example at $T=T_c/2$, $\frac{1}{2}(C_{es}-S_{es})\simeq C_{es}/3$. We therefore see that the so-called electronic term contains a large positive contribution from the kinetic energy of the ions in the lattice. This fact implies that considerable caution should be exercised in any attempt to interpret C_{es} in terms of a one-electron energy spectrum. On the other hand, it does not imply that such an interpretation is completely impossible. However, an alternative interpretation of this term would be that it arises from the excitation of elementary (charged) excitations across an energy gap. The magnitude of the gap may, and indeed must, depend on M. These excitations could be supposed to arise from the cooperative nature of the interaction between the electrons and the lattice vibrations. This kind of interpretation does not suppose that any separation of the nuclear and electronic motions is possible and there is no reason to identify the elementary excitations with electrons.

ACKNOWLEDGMENTS

It is a pleasure to thank Professor J. E. Mayer and Dr. A. B. Pippard for numerous conversations throughout the course of this work. The author would also like to thank the United States Government for the award of an F.O.A. research fellowship during the tenure of which this work was carried out.

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Observed Dependence of the Low-Temperature Thermal and Electrical Conductivity of Graphite on Temperature, Type, Neutron Irradiation, and Bromination*

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The thermal conductivity of various graphites in the temperature interval 10° to 300°K has been determined and the effect of neutron irradiation and bromination investigated. The thermal conductivity of large crystallite natural graphite and of nonpitch-bonded graphite is found to vary as T^2 at low temperatures, as does the specific heat, in accordance with the simple theory of lattice heat conduction. This is in contrast to the anomalous $T^{2.7}$ dependence exhibited by various pitch-bonded graphites. The anomaly is explained in a subsequent paper in terms of the effect of ungraphitized pitch on the total thermal resistivity of pitch-bonded graphites.

Neutron irradiation is observed to cause the thermal conductivity of graphite to decrease markedly at a rate which decreases with exposure time. Also, the exponent of the temperature dependence decreases with exposure. The effect of bromination on the thermal conductivity of graphite is determined and compared with the effect of neutron irradiation. The results indicate that the change in the concentration of conduction electrons is not the principal mechanism by which neutron irradiation decreases the thermal conductivity.

The electrical resistivity shows a negative temperature coefficient for all graphites, except the large crystallite natural graphite. Neutron irradiation increases the electrical resistivity to a saturation value and decreases the magnitude of the temperature coefficient.

I. INTRODUCTION

As a part of a general program[1] to study the effect of radiation damage on the properties of graphite, the thermal and electrical conductivity of various types of graphite have been determined as a function of neutron exposure and temperature in the interval 10° to 300°K. The thermal conductivity of unirradiated artificial polycrystalline graphite at low temperatures has been reported by Tyler and Wilson[2] and by Berman.[3] These authors reported an anomalous temperature dependence which has been confirmed by an independent experimental method[4] in the present study. Accordingly, graphite is the only nonmetallic substance known at present in which, at low temperatures, the thermal conductivity varies more rapidly with temperature (up to $T^{2.7}$) than the specific heat[2] (T^2). Klemens[5] has treated this anomaly as due to different vibrational modes being responsible for thermal conduction and specific heat in thin graphite plates. Smith[6,7] and Hove[8] have explained it as due to the presence of small regions of nongraphitic carbon, presumably in the pitch binder, in the artificial graphites. Since the latter explanation depends critically on the effect of the nongraphitic pitch binder, the behavior of graphites in which it is essentially absent has also

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[1] G. Hennig, and J. Hove, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, August, 1955* (United Nations, New York, 1956), Vol. 7, Sec. 13B, p. 666.
[2] W. W. Tyler, and A. C. Wilson, Jr., Phys. Rev. **89**, 870 (1953).
[3] R. Berman, Proc. Phys. Soc. (London) **65**, 1029 (1952).
[4] N. S. Rasor, Rev. Sci. Instr. (to be published).
[5] P. G. Klemens, Australian J. Phys. **6**, 405 (1953).
[6] A. W. Smith, Phys. Rev. **93**, 952 (1954); **98**, 1563(A) (1955).
[7] A. W. Smith, Phys. Rev. **95**, 1095 (1954).
[8] J. E. Hove, Phys. Rev. **98**, 1563(A) (1955).

been determined and is reported in the present paper. These explanations will be discussed in detail in the subsequent paper (II).

The production of lattice defects in graphite by high-energy neutron irradiation causes pronounced changes in its thermal conductivity.[9] This is presumably due to scattering, by the defects, of the lattice waves which conduct heat in graphite. The changes in the thermal conductivity and its temperature dependence reported herein are used in the subsequent paper (II) to obtain information on the rate of formation of the lattice defects introduced by neutron irradiation.

The change in the concentration of free electrons induced by neutron bombardment could conceivably cause the observed changes in the thermal conductivity, since electrons can also scatter lattice waves. This possibility has been explored by independently varying the free electron concentration through bromination of graphite and observing the effect on the thermal conductivity.

The electrical resistivity of various graphites was also determined as a function of temperature, neutron exposure, and bromination. This property is sensitive to changes in the Fermi level and to changes in the mean-free-path of the electrons. The interpretation of the observed effects of radiation damage on the electrical resistivity of graphite has been reported by Eatherly.[10]

The method of measurement used on all samples reported here, with the exception of the natural graphite crystals, has been reported elsewhere.[4] It will suffice here to say that the method used was the Kohlrausch method which utilizes the temperature rise resulting from the passage of an electrical current through the specimen. A "heat meter" method was used to determine the thermal conductivity of the natural graphite crystals and will be described in the present paper.

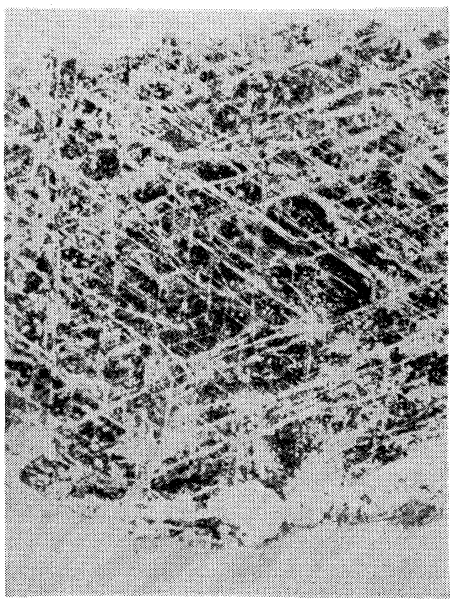

FIG. 1. Photograph of surface of a Canadian natural graphite sample.

[9] N. S. Rasor, and J. E. Hove, Phys. Rev. **100**, 1806 (1955).
[10] W. P. Eatherly, Phys. Rev. **98**, 1531(A) (1955).

II. THERMAL CONDUCTIVITY

A. Pitch-Bonded Polycrystalline Graphite

The temperature dependence of the thermal conductivity of various unirradiated artificial pitch-bonded graphites has been reported elsewhere[2–4] and the salient features which establish graphite as a lattice thermal conductor discussed. The results for type AGOT–KC, shown in Fig. 3, are typical of the pitch-bonded graphites. Failure to conform to the requirements of the simple theory (i.e., direct proportionality to the specific heat leading to a T^2 dependence at low temperatures) is apparent. This anomaly is discussed in (II) and is treated as due to the presence of non-graphitic carbon which is known to exist in pitch-bonded graphites.

B. Large Crystallite Canadian Natural Graphite

Magnetic susceptibility measurements indicate that little if any nongraphitic carbon is present in certain natural graphites. Since the explanation of the anomalous behavior of pitch-bonded graphites presented in (II) is based on the effect of nongraphitic material, the temperature dependence of the thermal conductivity of these natural graphites is of great importance to this hypothesis.

A number of fairly large flakes (about $\frac{1}{2}$ inch long) of Canadian natural graphite were obtained from J. C. Bowman of the National Carbon Company. This graphite has a very low ash content; a microphotograph of a typical flake is shown in Fig. 1. It can be seen that there are a large number of deformation lines. Assuming that these lines could be taken as the boundaries of the crystallites, it was estimated that the crystallites are about 10^{-2} cm in length. From the symmetry it appears that these lines lie in the basal plane; the thickness of the crystallites is unknown. Because of the irregular shape of these flakes, it is difficult to make an absolute measurement of the thermal conductivity and the results obtained here will only be a rough measure of the magnitude of these properties although relative measurements at different temperatures are good to better than 10%.

The apparatus used to determine the thermal conductivity of these flakes is shown in Fig. 2. A small carbon resistor, resting on Bakelite legs, was soldered to a heat meter which consisted of a piece of type AWG graphite whose thermal conductivity was well known. Between the AWG graphite and a copper block a flake of the graphite to be measured was placed. The flake

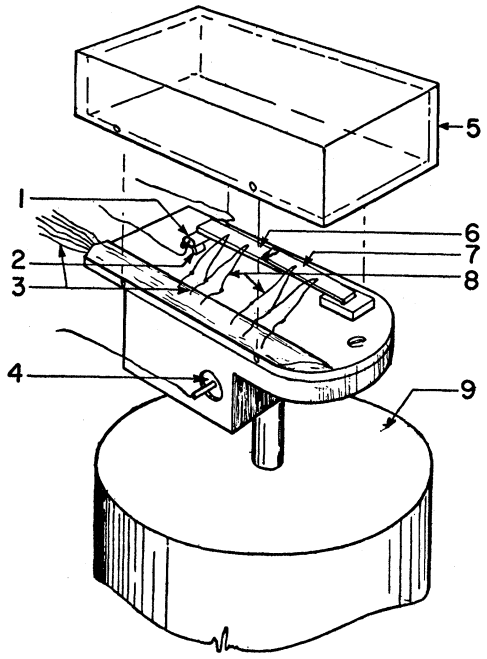

FIG. 2. Thermal conductivity apparatus used for Canadian graphite sample measurements. 1. Carbon resister heater. 2. Bakelite legs. 3. Insulated copper wire buried in Cerrolow solder. 4. Carbon resistor heater. 5. Radiation shield. 6. AWG-type graphite. 7. Natural graphite. 8. Chromel-constantan differential thermocouples. 9. Bottom of inside Dewar.

ends were electroplated with copper and soldered to the block and to the AWG with Cerrolow (117°F) solder. Differential thermocouples of 0.001-inch diameter chromel and constantan wire were cemented to both the AWG and the natural graphite with Epon (CD–200) cement so that the temperature gradient across each could be measured. These thermocouples could also be used to measure the temperature difference between the flake and the reference junctions. The reference junctions were Teflon-covered 0.003-inch diameter copper wires, which were brought through Cerrolow solder to obtain good thermal contact to the copper block. An additional thermocouple with an ice reference junction was then buried in this solder. Thus the absolute temperatures of the natural graphite and the AWG heat meter were measured as well as the two differential temperatures. From these data the thermal conductivity of the natural graphite is readily obtained. Heat leakage through the 0.001-inch diameter wires, through the rarified gas ($<10^{-5}$ mm Hg), and by radiation can be shown to be negligible. The size of the samples measured was approximately $\frac{1}{4}$ in.$\times$1/20 in. $\times$1/100 in. Temperature control was obtained by connecting the entire unit to a copper block containing a 100-ohm carbon resistor heater. This block was connected through a stainless steel rod to the bottom of a vacuum chamber immersed in a refrigerant bath, as shown in Fig. 2.

The results of the thermal conductivity measurements on three natural graphite flakes are shown in Fig. 3. The temperature exponent in all three cases is 2.0 ($\pm$0.1) in excellent agreement with the simple theory of lattice conduction. This result strongly implies that the presence of nongraphitic carbon is the cause of the anomalous behavior of pitch-bonded graphites.

The peak in the thermal conductivity occurs at about 80°K as contrasted to about 300°K for the artificial graphites such as AGOT–KC. This peak position may be used to estimate the order of magnitude of the average crystallite size. If it is assumed that phonons (lattice waves) are scattered only by boundaries and by other phonons (a qualitative discussion of these scattering mechanisms can be found in reference 3), and that the contribution of each of these to the thermal resistivity is equal at the temperature of the peak, then it is easily shown that

$$\frac{L_1}{L_2}=\exp\left[\frac{\theta}{2}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right].$$

Here L_1 and L_2 are the crystallite sizes of samples having peaks at temperatures T_1 and T_2, respectively, and θ is the Debye temperature. In the present case AGOT–KC has $T_1=300$°K and Canadian natural has $T_2=80$°K. Using $\theta=1000$°K, it is found that

$$L_2/L_1=100.$$

For AGOT–KC, L_1 is estimated, as will be discussed in the subsequent paper, as about 6×10^{-5} cm in which case L_2 is of the order of 0.6×10^{-2} cm. This agrees well with the estimate of 10^{-2} cm made previously from the lines on the microphotograph of a flake. In (II), reasons are presented which suggest that a Debye temperature of about 1600°K should be used instead of

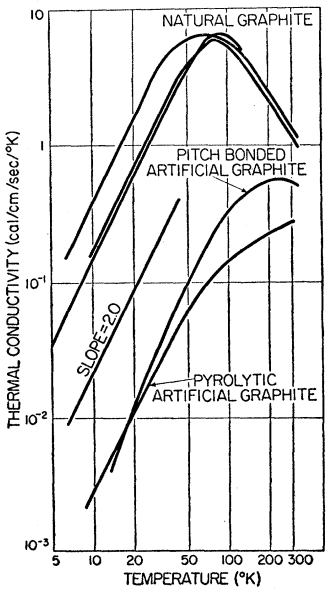

FIG. 3. Thermal conductivity of Canadian natural and pyrolytic graphites. For comparison, a typical pitch-bonded graphite is also shown.

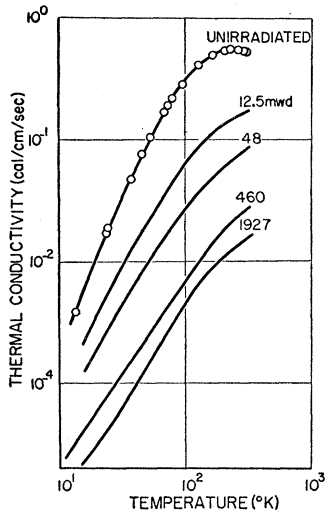

FIG. 4. Thermal conductivity of AGOT-KC graphite (in a direction parallel to the extrusion axis) with various neutron irradiations at about 30°C. The unit (megawatt-day) used represents about 10^{17} *nvt* of neutrons with energy greater than 0.5 Mev.

1000°K. This would give a value for L_2 of 6×10^{-2} cm. The agreement with the previous estimate is still reasonable, especially considering the crudeness of the latter.

One sample of Ceylon natural graphite has been measured[4] which has the anomalous ($T^{2.7}$) behavior. It is felt, however, that since this sample has a skew orientation and unknown purity, it does not represent the intrinsic conductivity of graphite. The fact that its conductivity at low temperature is of the order of one-hundredth that of the Canadian natural tends to indicate very small crystallites or very poor orientation.

C. Pyrolytic Graphite Filament

The thermal conductivity of a graphite formed by pyrolytic decomposition of a hydrocarbon has been obtained and is included in Fig. 3. The sample was prepared by J. Meers of the National Carbon Research Laboratory. This material has no pitch-bonding. It is a well-graphitized material differing from the natural graphite principally in having a small crystallite size. It can be seen that the thermal conductivity has a T^2 dependence at low temperatures, again giving evidence that nongraphitic carbon is responsible for the anomalous behavior of graphites which contain it.

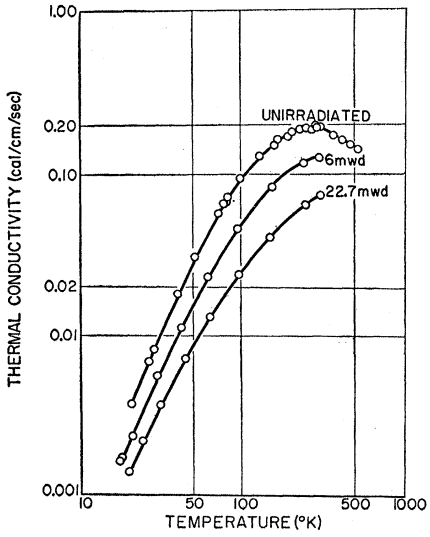

FIG. 5. Thermal conductivity of AWG graphite (in a parallel direction to the molding pressure) with various neutron irradiations at about 30°C.

D. Effect of Neutron Bombardment

Since the thermal conductivity of lattice conductors such as graphite is strongly dependent on the degree of lattice perfection, this property should be a sensitive means of studying the production of lattice defects by neutron bombardment. Three types of artificial pitch-bonded graphite have been subjected to neutron bombardment. Type AGOT-KC is a coke graphite with a density of 1.65. It is extruded and has an estimated size of 50 microns and a crystallite size of 0.3 micron or greater. Type AWG is a molded coke graphite with a density of 1.75, a particle size of 25 microns, and a crystallite size of 0.2 micron or greater. Type SA-25 is a pitch-bonded graphitized lampblack. It is molded and has a density of 1.55, a particle size of the order of 0.3 micron, and a crystallite size of about 0.05 micron. Several samples of each type were irradiated in a Hanford reactor in a cooled test hole (approximately 30°C) for varying lengths of time. Due to the necessity of using different samples for each exposure, the comparison between them is probably good only to the order of 10%. However, the relative accuracy of measure-

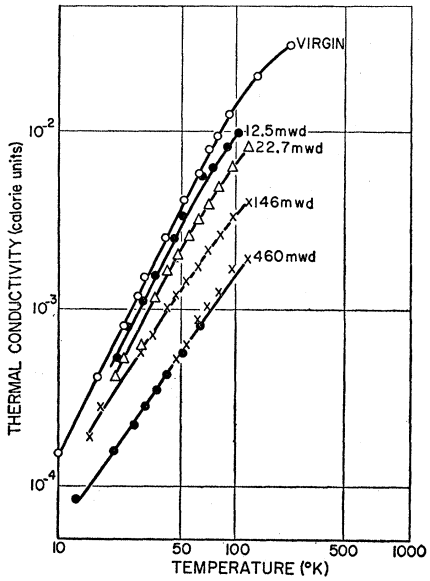

FIG. 6. Thermal conductivity of SA-25 graphite with various neutron irradiations at about 30°C.

ments on each sample is better than this. This is discussed more extensively elsewhere.[4]

The effect of neutron bombardment can be seen in Figs. 4, 5, and 6. The unit of exposure used in these figures (Mwd) is roughly equivalent to an integrated flux of 10^{17} *nvt* of neutrons with energies greater than 0.5 Mev. The relative decrease in the thermal conductivity is greater for samples with a high conductivity. In the case of the AGOT-KC, a decrease by a factor of 100 is observed at 20°K for the longest exposure although the temperature dependence does not change to a large degree, going from a maximum of $T^{2.7}$ down to $T^{1.8}$.

Since introduction of imperfections at a constant rate should increase the thermal resistivity at a constant rate, it is instructive to plot thermal resistivity *vs* exposure. This is done in Fig. 7 for the room temperature values. It can be seen that the rate of increase is not linear but becomes linear at long exposures. This is felt to be due to the thermal annealing which occurs during exposure at room temperatures. While no attempt will be made here to introduce a model of radiation damage for graphite, it can be said that the migration, during irradiation at constant temperatures of single imperfections to double or larger groups of imperfections, will give curves which fit the data in Fig. 7. In this connection it should be mentioned that similar (unpublished) measurements on samples of AWG graphite irradiated at liquid nitrogen temperatures have been made by G. Deegan and V. Martin at this laboratory. The samples were irradiated in the Brookhaven reactor, transferred to this laboratory, and measured without being warmed above liquid nitrogen temperatures. The thermal resistivity in this case was linear with exposure over the entire exposure interval (approximately 75 Mwd). These samples also showed appreciable annealing on warming to room temperature.

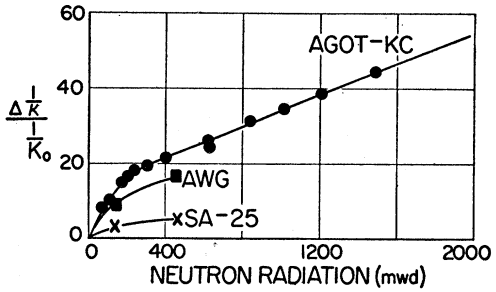

FIG. 7. Variation of the fractional increase of thermal resistivity of graphite with neutron exposure. Both irradiation and measuring temperatures are about 30°C.

E. Brom-Graphite Residue Compounds

Brom-graphite compounds and their electronic properties have been extensively studied by Hennig[11] and will not be discussed here in any detail. Briefly, bromine is allowed to react with graphite forming relatively unstable lamellar compounds in which the bromine forms layers between the graphite basal planes. When these compounds are allowed to decompose some of the bromine always remains in the graphite unless the temperature is raised almost to the graphitizing point (approximately 2200°C). The graphite plus this remanent bromine is called a residue compound. For type AGOT-KC graphite, a residue compound with up to about 1 atomic percent of bromine has almost all of the bromine residing at boundaries and other discontinuities (x-ray measurements indicate[11] that, at most, 6% of the bromine is between the graphite planes inside the crystallite). Residue compounds of greater than about 1.2% cannot be prepared without producing permanent distortion and damage of the graphite crystallites. In the residue compounds, about 18% of the bromine atoms are ionized,[11] thus removing electrons from the graphite conduction band. With the bromine only at boundaries, it is assumed that little change is made in the band structure of graphite. Since electrons are also removed from the conduction band by neutron bombardment,[10] studies of the thermal conductivities of the brom-graphite residue compounds were undertaken to see if the effect of neutron damage on the thermal conductivity was principally due to scattering of phonons by the electrons. It was assumed *a priori* that the bromine atoms themselves would not greatly affect the thermal conductivity greatly as long as they are located on boundaries.

A number of samples of type AGOT-KC graphite was brominated by N. Dzurus of the Argonne National

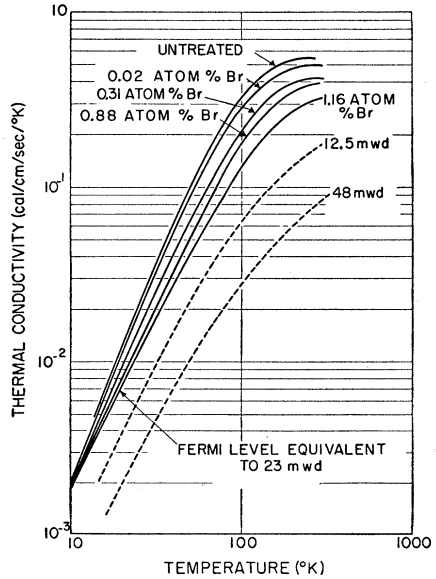

FIG. 8. Thermal conductivity of brom-graphite samples of AGOT-KC. Two neutron-irradiation curves are shown also, for comparison. The Fermi level equivalence was obtained from magnetic susceptibility measurements.

[11] G. Hennig, J. Chem. Phys. **19**, 922 (1951); **20**, 1438, 1443 (1952).

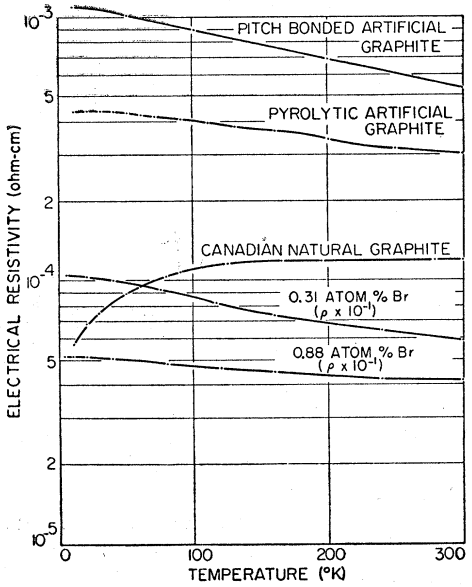

FIG. 9. Electrical resistivity of Canadian natural and pyrolytic graphites. A pitch-bonded (AGOT–KC) graphite and two brominated samples are also shown for comparison. Note change in scale in the latter two curves.

Laboratory. The thermal conductivities as a function of temperature of four of these samples are shown in Fig. 8 which also includes curves for an untreated sample and for two neutron-irradiated samples. For the purpose of this plot the curves were normalized at 10°K. This changed the values by less than 10%. It can be seen that the low-temperature slope of these curves decreases as the bromine concentration increases. The maximum slope changes from about 2.6 for the untreated sample to about 2.0 for 1.16 atom percent bromine sample. The 12.5-Mwd (megawatt-day) neutron-irradiated sample has a slope of just over 2.0. These slopes, of course, represent the temperature exponent of the thermal conductivity. On the basis of magnetic susceptibility and Hall coefficient measurements, an equivalence factor between electron concentration changes caused by neutron irradiation and bromination has been determined. Approximately 20 Mwd correspond to 1.0 atom percent of bromine. From Fig. 8 it can be shown that the change in thermal conductivity due to bromination is less than one-third of that caused by an equivalent neutron exposure. Thus the thermal resistance due to scattering of phonons by electrons cannot cause more than one-third of the change observed on neutron irradiation. Probably, the bromine atoms located at the boundaries do scatter phonons to a slight extent and cause the observed effect.

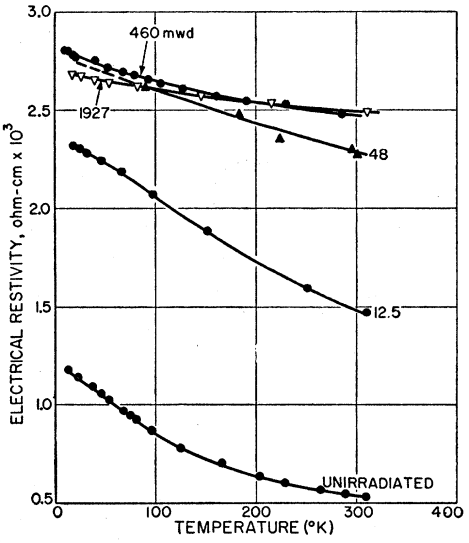

FIG. 10. Electrical resistivity of AGOT–KC graphite for various neutron-irradiations (at about 30°C).

III. ELECTRICAL RESISTIVITY

Although the primary object of this research was the measurement of thermal conductivity, the use of the Kohlrausch method gives the electrical resistivity also. The electrical resistivity of the Canadian natural graphite was measured separately both for completeness and because the electrical resistivity is very sensitive to sample perfection. The electrical resistivity of single-crystal graphite has been investigated by Primak and Fuchs.[12] They find a positive temperature coefficient of resistance as did Kinchin.[13] Artificial graphite as well as small crystallite natural graphite shows a negative temperature coefficient of electrical resistance.

The resistivity of the Canadian natural and the pyrolytic filament is shown in Fig. 9. The Canadian natural has a temperature dependence similar to that

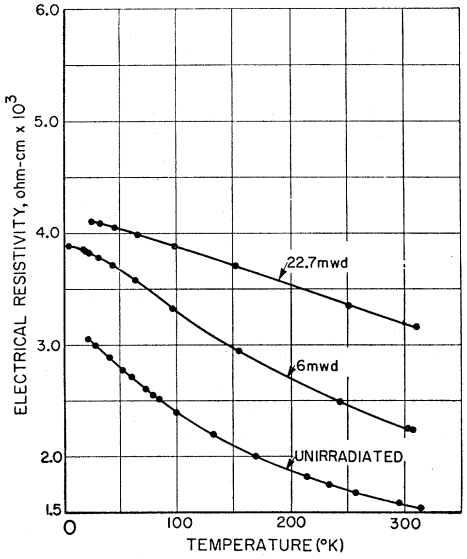

FIG. 11. Electrical resistivity of AWG graphite for various neutron irradiations (at about 30°C).

[12] W. Primak and L. H. Fuchs, Phys. Rev. **95**, 22 (1954).
[13] G. H. Kinchin, Proc. Roy. Soc. (London) **A217**, 9 (1953).

found by Primak and Fuchs, although the curve is flatter in the higher temperature region than that of Primak and Fuchs. The pyrolytic filament has a negative coefficient presumably because of the small crystallite sizes.

The effect of neutron bombardment on the electrical resistivity is shown in Figs. 10, 11, and 12. It can be seen that the primary effect is to increase the resistivity up to a maximum value with a very slight decrease for long irradiations. This saturation is presumably due to the counteracting effects of the simultaneous increase in scattering and increase in number of charge carriers.[10] The resistivity decreases when only the number of charge carriers is increased, as in the brom-graphites. The decrease in the magnitude of the temperature dependence is probably due to the shift in the Fermi level away from the zone boundary. The effect of changes in the Fermi level alone can be seen by the change in resistivity on bromination. Hennig has shown[11] that there is little increased electronic scattering on bromination. Thus, the resistivity is decreased for low brominations. For brominations greater than 1 atom percent, this conclusion does not hold since extensive damage to the crystallites begins to appear. The results in Fig. 13 agree with those obtained by Hennig and extend the measurements below liquid nitrogen temperature.

IV. SUMMARY

The anomalous temperature dependence ($T^{2.7}$) of the thermal conductivity of pitch-bonded graphites reported elsewhere has been verified by an independent experimental method and in different types. However, the thermal conductivity of graphites in which significant amounts of nongraphitic carbon are not present (natural crystals and pyrolytically formed) has the temperature dependence (T^2) required by simple lattice-conduction theory. It is thus strongly implied that the nongraphitic carbon present in pitch-bonded graphites is responsible for its anomalous behavior.

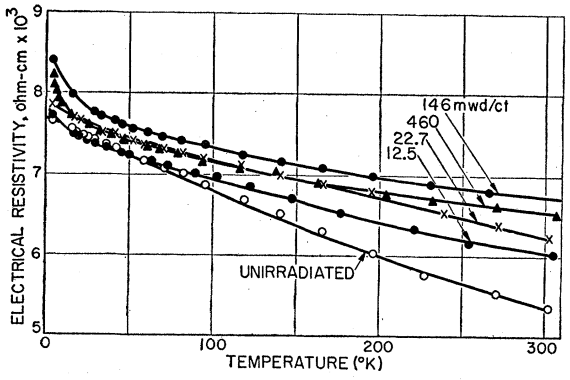

FIG. 12. Electrical resistivity of SA–25 graphite for various neutron irradiations (at about 30°C).

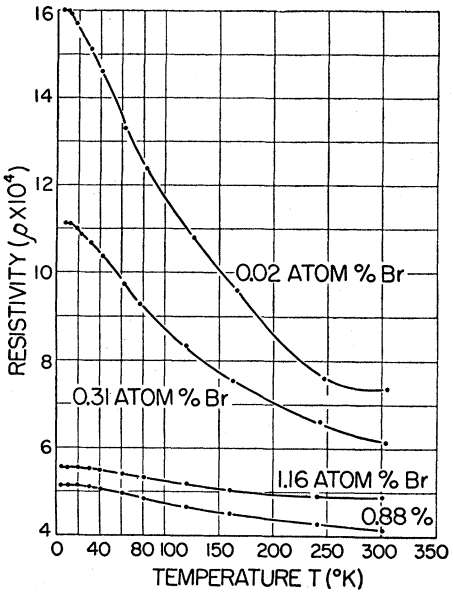

FIG. 13. Electrical resistivity of brominated AGOT–KC graphite.

At a given temperature, the thermal resistivity of graphite initially rises rapidly with exposure to neutron irradiation, but soon increases linearly at a slower rate. There is no evidence of saturation up to the highest exposures obtained, corresponding to a hundredfold reduction of the thermal conductivity. The exponent of the temperature dependence also decreases with exposure. By comparison with the effect of bromination, it is concluded that the change in electron concentration due to neutron irradiation cannot alone account for the major part of the reduction in thermal conductivity induced by neutron irradiation.

A semiempirical quantitative analysis of the observed temperature dependence and effect of neutron irradiation on the thermal conductivity of pitch-bonded graphites will be presented in the subsequent paper (II). The principal hypotheses used, i.e., that nongraphitic carbon plays a critical role and that electron-phonon interaction may be neglected, are very well supported by the present data.

The temperature dependence of the electrical resistivities of the unirradiated graphite samples used here are in agreement with those reported by other workers on similar materials. The primary effect of neutron irradiation is to increase the resistivity to a maximum value with a very slight decrease for long irradiations. These results and those for brom-graphite illustrate the competing effects of the trapping and scattering of conduction electrons by defects, in accord with existing theories correlating the electronic properties of graphite.

FIG. 1. Photograph of surface of a Canadian natural graphite sample.