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The effect of extrinsic defects in pyrolytic graphite on the *a*-axis resistivity

C. ZELLER*, G. M. T. FOLEY†, F. L. VOGEL
Moore School of Electrical Engineering and Labarotory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA

A contactless r.f. resistivity technique is shown to be well suited to the measurement of room temperature *a*-axis resistivities in lamellar compounds, particularly those of graphite. The method is used to investigate the relative damage induced by different techniques employed in cutting of samples.

1. Introduction

Graphite is a highly anisotropic material in both its mechanical and electrical properties. Recently, intercalation compounds of graphite have become the subject of much interest with regard to their *a*-axis conductivity (conductivity in the basal plane). Contactless measurements of conductivity such as we shall describe are essential in the investigation of these materials which are difficult to handle and in general highly unstable in air. More important, as recent work on AsF_5 graphite has indicated [1], is the enormous anisotropy of the electrical conductivity in acceptor compounds of graphite coupled with the very high basal plane conductivity make conventional 4-point d.c. bridge measurements impractical. In the course of our work on intercalation compounds it became of interest to determine the quality of our starting material and the degree to which sample preparation techniques, i.e. the manner in which samples are cut to shape, affected the room temperature *a*-axis resistivity ρ_a. The r.f. technique which we describe is eminently suited to this investigation.

The purpose of this paper then, is two-fold. Firstly, by measurement of the *a*-axis resisitivity of highly oriented pyrolytic graphite (HOPG) it is our intent to establish that the r.f. method is a valid technique for measurement of basal plane conductivities in quasi-two-dimensional materials. Secondly, in presenting the results of such measurements we graphically illustrate the importance of minimizing extrinsic defects in samples by an appropriate choice of sample cutting technique.

Except for the measurements of Dutta [2] who used an eddy current technique, the majority of studies of graphite resistivity have been classical four-point resistivity measurements. Both natural single crystals and synthetic HOPG have been studied. The in-plane *a*-axis resistivity ρ_a, is somewhat simpler to measure than the *c*-axis resistivity ρ_c, and has been studied in greater detail [2–17]. Table I summarizes results of a number of authors for the room temperature resistivity in the two principal directions.

Values of ρ_a are seen to be widely scattered and in many cases insufficient detail makes it difficult to assess the reliability of a published value. However, if we make the assumption that the smallest values represent those crystals closest to the ideal then we may judge the most likely value of ρ_a to be in the range $37–41 \times 10^{-6}\,\Omega\,\text{cm}$ for both natural and synthetic graphite. The spread in *c*-axis resistivity is generally much greater and its value is still a matter of some controversy [18]. Room temperature measurements on synthetic materials always give a ratio ρ_c/ρ_a greater than 10^3 while natural crystals give values between 10^2 and 10^4.

Sample damage may be incurred in a variety of ways. Even the straightforward purification of a single crystal by strong acids significantly affects

*Nato exchange visitor, University of Nancy, France.
†Present address: Wilson Center for Technology, Xerox Corporation, Webster, New York, USA.

TABLE I Principal resistivities for natural single crystal graphite (SC) and highly oriented pyrolytic graphite (HOPG)

Reference	$\rho_a(\Omega\,\mathrm{cm})$	$\rho_c(\Omega\,\mathrm{cm})$	ρ_c/ρ_a	Type of graphite
Dutta [2]	9.9×10^{-5}	1.0	10^4	SC
Ryschewitsch [3]	$3.9-6.0 \times 10^{-5}$			SC
Pirani and Fehse [4]	3.9×10^{-5}			SC
Ganguli and Krishnan [5]	$\sim 10^{-4}$	~ 1	10^4	SC
Kinchin [6]	$4-7 \times 10^{-5}$			SC
Primak and Fuchs [7]	3.8×10^{-5}	~ 0.01	250	SC
Primak [8]	4.1×10^{-5}	5×10^{-3}	120	SC
Soule [9]	4.1×10^{-5}			SC
Brown and Watt [10]	6×10^{-5}	0.5	0.8×10^4	HOPG
Bhattacharya [11]		4–14	10^4-10^5	SC
Blackman *et al.* [12]	$3.5-5.0 \times 10^{-5}$			HOPG
Klein [13]	4.2×10^{-5}			HOPG
Spain *et al.* [14]	$3.7-5.1 \times 10^{-5}$	0.1–0.3		HOPG
Murray and Ubbelohde [15]	$4.1-5.3 \times 10^{-5}$	0.23–0.31	$4.3-7.5 \times 10^3$	HOPG
Ubbelohde [16]	3.7×10^{-5}	8.8×10^{-2}	2.3×10^3	HOPG
Foley [17]	4.0×10^{-5}	8×10^{-2}	2×10^3	HOPG

the measured ρ_a [11, 19]. Ott [20] has shown that even the stirring of the acid during purification is sufficient to modify the X-ray diffraction patterns of the purified material. The introduction of defects by means of fast neutron irradiation substantially changes both ρ_a and ρ_c. More importantly, mechanical stress from cutting or cleaving of crystals has, as shown in this work, a very definite effect on crystal perfection. Since the electrical resistivity is a parameter of primary interest in our study of intercalation compounds of graphite, the minimization of additional sample damage during preparation is of the utmost importance.

2. Experimental technique

The method which we shall describe is particularly sensitive to the type of defect introduced in sample preparation. Such defects are confined largely to the sample perimeter, the region of peak current density in the eddy current technique which we employ. As the very small scatter in our final results indicates, rather than representing a limitation of the technique, the sensitivity to such defects allows samples of low quality to be easily detected and rejected.

The principle of the method is based on the fact that eddy currents are induced in a conductor placed in a changing magnetic field $\mathbf{B}_{rf}$. If the sample is coupled to the electromagnetic field in a circuit then such eddy currents will effectively reduce the incident magnetic flux and produce a change in the circuit impedance. Eddy current techniques are well known [21, 22]. The perturbation which the eddy currents in the sample represent are generally observed as an imbalance in an a.c. bridge circuit. For various reasons [23] we have adopted a simpler scheme which provides more than adequate sensitivity for the measurements necessary to our investigation.

The system comprises an oscillator in which the inductor is wound of a ferrite core having a small air gap. Introducing a conducting sample into the gap provides coupling between the sample and the magnetic circuit and the corresponding change in inductance is evident as a change $\Delta\omega$ in the frequency of oscillation.

For square samples in the form of a thin sheet, whose area is smaller than the cross-section of the air gap, it is possible to calculate the change of period ΔT ($T \equiv 2\pi/\omega$) for the case where the skin effect is negligible. The difference in period with and without the sample is given to a good approximation by

$$\Delta T = s\left[K_1\left(\frac{es}{\rho}\right) + K_2\left(\frac{es}{\rho}\right)^2 + \ldots\right] \qquad (1)$$

where K_1 and K_2 are constants which depend on the air gap and the coupling between the sample and the circuit; ρ is the resistivity of the sample in the plane perpendicular to the applied magnetic field, e the sample thickness and s the surface area of sample. K_1 is always larger than K_2, and in our experiments K_1/K_2 is about 50 at 100 kHz. It can be shown that K_1 varies with $1/Q$ (where Q is the quality factor of the circuit), while K_2 varies hardly at all with this parameter. For sufficiently small Q therefore, the response is essentially linear in es^2/ρ.

We have verified experimentally that the skin effect may be ignored provided the sample thick-

ness e is less than twice the skin depth δ. This condition is easily satisfied in our experiments with HOPG [24]. At 100 kHz the skin depth is about 1 mm.

We can consider two types of defect, those in the basal plane and those perpendicular to it. Exfoliation of the lamellar structure is an example of the latter and is the major type of transverse defect. Experiments with multilayer laminations of copper foil show that exfoliation has no observable effect on the calculated resistivity in the plane for the low Q situation where the response is essentially linear in the thickness. This is to be expected since the eddy currents are confined to the plane $\perp \mathbf{B}_{rf}$. Delamination of the graphite layers, a feature frequently encountered in the intercalation compounds, in principle, therefore, has negligible effect on these measurements of the a-axis resistivity, the parameter of interest.

In-plane defects, on the other hand, can have serious effects on the magnitude of the observed signal. Scratches in the sample surface and flexing of the sample can result in a signal reduction by as much as a factor of 10. A small edge imperfection may have significant effect because the induced surface currents are largely confined to the sample perimeter. Imperfections resulting from the cutting of the samples, which necessarily lie in the region of the sample edge, are thereby magnified.

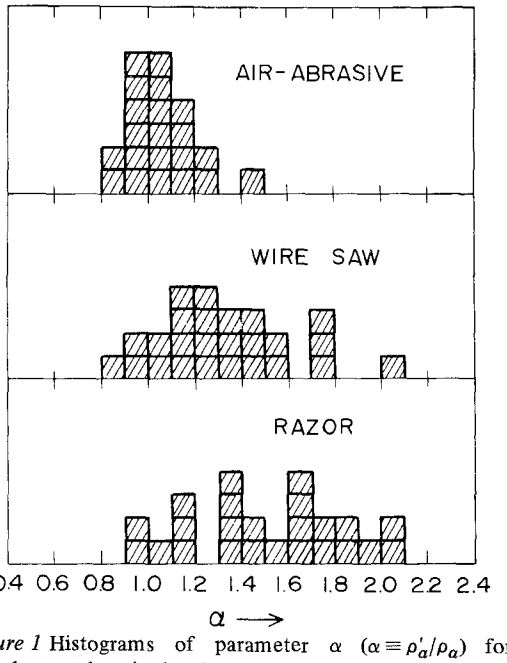

Figure 1 Histograms of parameter α ($\alpha \equiv \rho_a'/\rho_a$) for samples cut by air-abrasive, wire saw and razor prior to density correction.

We may suppose that the intrinsic a-axis resistivity ρ_a becomes ρ_a' due to the presence of extrinsic defects, where

$$\rho_a' = \alpha\rho_a. \tag{2}$$

Then the change in period ΔT in Equation 1 may be written

$$\Delta T \simeq s\left[K_1\left(\frac{es}{\alpha\rho_a}\right) + K_2\left(\frac{es}{\alpha\rho_a}\right)^2\right]. \tag{3}$$

Values of K_1 and K_2 at a chosen Q value are provided by calibration of our apparatus with materials of known resistivity. The procedure is described elsewhere [23], A measurement of ΔT for the intrinsic ρ_a is assumed.

3. Results and discussion

Our samples were all HOPG. Pieces were razor cleaved to approximately the desired thickness and then tape cleaved to provide mirror like c-faces on each sample. The plate-like samples were cut to size along the c-axis using three different methods:

(i) razor,

(ii) wire saw,

(iii) Air-abrasive technique (dental sandblast tool) [25] employing 27 μm powder.

The samples had c-faces the order of 5 mm on a side and were 0.1–0.5 mm in thickness. About twenty samples were cut by each method and subsequently measured. Fig. 1 shows histograms of the calculated α for each technique assuming (somewhat arbitrarily) $\rho_a = 43.1 \times 10^{-6}\,\Omega$ cm for the intrinsic a-axis resistivity of the starting graphite. Maximum values for α for the wire saw and razor are seen to be in excess of 2 while that for the air-abrasive technique is a little less than 1.5. The indication is that the air-abrasive technique is much superior to the other methods. Further investigation showed that a substantial part of the scatter could be ascribed to differences in the densities of the samples which were found to be as much as 10% less than the ideal value. If, instead of taking the measured sample thickness, we use a value computed from the sample weight and surface area, and the density of ideal graphite, a significant reduction in scatter is observed in the calculated resistivities for the wire saw and sandblast cut samples. The improvement is dramatic for the wire saw cut material which formerly showed relatively large scatter. Fig. 2 is a histogram for a group of wire saw cut samples similar to those used in the data of Fig. 1. The scatter is compar-

able to results from sandblast cut samples for which the density correction has also been applied. In addition the overall scatter is much less than that observed even for the best of the uncorrected data of Fig. 1. Application of a density correction to razor cut sample data provides only marginal improvement in terms of reduced scatter.

We have measured the density of our starting material and found it to correspond closely to the ideal value, $2.27\,g\,cm^{-3}$. We therefore make the following inferences on the basis of our measurements. Subtle delamination of samples occurs in the process of cutting them which leads to materials of less than ideal density. This effect is found in material cut by all three methods and is to be distinguished from gross delamination of samples which is readily observable visually. While the delamination has negligible effect on the measured signal it must be accounted for in calculation of effective sample thickness. The remaining α-scatter for the razor cut samples can be accounted for only in terms of additional basal plane defects. These defects are apparently largely absent in material cut by the other techniques.

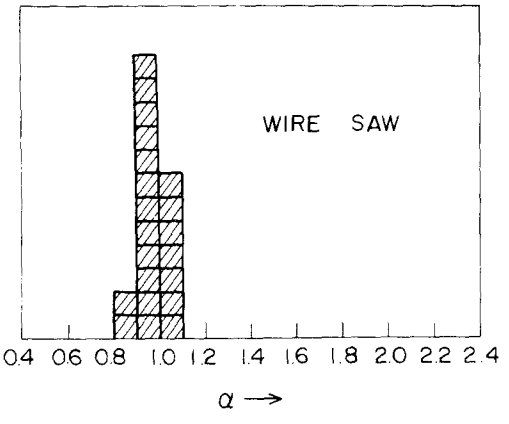

Figure 2 Histogram of parameter α ($\alpha \equiv \rho_a'/\rho_a$) for set of wire saw cut samples including density correction.

It is interesting to note however, that the measured minimum resistivity ρ_a, is approximately the same for each of the three techniques ($38 \pm 1 \times 10^{-6}\,\Omega\,cm$). This value may justifiably be regarded as that most closely approximating the resistivity of an ideal crystal. It corresponds precisely to that found previously by d.c. techniques for both natural and synthetic graphite. Further, the range of values of ρ_a for the razor cut samples corresponds to that found in Table I suggesting that extrinsic defects could account for much of the spread in published values.

4. Conclusions

Published values of a-axis resistivity for natural and synthetic graphites show considerable scatter. Our investigation indicates that, when only a small number of samples are examined, defects induced in sample preparation techniques may well lead to erroneous values for the ideal ρ_a. We suggest that as much of the scatter in previously reported values may be due to improper handling as is due to intrinsic differences in starting graphite. We conclude further that, in general, air-abrasive techniques are preferable for the cutting of material but that either that method or wire saw techniques will provide good data when density corrections are made in the manner in which we describe. This concurs with the work of Spain *et al.* [14].

Our investigation appears to indicate that $\rho_a = 38 \times 10^{-6}\,\Omega\,cm$ is an appropriate value for ideal starting material, in agreement with the smallest values derived by conventional 4-point d.c. methods in previously published work. The small scatter observed in our results for sandblast and wire saw cut samples after density corrections, suggest that starting material with an α outside the range 0.8–1.1 should be rejected. The establishment of criteria for sample acceptibility is not new but the simplicity of the procedure with the r.f. technique is an attractive feature.

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