irradiated artificial graphite, and further irradiation then produces a slight increase in conductivity (Woods, Bupp, and Fletcher[4]). This may be related to the behavior of the *c*-axis resistivity which shows a similar behavior (though more pronounced) at about the same dosage.

## ACKNOWLEDGMENTS

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# *C*-Axis Electrical Conductivity of Graphite*

W. Primak
*Chemistry Division, Argonne National Laboratory, Lemont, Illinois*

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Small crystals of natural graphite showing no evidence of twinning were found in a sample of marble from the Lead Hill mine (Ticonderoga, New York). They were isolated, handled very carefully to avoid deformation, and their *c*-axis conductivity determined. It was found to be about $2\times10^2$(ohm cm)$^{-1}$, in accord with previous measurements of less perfect crystals. It is shown that much of the variability in the measurements of larger, less perfect crystals is caused by nonuniform current flow. However, evidence is adduced to indicate that the actual *c*-axis conductivity of natural graphite crystals does vary somewhat.

## INTRODUCTION

THE electrical conductivities of graphite and their ratio for crystals isolated from several North American marbles were carefully determined by Primak and Fuchs.[1] (References to earlier work may be found in their paper.) All of the crystals which they measured possessed the gross twinning usually assigned to the $11\bar{2}1$ plane.[2] Since the twin zones were large compared to the mean free path of electrons in a solid, it was assumed that the gross twinning would have only a small effect on the electrical conductivities. The measurements of the *a*-axis conductivity were quite reproducible, and the results fell in a narrow range (10 to 15%); but the *c*-axis conductivity measurements were much less reproducible, and the average values of the results obtained for individual crystals covered a much larger range (about 40%). The electrical conductivities were in reasonable agreement with most of the previously published values, with two exceptions. Krishman and Ganguli[3] and also Dutta[4] reported results for the *c*-axis conductivity of Ceylon natural graphite crystals (which they claimed were very perfect, though without detailing evidence for it) two orders of magnitude lower. Accordingly, when some graphite crystals were found which were morphologically more perfect than the ones studied by Primak and Fuchs, the *c*-axis electrical conductivity of these crystals was investigated.

A small piece of marble from the Lead Hill mine find containing crystals which were considered at that time to be too small for electrical measurements was furnished to Dr. Fritz Laves (then at the University of Chicago, now at the Mineralogisch-petrographisches Institut Eidg. Techn. Hochschule, Zurich, Switzerland) for x-ray studies. He separated the crystals by dissolving the marble in hydrochloric acid and examined them by means of Laue and precession photographs. He reported them to be among the best crystals he had encountered; the spots were sharp; some crystals were free from twinning. He found that he could induce twinning and various disorders by rather gentle mechanical deformation.[5]

A further search was made for additional specimens of rock of the sort furnished Dr. Laves. After dissolving many specimens of rock and meticulously separating the crystals under a microscope, it was found that there was a well defined vein of the original boulder of the Lead Hill mine find in which the small high-quality crystals occurred. Additional rock was then dissolved, and a number of the crystals were separated. The greatest care was employed to avoid deformation of the crystals. Only small samples of rock were dissolved in a vessel, and no large amount of residue was permitted to collect. The graphite crystals were kept immersed in liquid during the whole operation of solution of the rock in hydrochloric acid and the subsequent washing with water. The crystals were retrieved under the microscope with a $\frac{1}{16}$-inch diameter applicator stick on the end of which was a dab of stopcock grease. They were then transferred to a benzene-water interface in a small dish.

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* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[1] W. Primak and L. H. Fuchs, Phys. Rev. **95**, 22 (1954).

[2] C. Palache, Am. Mineralogist **27**, 713 (1941).

[3] K. S. Krishnan and N. Ganguli, Nature **144**, 667 (1939).

[4] A. K. Dutta, Phys. Rev. **90**, 187 (1953).

[5] A preliminary report may be found in a progress report (U. S. Atomic Energy Commission Report COO-150, 1955; to be submitted for publication).

When the stopcock grease had dissolved, most of the liquid was removed with a pipette and replaced with acetone. The crystal was then washed (using the same technique) several times (successively) with benzene and acetone, and then it was stored under water. In order to transfer it, the crystal was picked up with a wet fine camel's hair brush; and it was transferred either in a drop of water held on the brush or held on a loop of wire. All of the crystals whose numbers are prefixed by *SP* were prepared and handled in this way.

## EXPERIMENTAL

### A. Resistivity of Special Crystals

The *SP* crystals were 0.01 cm thick and 0.15-cm diameter. If they possessed resistivities of the order of magnitude reported by Krishnan and Ganguli and also by Dutta, they would have had a *c*-axis resistance in excess of $\frac{1}{2}$ ohm. In the first set of measurements eight crystals were examined by placing them on a mercury drop, touching them with a mercury drop held in a tube [Fig. 1(A)], and measuring the resistance between the two mercury drops. For only two crystals was there found a resistance large enough to give a resistivity of the order of magnitude reported by Krishnan and Ganguli and also by Dutta. One of these was examined under the microscope and found to possess a wide groove on one basal plane, and it was assumed it made poor contact to the mercury drops. The other crystal which gave a high resistance between mercury drops and a third crystal from this lot were examined in the manner indicated in Fig. 1(B) and 1(C). With the arrangement shown in Fig. 1(B), the current increased over a period of half an hour and the potential drop decreased so that in one case the computed value of $E/I$ (potential drop $E$, current $I$ fell from 0.37 to 0.16, while with the arrangement of Fig. 1(C) the value of $E/I$ was 0.012. It was evident that there was an appreciable potential drop across the mercury graphite contacts.

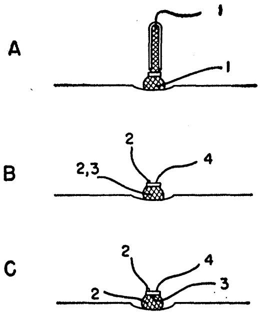

FIG. 1. Arrangements used in an attempt to check the resistances of *SP* crystals; (1) ohmmeter leads, (2) current leads, (3) fixed potential probe, (4) movable potential probe; cross-hatching indicates mercury (not to scale).

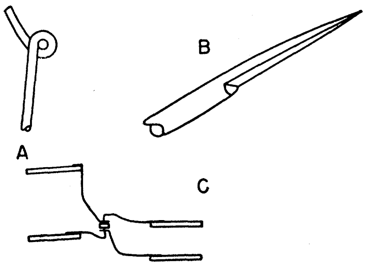

FIG. 2. Apparatus used to measure the *c*-axis electrical resistivity of small crystals, (A) the loop of wire used to form a current electrode before the loop was hammered flat and the unwanted end snipped off, (B) current electrode hole reamer made from a fine sewing needle, (C) assembly sketch of the apparatus with a crystal in place (not to scale).

To eliminate the effects of the contact resistance with the current electrodes an apparatus similar in principle to the *c*-axis apparatus used by Primak and Fuchs[1] was constructed. The current contacts were made by forming a small loop of No. 32 B. and S. gauge copper wire [see Fig. 2(A)], hammering it flat, clipping off the unneeded end, amalgamating the flat portion, and placing a drop of mercury upon it. The drop of mercury could be formed into a doughnut shape on this holder (with a hole in the center). A reamer for shaping the hole was made by honing away half the cross section of a sewing needle. The potential probes were made of No. 36 B. and S. gauge copper wire, the ends of which were sheared off to form a flat surface. The flat surface was amalgamated, and a droplet of mercury was placed upon it. The parts were placed on micromanipulators and positioned under a binocular microscope. Two *SP* crystals which showed no evidence of twinning were selected. For the first, *SP*-17: area of the basal plane 0.0034 cm$^2$, thickness 0.0118 cm, current 0.0189 amp, potential drop 0.000304 volt; hence the calculated resistivity was 0.0046 ohm cm. For the second, *SP*-18: area of basal plane 0.0022 cm$^2$, thickness 0.0165, current 0.0189, potential drop 0.000470 volts; hence the calculated resistivity was 0.0054 ohm cm.

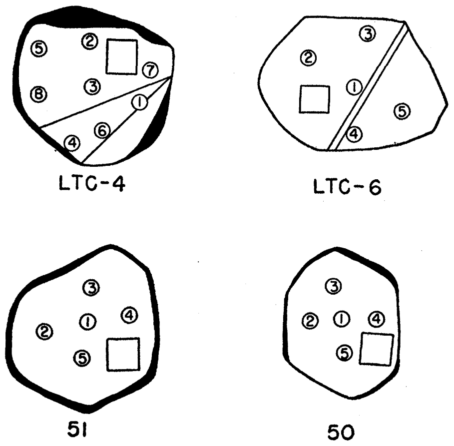

FIG. 3. Camera lucida sketches of graphite crystals showing approximate positioning of potential probes. The small square is $\frac{1}{4}$ mm$^2$.

### B. Measurements of Other Crystals

The crystals measured by Fuchs and Primak[1] were placed into their *c*-axis apparatus in a loosely fitting plastic mask of the thickness of the crystal. A micromanipulator held the mask which could thus be moved to position the crystal with respect to potential probes. In their measurements Fuchs and Primak attempted to locate the potential probes at the center of the crystal. A set of measurements was now made with the crystal purposely displaced in definite patterns. The patterns of potential probe locations are shown in Fig. 3 and the results of the measurements are given in Table I. Some of the results are for irradiated crystals.

## DISCUSSION

The measurements of the *c*-axis resistivity of undeformed natural graphite crystals showing no visible morphological defects obtained from a group of crystals which gave good x-ray patterns showed a maximum *c*-axis electrical resistivity about $5(10^{-3})$ ohm cm, in the middle of the range of the values found by Primak and Fuchs[1] for less perfect crystals.

TABLE I. $E/I$ for crystals positioned in the *c*-axis apparatus as shown in Fig. 3.

| | $E/I$ at various positions ($10^{-5}$ ohm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Crystal | 1 | 2 | 3 | 4 | 5 | 1 | Wt (mg) | Area (mm²) |
| *LTC*-4 | 192 | 141 | 296 | 302 | 166 | | 2.55 | 4.57 |
| *LTC*-6 | 170 | 142 | 161 | 145 | 229 | 162 | 4.78 | 7.10 |
| 51[a] | 634 | 423 | 558 | 1363 | 475 | 648 | 2.41 | 4.22 |
| 50[a] | 1060 | 629 | 312 | 1320 | 1386 | 977 | 1.58 | 3.22 |
| | 1 | 2 | 6 | 7 | 8 | | Wt (mg) | Area (mm²) |
| *LTC*-4[a] | 414 | 294 | 301 | 338 | 233 | | 2.55 | 4.57 |

[a] After irradiation in a nuclear reactor.

The measurements of $E/I$ for less perfect crystals given in Table I cannot be directly interpreted as resistance of the crystal. The current flow must be directed through the sections of lower resistance, and across these sections there must be found the greatest potential drops. Thus the highest values of $E/I$ may be associated with the smallest resistances. It is evident that the flow of current through most of the crystals measured in the *c*-axis apparatus was not uniform, and this would account for the variations in the measurements. In the case of one crystal for which data are given in Table I, there are measurements before and after irradiation, and the current flow pattern appears to have shifted as indicated in Fig. 4 as a result of the irradiation. Such an effect will account for some of the variability of the results reported by Primak and Fuchs[6] for irradiated crystals.

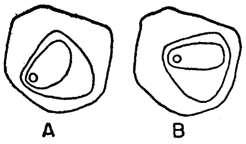

FIG. 4. Apparent current flow distribution in *LTC*-4, (a) before irradiation (b) after irradiation.

Since much of the variability in the measurements reported for *c*-axis crystals can now be assigned to nonuniform current flow, and since morphologically good crystals seem to possess a conductivity in the middle of the range of previous measurements, is any of the gross variability in the measurements of the *c*-axis resistivity to be assigned to a variability of the actual conductivity of the crystals? In some cases it was apparent that some of the nonuniform current flow was associated with variations in the thickness at different points in the specimen. However the variations shown by $E/I$ for different positions is far greater than the observed variations of the contact resistance of the current electrodes, for the gold leaf current electrodes were deformed at each resetting of the crystal, and after a series of resettings the value at a previous position could be reproduced (as shown in Table I). Further, the differences in the temperature dependence of the *c*-axis conductivity for different crystals (these measurements were made without disturbing the crystal and hence are for one position) and the differences in their irradiation behavior (these were averages taken for many resettings) are indicative of an actual variability in the conductivity. However, in the good natural graphite crystals used in the present studies it seems to be less than 40%. Nothing approaching a conductivity two orders of magnitude lower, as reported by Krishnan and Ganguli and also by Dutta, has been found.

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[6] W. Primak and L. H. Fuchs, Phys. Rev. **103**, 541 (1956) preceding paper.