Radiation Damage to the Electrical Conductivities of Natural Graphite Crystals*

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When natural graphite crystals were exposed in nuclear reactors, it was found that the a-axis electrical conductivity decreased progressively and monotonically, eventually about twenty-fold. The c-axis electrical conductivity decreased by a factor of about three to a minimum and then slowly increased somewhat. Very early in the irradiation, the temperature dependence of the conductivities altered to a negligible dependence on temperature, indicating the spacing of fixed scattering centers in the original crystals was at least hundreds of atomic spacings. The approximate values of the crystallite conductivities in artificial graphite are inferred from the results obtained for the natural graphite crystals.

INTRODUCTION

RADIATION damage to the electrical conductivity of artificial graphite was first observed at the Metallurgical Laboratory of the University of Chicago.[1,2] There are a number of more recent investigations of the effect of irradiation on artificial graphite.[3,4] Neubert and his co-workers investigated the radiation damage to the electrical conductivity of Ceylon natural graphite (consisting of crystal aggregates) samples cut in the direction of maximum electrical conductivity and similar samples cut in a direction perpendicular to the direction of maximum conductivity.[5] The authors briefly mentioned the effects of neutron irradiation on graphite crystals in a previous article.[6]

EXPERIMENTAL

The graphite crystals which were used were the same as those described before.[6]

The electrical measurements were performed by some of the methods described previously.[6] The c-axis resistivities which are reported here are the reciprocals of σ_c as reported previously. The a-axis resistivities which are reported here are the reciprocals of σ_a/δ reported previously. Since the ratio of the conductivities were found to alter with irradiation, δ is affected. However, it was shown that δ for the crystals which were used was probably between 1 and 1.1. The change in δ with irradiation would bring it closer to unity. Its effect is therefore negligible in comparison to the changes induced by irradiation. Since the experiments were conducted over a long period of time (several years), it was considered desirable to measure a set of standards with each set of determinations. These were several crystals of the same kind which were irradiated. The results reported here were obtained by multiplying the measurements by a constant which restored the measurements of the standards to their original value.

The progressive irradiations were conducted in the central thimble of CP-3 the Donuts at X-10, the converter at X-10, and the converter of CP-3′. A single irradiation of another set of crystals was performed in a Hanford test hole. The effects which were observed were certainly initiated by fast neutrons. The irradiation dosage for the progressive irradiations was obtained by the use of spectroscopic graphite rods as monitors in the manner described by Primak and Fuchs.[7] It is reported here in terms of the percent electrical conductivity decrease which would have been sustained by the spectroscopic graphite rods used by the writers if the initial rate of decrease had continued and is labeled in Initial Units (IU; an IU is equivalent to about 4.5×10^{15} neutrons/cm^2 effective in producing damage). The use of electrical conductivity dosage rods would in the present case serve to correct in part for temperature effects on the damage rate. The temperatures of irradiation were probably all in the range of 35°C to 60°C.

The effect of irradiation on the conductivities of natural graphite crystals is shown in Figs. 1 and 2. For comparison, the effect on the conductivity of arti-

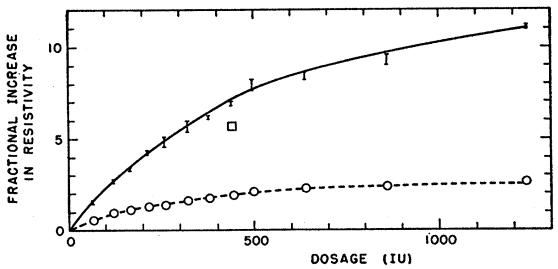

FIG. 1. The effect of irradiation on the a-axis resistivity of natural graphite (solid line) and on the resistivity of spectroscopic artificial graphite (dotted line).

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.
[1] M. Burton, J. Phys. & Colloid. Chem. **51**, 618 (1947).
[2] T. J. Neubert, post-deadline paper presented at the American Physical Society Meeting, Baltimore, March 17, 1955; M. Burton and T. J. Neubert, J. Appl. Phys. (to be published).
[3] G. H. Kinchin, J. Nuclear Energy **1**, 124 (1954).
[4] Papers presented at the International Conference on the Peaceful Uses of Atomic Energy at Geneva (United Nations, New York, 1955); G. H. Kinchin, A/Conf.8/P/442; Woods, Bupp, and Fletcher, A/Conf.8/P/746; G. R. Hennig and J. E. Hove, A/Conf.8/P/751; Mayer, Perio, Gigon, and Tournarie, A/Conf.8/P/362.
[5] T. J. Neubert *et al.*, *Neutron-Induced Discomposition of Graphite*, ANL 5472 (available from the Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C., 1956).
[6] W. Primak and L. H. Fuchs, Phys. Rev. **95**, 22 (1954).
[7] W. Primak and L. H. Fuchs (to be published).

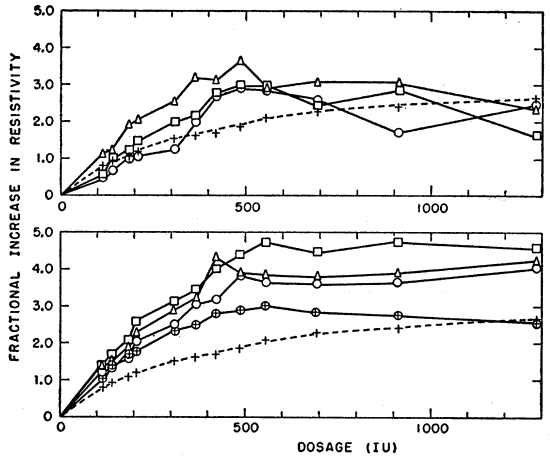

FIG. 2. The effect of irradiation on the c-axis resistivity of natural graphite. In the upper figure the crystal designations are: triangle 26, square 25, circle 33; in the lower figure they are: square 27, triangle 30, circle 29, crossed circle 28; and in both figures the crosses are the results for spectroscopic artificial graphite (dotted line).

ficial graphite (spectroscopic graphite rods[7]) is also shown in these figures.

A set of samples were also irradiated in a Hanford test hole for 344 Mwd/aT (megawatt days per adjacent ton) an exposure which would have resulted in a dosage of about 14 000 IU. The results are given in Table I.

The electrical resistivities were determined as a function of temperature for several irradiated crystals. The low-temperature relative resistivities of crystals *LTA*-3 and *LTC*-4 were reported previously.[6] Their relative resistivities after an irradiation in which the room temperature resistivity of *LTA*-3 increased 67% and *LTC*-4 increased 40% are shown in Fig. 3(a) and (b). The relative resistivities of crystals 9*A* and 33 which had been irradiated for about 1300 IU are shown in Fig. 3(c) and (d). The relative resistivity of crystal 11*A* irradiated for 344 Mwd/aT in a Hanford test hole is shown in Fig. 3(e).

TABLE I. Effect of an exposure of 344 Mwd/aT in a Hanford test hole on the electrical resistivities of graphite.

Crystal (No.)	R_0 [a] (10^{-5} ohm)	R_i [b] (10^{-5} ohm)	Increase $100[(R_i/R_0)-1]$ (percent)
	c axis		
34	168	715	326
35	163	451	177
36	250	762	204
37	161	465	189
38	171	659	285
39	102	251	146
	a axis		
10*A*	8.7	178	1948
11*A*	16.9	347	1950
12*A*	22.8	438	1820
13*A*	7.9	145	1720
	Spectroscopic graphite rods		
1	393	1799	358
2	406	1790	342
3	378	1788	373
4	380	1784	370

[a] R_0—resistance before irradiation.
[b] R_i—resistance after irradiation.

DISCUSSION

The progressive irradiations reported here consisted of a series of irradiations each of 1 to 3 weeks duration at irregular intervals, the series extending over a period of about 2 years. Since annealing of about 20% of the induced change in the resistivity of artificial graphite in a year following a short irradiation has been found,[5] it may be assumed that some annealing occurred during the series of progressive irradiations. However the changes are so large that the general nature of the effects found here would not be altered by the annealing correction. For a discussion of the annealing phenomena see an article by Primak.[8]

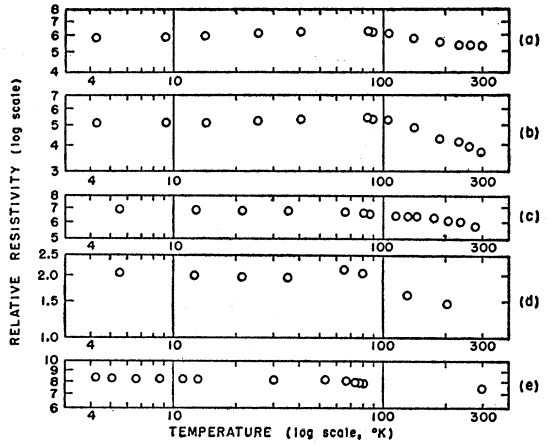

FIG. 3. Temperature dependence of the electrical resistivity of irradiated natural graphite; (a) a-axis crystal *LTA*-3, (b) c-axis crystal *LTC*-4, (c) a-axis crystal 9-*A*, (d) c-axis crystals 33, (e) a-axis crystal 11-*A*.

The variations found in the measurements of the c-axis conductivity are greater than any reasonable annealing effects as can be seen by a comparison of the irradiation curves for them with the curve for artificial graphite samples. These variations were investigated by Primak[9] who showed that they are largely due to nonuniformity in the crystals. Although the variations in measuring individual crystals is large, the changes induced by irradiation are so much greater that it is not difficult to see the latter.

Under irradiation, the a-axis conductivity decreases monotonically, and it is found that the resistivity as a function of dosage closely obeys a law due to Novick,[5,7]

$$y^{-1}=ax^{-1}+b,$$

where y is the percent change in resistivity, x is the dosage, and a and b are constants. The data of the

[8] W. Primak (to be published).
[9] W. Primak, Phys. Rev. **103**, 544 (1956) following paper.

progressive irradiations indicate saturation according to this law at 1800% change, close to the value found in the Hanford irradiation.

The c-axis conductivity behaves in a more complex fashion. It decreases much less rapidly than the a-axis conductivity, reaches a minimum at about 500 IU, and then increases again slowly. The actual changes vary considerably. The conductivities of the crystals have been reported,[6] and it is seen that the irradiation-induced changes tend to be greater in the crystals of greater original conductivity (with exceptions). Although the extreme deviation of the minimum conductivities reached on irradiation are greater than the extreme deviation of the original conductivities, if the two extreme results are cast out (crystals 27, 33), the remainder have nearly the same minimum c-axis conductivity, 57 ± 3(ohm cm)$^{-1}$. The increase in the measured values of the c-axis conductivity as the irradiation proceeds beyond this point seems quite real, for the c-axis conductivity of the Hanford irradiated crystals is at a noticeably greater level than those at the end of the progressive irradiations.

As a result of irradiation, the anisotropy of the electrical conductivities decreases. A decrease of anisotropy due to radiation damage seems to be quite general.[10,11] The original anisotropy was about 140. As a result of irradiation, the a-axis conductivity decreased about nineteen-fold and the c-axis conductivity two- to threefold. Hence the final anisotropy is about 20.

As the anisotropy of the electrical conductivities decreases, any nonuniformity of conduction in the experimental arrangement used to determine the c-axis conductivity should become more severe. If this merely meant that some portion of the cross section of the crystal were not effective in conducting current, then the apparent resistance would increase, and it would be argued that the decline from the maximum resistance which is observed in long irradiations is surely real. On the other hand, if the conduction were nonuniform to begin with, there might be an alteration in the conduction pattern on irradiation, and the result would be uncertain. Correspondingly, the results should then be random, some crystals increasing in resistivity and some declining, rather than showing the general decline which was observed.

The change in the temperature dependence occurs very early in the irradiation. It appears as if the leveling off (proceeding to lower temperatures) of the logarithm of resistance *vs* logarithm of temperature which occurs below about 15°K is extended to higher temperatures. The effect is in accord with the previous assignment[6] of this resistance to fixed scattering centers. In the short irradiations which are sufficient to alter the temperature dependence, the carrier concentration does not alter appreciably (see Hennig and Hove,[4] and Woods, Bupp, and Fletcher[4]; note values of the Hall coefficient; 1 Mwd is equivalent to about 40 IU). Accordingly, the alteration in the resistance at this time is to be attributed to the introduction of scattering centers. The rate of accumulation of displacements in graphite under the conditions used in the irradiations described here[12] is about 2.7×10^{-5} per atom IU, and therefore about 7×10^{-4} displacements per atom were present in the shortest irradiation in which the temperature dependence of the electrical conductivities was examined. Many of the displacements are grouped,[13] and hence their scattering effectiveness is uncertain. However the closest possible average spacing of scattering centers introduced by the shortest irradiation would be about thirty atomic spacings in the graphite planes. The mean free path for electrons in the unirradiated graphite crystals must be much greater, a fact which might be inferred from the electron theory of conduction.

The change in the temperature dependence of the c-axis conductivity at low temperature caused by the introduction of additional fixed scattering centers seems to cause the temperature of maximum resistance to shift to lower temperatures. It seems reasonable, therefore, to attribute the variability in the position of this temperature of maximum resistance in unirradiated crystals to variations in the number of scattering centers. It seems reasonable to attribute the variability of the c-axis electrical conductivity temperature dependence among different crystals to the same cause and also some of the variability in the room temperature conductivity of different crystals.

The electrical conductivity of artificial graphite has a temperature dependence much like that of irradiated natural graphite. Because of the high value of the electrical conductivity of artificial graphite, it must be considered to represent mainly a-axis conductivity. It is concluded that the crystallites of artificial graphite possess more scattering centers than natural graphite crystals but not more than would decrease the effective a-axis conductivity of the crystallites by $\frac{1}{2}$ to $\frac{1}{3}$. The following will account for the effect of irradiation on the electrical conductivity of artificial graphite: that the original crystallites have an effective conductivity ratio 50 to 75, an a-axis conductivity $\frac{1}{2}$ to $\frac{1}{3}$ that of natural graphite, and 0.95 to 0.97 of the effective conduction is along the a-axis; that in the irradiated artificial graphite, when the change has saturated, the conductivity ratio is about 15, the a-axis conductivity is 1/19 that of natural graphite, and about 0.9 of the effective conduction is along the a-axis. There appears to be a minimum conductivity which is reached by

[10] A. Pabst, Am. Mineralogist **37**, 137 (1952).
[11] Primak, Fuchs, and Day, J. Am. Ceram. Soc. **38**, 135 (1955).
[12] W. Primak (to be published).
[13] W. Primak (to be published).

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.

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C-Axis Electrical Conductivity of Graphite*

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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 2×10^{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.

* 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).