of this term is shown as the full curve in Fig. 3, and we note that the agreement with experiment is excellent, considering the simplicity of the model. At very low temperatures we must also take into account the residual resistivity term. If we assume that the pressure coefficient of τ_0 is now close to $d \ln c/dp$, in analogy with our assumption for the in-plane resistivity above, we find the dotted curve, which of course differs little from the curve already shown at temperatures above about 60 K, where ρ_{imp} can be neglected.

The simple models above thus give surprisingly good agreement with experiments in spite of the many simplifications used, especially when we consider that *no adjustable parameters* have been introduced. To moderate this statement we agree that two parameters, Θ_D and $d \ln |\gamma_2|/dp$, are in principle “free,” but for both of these we have chosen standard accepted values. Data for the low- T thermal properties give constraints on realistic values for Θ_D , while data for $d \ln |\gamma_2|/dp$ differ strongly between different studies. The value 0.24 GPa^{-1} used here is close to the average of the values discussed in recent reviews,^{4,12} but we could equally well have chosen the value 0.42 GPa^{-1} given by Dillon, Spain, and McClure,²⁰ which would have given a less good numerical agreement with experiment for ρ_a at low T . We have also naively assumed that ρ_a is mainly limited by scattering by in-plane phonons and ρ_c by c -axis phonons, which may not be correct, and some of the differences observed

above 300 K between the theoretical and experimental values of $d \ln \rho_c/dp$ might be due to an increasing effect of pressure-insensitive in-plane phonons on ρ_c . However, the results allow us to conclude that the band-conduction model is probably correct for single-crystal graphite, since it correctly predicts *both* the T and p dependence over a wide range in T . Unfortunately, no data could be obtained below 77 K, the range where $d \ln \rho_c/dp$ shows a change in sign of the slope. While such low- T data would be quite interesting because of the possibility to obtain new information on the pressure dependence of ρ_c , and thus possibly on the type of imperfection dominating this term, it should be noted that such data would not give any additional information about the transport mechanism active above 77 K. The exact position of the minimum in $d \ln \rho_c/dp$, as well as the exact values of $d \ln \rho_c/dp$ below this, depend on the relative magnitude of ρ_0 and are thus sample dependent, which makes a detailed analysis of the low- T range less attractive. Finally, the c -axis properties of HOPG are found to be very different from that of single-crystal graphite, probably because HOPG consists of an aggregate of crystallites separated by regions with translational and rotational disorder that evidently have large effects on electronic transport. More work is clearly needed in order to establish the true mechanism behind the large but temperature-independent pressure coefficient of this material.

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