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The Electrical Resistance of Graphite at Low Temperatures*

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The resistance of natural graphite and of high purity polycrystalline graphite has been measured over a range of temperature from room temperature down to 1.35°K. The resistance of large-crystal natural graphite was found to increase with increasing temperature over the entire range. For polycrystalline graphite the resistance was found to increase smoothly as the temperature was lowered to about 20°K. At this temperature the resistance begins to level off until around 5°K it is virtually independent of temperature, at a value about double the room temperature resistance. Below 5°K the resistance seems to fall slightly.

INTRODUCTION

THE electrical resistivity of large crystals of graphite is similar to that of a poor metal both in magnitude and temperature dependence.[1,2] However, by developing the band theory for graphite, Coulson[3] and Wallace[4] have shown that along its cleavage plane an infinitely large graphite crystal is a semiconductor with zero activation energy. Though Wallace has also shown that the results of measurements in natural graphite crystals are not inconsistent with the theory, such measurements are not capable of exact theoretical interpretation because of the lack of purity and the crystal imperfections of natural graphite.

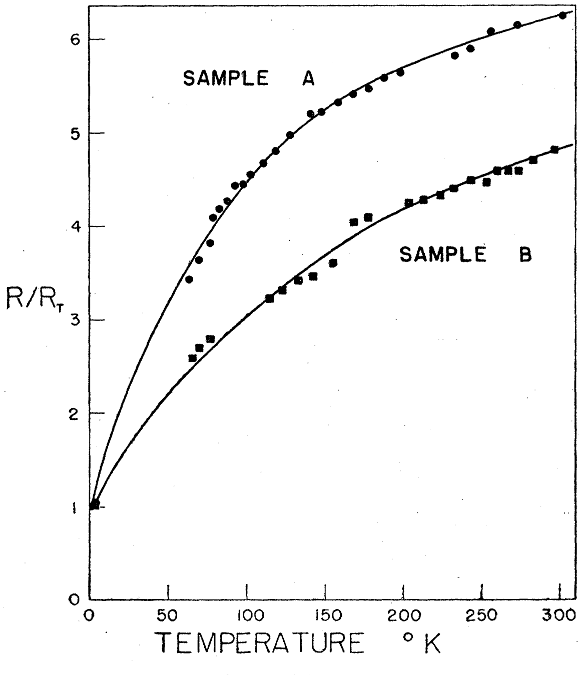

FIG. 1. Resistance of natural graphite.

Polycrystalline graphite of high purity may be produced artificially and measurements on the resistance of polycrystalline graphite have been made over a wide range of temperature.[5–7] The resistivity of polycrystalline graphite is of course always considerable larger than that of single crystals along the graphite plane, but a more striking difference exists in the temperature dependence of the resistance. While the resistance of single crystal graphite increases approximately linearly with temperature over the entire range, this is true for polycrystalline graphite only at high temperatures. The resistance-temperature curve for polycrystalline graphite shows a minimum around 1000°K, the exact value of the temperature depending strongly on the grain size of the sample.[6] At lower temperatures the resistance has an inverse temperature dependence. Several attempts have been made to extend or modify Wallace's theory to account for the observed temperature dependence of the resistance of polycrystalline graphite. Mrozowski assumes for polycrystalline graphite a nonzero activation energy, ($E \sim kT$ where T is the temperature of the minimum) and a constant number of free electrons in the conduction band in addition to those thermally activated into the conduction band. Bowen,[8] on the other hand, simply adds to Wallace's theory a temperature independent term for scattering from the crystallite boundaries. Semi-empirical equations based on either formulation may be fitted to the data within a few hundred degrees of the minimum, but both depart markedly from the data below about 150°K. By assuming that, due to impurity or surface states, the Fermi surface is displaced from the zone boundary,[7,9] the fit of Bowen's formulations may be improved somewhat at lower temperatures.

An important feature of any theory of graphite is its prediction of how the electrical resistance approaches the absolute zero temperature axis. The results reported here extend the data on the resistance of graphite down to 1.3°K.

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* Supported by the National Science Foundation.

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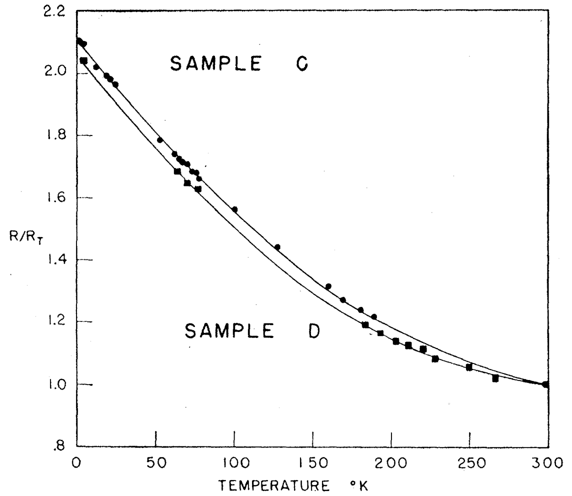

FIG. 2. Resistance of polycrystalline graphite.

PROCEDURE

The ends of the graphite sample were copper plated and current and potential leads were attached. The samples were mounted on a Lucite frame and placed in a Dewar flask in direct contact with the liquid bath. Temperatures in the ranges 1° to 4.2°K and 66° to 78°K were maintained by baths of liquid helium and liquid nitrogen, respectively. Temperatures in the liquid helium range were determined from the Mond[10] vapor pressure tables, and in the liquid nitrogen range they were determined from the *International Critical Tables*[11] vapor pressure tables.

To minimize thermal emf's the current and potential leads were brought out of the vacuum tight flask cap through an 8 inch long, thin wall, stainless steel tube, which was stuffed with cotton to prevent convection currents. The leads were soldered to the terminials of a hermetic seal at the end of the tube which was

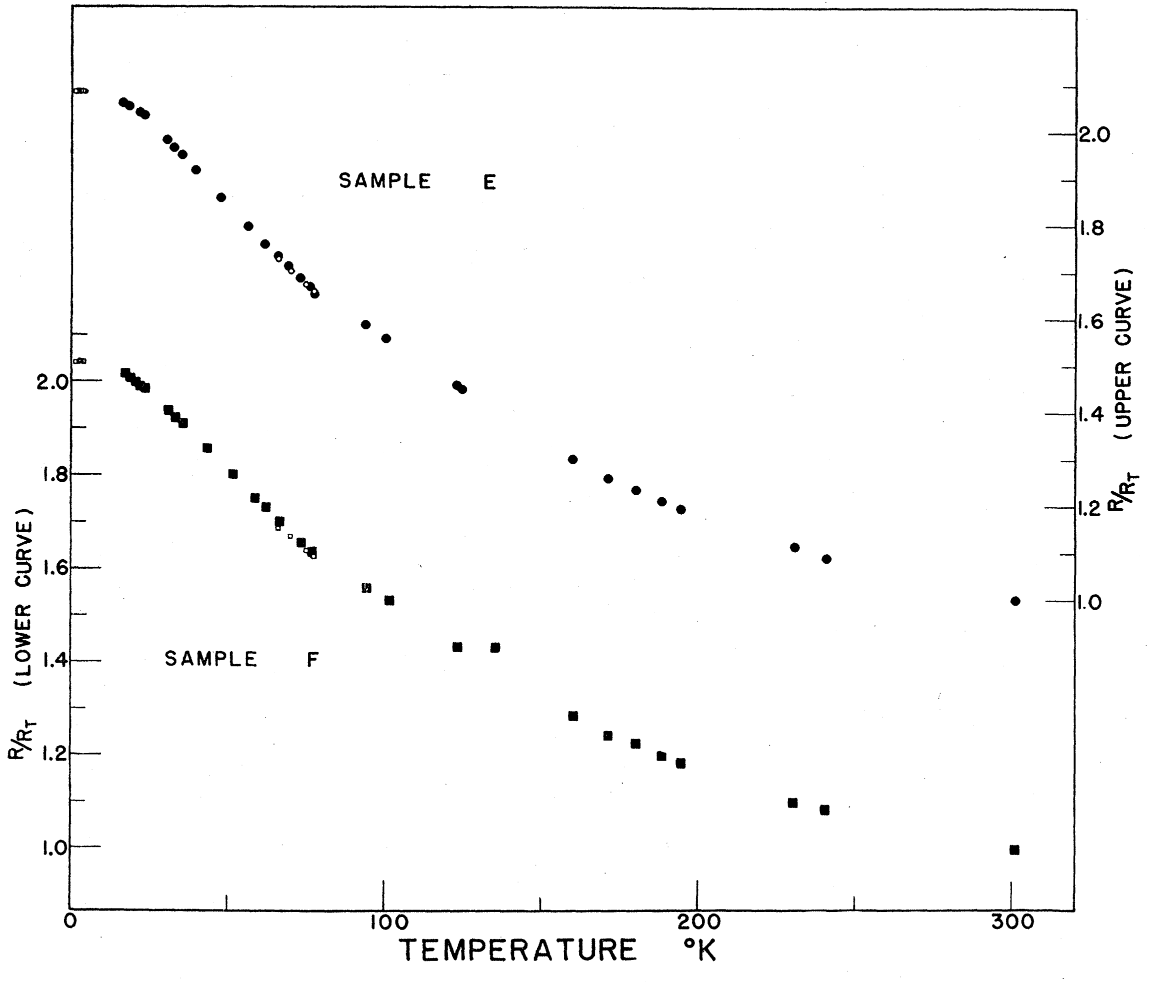

FIG. 3. Resistance of polycrystalline graphite. The solid points are taken from warmup data. The open points were taken while the samples were in liquid baths.

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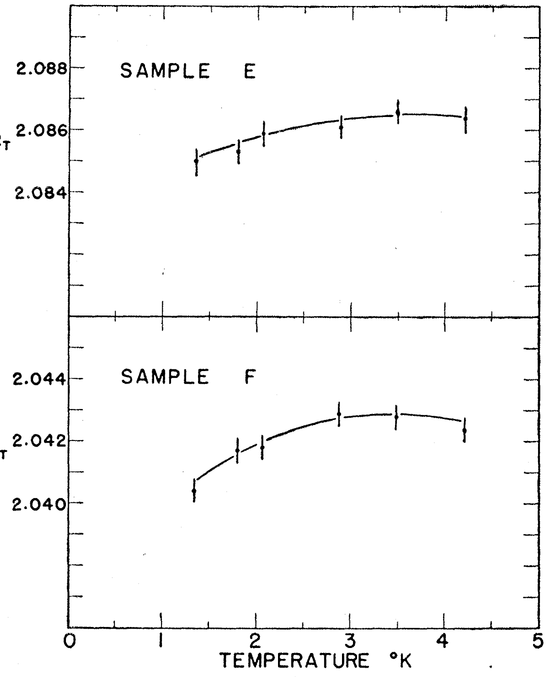

FIG. 4. The low-temperature points from Fig. 3.

effectively at room temperature. The thermal emf's were generally less than 0.5 microvolt and constant to within the sensitivity of the measuring apparatus during any set of measurements. Currents and potentials were measured on the two sides of a White double potentiometer with a dc breaker amplifier being used as the null indicator.

Points in ranges of temperature not obtainable with liquid helium or liquid nitrogen were taken from warmup data. The warmup rate was about 12° per hour from 15° to 65° and about 8° per hour from 65° up to room temperature. During the warmup runs, temperatures were determined by means of a calibrated copper-constantin thermocouple and the emf developed across the sample, carrying a constant current, was tracked by means of a Brown recording potentiometer.

For some of the preliminary measurements reported here (Figs. 1 and 2) the breaker amplifier was not available and a rather insensitive galvanometer was used. No effort was made to eliminate thermal emf's in these measurements. These two things are responsible for the scatter of points from these measurements.

RESULTS

Natural Graphite

The samples of natural graphite were flakes, about 3 by 5 mm and 4 by 6 mm and each about 0.5 mm thick, cleaved from specimens of natural flake graphite from Ceylon. The crystallites were a millimeter or so in size. X-ray examination showed them to be very imperfect crystals with much twinning and strain. The chemical purity was not checked, though it was probably not very good. The crystals were so fragile that it was extremely difficult to get good copper plate electrical contacts to the samples. The nature of the samples did not seem to warrant refinement of measurements on them, so only preliminary measurements were taken. The results on two samples are shown in Fig. 1. The results are in qualitative agreement with other measurements[1,2] and with Wallace's theory.[4]

Polycrystalline Graphite

The polycrystalline graphite used in these measurements was high purity commercial graphite. Spectrographic analysis, performed on both the bulk material and the actual samples after the experiments, showed the purity to be greater than 99.99 percent. X-ray photography of the bulk material showed a preferred plane for the *c*-axis but little or no preferred direction in the plane. The grain size of the graphite was determined by the Debye-Scherrer method to be around 10^{-4} cm.

The samples were machined to square cross sections of $\frac{1}{16}$ inch by $\frac{1}{16}$ inch and were 3 to 4 inches long. Each end of each sample was copper plated. The plating covered the extreme $\frac{1}{8}$ inch of each end. To check whether or not the copper penetrated the sample, one of the samples, which had been used in a run, was broken off $\frac{3}{8}$ inch from one end and the tip burned in the spectrometer. The spectrum showed less than 0.01 percent Cu.

The results of preliminary measurements on two samples are shown in Fig. 2. The probable error of the points is about the size of the points. These measurements agree with those of Goetz and Holser[5] and Tyler and Wilson.[7] Though these measurements extend the data to the liquid helium range of temperature, they do not show how the resistance approaches the absolute zero temperature because the resistance of the graphite is so insensitive to temperature that the accuracy of the resistance values is not great enough to detect a trend over a few degrees.

Subsequent measurements on the graphite, using more refined apparatus, as described above, yielded the results seen in Fig. 3. Sample *E* referred to in the upper curve was cut from the bulk graphite so that the sample axis lay in the preferred plane for the *c* axis of the crystallites. The lower curve refers to sample *F* whose axis was perpendicular to this plane. The resistances are plotted as R/R_T, where R_T is the resistance of the sample at room temperature. The room

TABLE I. Room temperature data.

Sample	Dimensions (cm)	Resistance R_T (ohm)	Resistivity ρ_T (ohm-cm)
E	$0.182 \times 0.181 \times 4.77$	0.1637	11.32×10^{-4}
F	$0.182 \times 0.185 \times 5.17$	0.0851	5.55×10^{-4}

temperature data on these two samples are given in Table I.

It is interesting to note that although the resistivity of sample E is about twice that of sample F, there is no significant difference in the temperature dependence of the resistance of the two samples. The curves for R/R_T for the two samples almost coincide and were separated by arbitrary distances in Fig. 3 for clarity in presentation. At temperatures above 20°K these curves agree remarkably with those of Tyler and Wilson[7] on their sample B, where their sample B is most nearly like our polycrystalline graphite. These measurements, like those of Tyler and Wilson, do not seem to be simply interpreted by present theory.

In both curves in Fig. 3 the open symbols represent data taken while the sample was at a constant temperature in a liquid bath and the solid symbols represent values obtained from warmup data. While the sample was in liquid helium the temperature was controlled to 0.001°K, and in liquid nitrogen it was controlled to 0.1°K. The temperature values *for the warmup points* are only known to within a few degrees. However, in Fig. 3 the warmup points from 66° to 78°K match the bath points fairly well.

In Fig. 3 the resistance is seen to rise as the temperature is lowered, as previously observed, but below 10°K it levels off. Actually, below 5°K, the resistance seems to fall very slightly. The points below 5°K have limits of error which are considerably smaller than can be seen in Fig. 3. Figure 4 shows these points on a much expanded scale. One could draw a horizontal line through these points, but curves of positive slope fit somewhat better. Even so, these curves extrapolate to absolute zero temperature almost horizontally and at resistance values slightly greater than twice the resistance at room temperature.

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Photoionization Cross Section of Nitric Oxide

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The photoionization cross section of the NO molecule was measured in the spectral region 1070–1343A, at intervals of one to five angstroms, using a vacuum monochromator (band width 0.85A), an absorption cell with ion collector, and a detector calibrated against a thermocouple. The ionization continuum showed some structure which was ascribed partly to preionization of several bands in the region 1070–1150A and partly to vibrational levels of the ground state of NO^+ ion. The photoionization cross section at Lyman alpha was 1.24×10^{-18} cm^2, about one-half the total absorption cross section. The first ionization potential, 9.23 ± 0.02 ev, was obtained from the long wavelength limit of the ionization continuum. Application of the method to other molecules appears promising.

INTRODUCTION

"Although experiments on the photoionization of air and other permanent gases have been carried out intermittently ever since the photoelectric effect was first discovered, it must be admitted that the state of our knowledge regarding the ionization of these gases is extremely unsatisfactory." This statement made by Hughes and DuBridge[1] about twenty years ago seems to be still applicable. Experiments on photoionization have been conducted in the past mostly with vapors of the alkali metals, for their ionization potentials are low enough to permit measurements in a relatively accessible region of the spectrum between 2000 and 3200A. In spite of the careful measurements, particularly by Mohler and co-workers (see reference 1), a review[2] of the data suggests that even for these atoms more consistent experimental values are desirable. Recent progress, however, has been confined almost entirely to theoretical calculations of cross sections of certain neutral and ionized atoms. The methods, results, and limitation of these calculations are discussed in papers[3] by Bates and Seaton. For molecules the available information on photoionization cross sections, both experimental and theoretical, is very meager.

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