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NEUTRON-INDUCED DISCOMPOSITION OF GRAPHITE

by

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PREFACE

These papers describe the results of the first investigations of the effect of fast neutron bombardment on the physical properties of graphite. The experimental work was done during and shortly after the Second World War at the Metallurgical Laboratory of The University of Chicago, the precursor of the Argonne National Laboratory. Texts of the various papers were prepared, for the most part, several years ago and no extensive re-writing has been done. The experimental data are invariant but the interpretation has tended to change in emphasis one way or another as time passed. A summary of these papers, from a point of view not inconsistent with current thinking, has been submitted for publication in the Journal of Applied Physics and should appear sometime during 1956.

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NEUTRON-INDUCED DISCOMPOSITION OF GRAPHITE^{a,b}I. FUNDAMENTALSMilton Burton^c and T. J. Neubert^{d,e}ABSTRACT

Fast neutron bombardment of graphite causes displacement of carbon atoms from normal lattice sites (Wigner effect); vacancies are produced and some of the displaced atoms are captured at interstitial positions and other trapping centers. The process is called discomposition. Elastic modulus, electrical resistance, breaking strength, and crystallite volume increase, and thermal conductivity decreases. The effects of heating are described. Results are interpreted in terms of a working model based on the activation energy required for the removal of the various effects. Contributions of various workers to the development of the model are reviewed.

^aBased on work done in the Radiation Chemistry Section, Metallurgical Laboratory, University of Chicago (now Argonne National Laboratory), during the period 1942 - 1946.

^bThis article was originally intended for publication as Chapter IV of Vol. 10A, Radiation Chemistry, of the National Nuclear Energy Series (Plutonium Project Record) under the editorship of Milton Burton.

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^eAlthough the name of Professor James Franck does not appear as an author, the writers are indebted to him for stimulation of this paper and for notable contributions to development of the ideas expressed. The importance of his gentle advice and persistent interest during the course of this work cannot be exaggerated.

1. Introduction

1.1 The Wigner Effect

In the early days of the Metallurgical Project, very little information existed about the effects of high intensity radiation. Consequently, all materials of construction conceivably subject to the influence of radiation were regarded as suspect, and some rather imaginative suggestions were made regarding possible difficulties. For example, a very early design of an atomic power plant showed small cylinders of uranium or of a uranium compound mounted in graphite bars. The plan included removal of stringers of such bars by simply pushing after a sufficiently long exposure. One question proposed (by E. Teller) concerned the possibility of freezing of the bars one to another as a result of irradiation. Conceivably, such freezing might occur as a result of opening and closing of carbon valence bonds at the surfaces of the bars. The suggestion could not be discarded lightly, because simple calculation showed that in plants operated as proposed enough energy was produced, and dissipated in the graphite, to open all the bonds at least once. An effort was made to produce such an effect artificially by exposure of graphite wedges under pressure before a deuteron beam, but no effect of the kind feared was detectable. Even yet, however, there is no certainty that such an effect would not be produced given a proper set of conditions.

In November, 1942, Wigner aroused much concern by announcement of an anticipated effect of fast particles on solids.⁽¹⁾ He showed, briefly, that such fast particles should act as projectiles and thus displace atoms from their normal lattice positions. According to early calculations, it appeared that fast neutrons produced in the fission of uranium would possess enough energy to displace either directly or indirectly ca 2×10^4 carbon atoms per neutron.⁽²⁾ Inside uranium a similar effect would be produced by fission recoils.

1.2. Definitions

Much has already been written about this subject.^(2,3) During the more than a decade that has elapsed since its activation, there have been created usages of expression foreign to the original workers and, in some respects, not conducive to understanding of the history of the subject and its development. For convenience, we therefore redefine some terms and use them in their original sense throughout this paper.

1.2.1 - The Wigner Effect, in its more general meaning, is the displacement of an atom from its position in a molecule or lattice as the result of momentum transfer in a collision involving an energetic particle.

1.2.2 - Discomposition is the displacement of an atom from its position in a crystalline lattice and its entrapment at a non-lattice point. This paper discusses Wigner-effect discomposition, but discomposition is not restricted to this class of phenomenon.

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1.2.3. - Bombardment - This series of papers is concerned exclusively with the effects of bombardment of graphite by neutrons. In the ensuing discussion the terms "bombardment," "exposure to radiation," and "irradiation" refer exclusively to bombardment by neutrons.

1.3. Early Experiments

The first calculations of the anticipated extent of the Wigner effect were of necessity of a very simple nature, so selected as to give high results. Nevertheless, the estimates so obtained gave little assurance that with the radiation sources then available a detectable effect could be produced in a reasonable time.^(1,4) It was decided to make neutron bombardments of small graphite samples at the highest energies then available for the work (the Washington University cyclotron at St. Louis) and to examine the effects of such bombardment by very sensitive tests of changes in structure. One rather obvious method was the measurement of electrical resistance; Paper III in this series relates the precautions adopted in the early work for prevention of adventitious and misleading changes not related to effects in the interior of the graphite. The more subtle method of examination of elastic modulus (Paper II of this series) was suggested by Dr. V. C. Hamister, Director of Research of the National Carbon Company. For the early testing work in this category, the Radiation Chemistry Section sought and obtained the assistance of Dr. E. U. Condon, Associate Director of Research, Dr. S. Siegel, and Dr. L. P. Hunter of Westinghouse Research Laboratories, East Pittsburgh, Pa.

The first bombardment took place in the period February to April 1943. The startling and unexpected feature of this early work was the easily measurable nature of the changes produced. It was immediately evident that a new tool for production of physical changes in solids had been discovered.

1.4. Objectives of This Paper

This is one of a sequence of papers, all the remainder of which are experimental. Papers II to VIII, are by former members of the Solid Elements Group of the Radiation Chemistry Section; Papers IX and X are by members of the Radiation Physics Section and their collaborators at Carnegie Institute of Technology. The purpose of this paper is to show the relationship of these investigations to each other in terms of the model current at the time of the work. It is impossible to avoid some modification of the original model resultant simply from maturation of ideas. However, throughout this report an effort is made to avoid implication of preknowledge, particularly because better understanding may be based on data or information acquired after 1946; for this reason the authors have leaned heavily on the precise wording of documents prepared prior to that time.

2. Graphite

2.1 The Ideal Lattice

Graphite has a layer lattice structure, as shown in Fig. 1. Carbon atoms are arranged in planes, the atoms within a plane forming a network of hexagons. From another view (conventional for the crystallographer) a plane is arranged in rhombi with atoms at corners and one atom one-third of the way along the long diagonal. In successive layers alternate corners of each hexagon lie above and below the centers of hexagons. Details of periodicity of the structure appear to be incompletely established.⁽⁵⁾

Fig. I. 1.

Two layers of the graphite lattice. The rhombus (base of unit cell) shown in layer 1.

The two fundamental constants in the graphite lattice are a_1 , a characteristic distance between carbon atoms in the planes (shown in Fig. 1), and a_3 , the distance between alternate planes. The precise values of the distances vary. The values of a_1 vary less than do those of a_3 . There seems to be some relationship between the value of a_3 and perfection of crystallization. Typical values in Angstroms are:

	a_1	a_3
Natural graphite	2.456	6.70
Artificial graphite	2.457	6.71
Lampblack	2.450	6.77

2.2 The Real Lattice

Natural graphite is by no means sufficiently pure for the purposes of a graphite-moderated atomic power unit. However, the crystals of which it is composed are larger than any crystals of artificial graphite yet synthesized. On the other hand, neither natural nor artificial graphite contain absolutely flat or perfect planes. Simple theoretical considerations⁽⁶⁾ suggest that vacancies occur in any "perfect crystal" at normal temperatures. In graphite such vacancies involve not only the absence of a carbon atom from its lattice position, but also the outward displacement from that position of all the adjacent carbon atoms. The latter are actually pulled away from the hole by the outer ring of atoms which in turn surrounds them. This greater density of atoms in the vicinity of the hole exerts a greater-than-normal attraction on the atoms in the adjacent planes. The anticipated result is a waviness in each of those planes in such a neighborhood, somewhat as shown in Fig. 2.

Fig. I. 2. Appearance of planes in the vicinity of a vacancy.

The probability of existence of interstitial atoms between the planes of normal graphite appears to be remote. If present by some chance in the original magma they should not be able to survive graphitization temperatures. There is good reason to believe that they do not survive heating to 500° and certainly cannot endure beyond 1500° (cf section 4.4,4.7).

Natural graphite contains a high percentage of impurity; but it is unlikely that this impurity lodges between the planes, because the dimension a_3 is less for natural graphite than for the purer forms. Consequently, the impurity atoms in natural graphite must lodge between crystallites.

In natural graphite the crystallites are large and, to the uncritical eye, appear of visible dimensions. In artificial graphite, the crystallites may be likened to stacks of decks of playing cards, with the individual decks not too carefully packed on top of each other.⁽⁷⁾ Each crystallite contains about three or four decks about 50A thick and greater than 1000A across.

The individual crystallites are separated from each other by, and contained in, a magma of smaller, less completely organized crystallites of graphite. The best evidence available⁽⁸⁾ indicates that the crystallites in artificial graphite do not grow significantly during the process

of graphitization of the coke from which they are produced. Seemingly, they remain approximately the same size as the crystals in the original coke fragments, but their perfection increases during the process of graphitization. The magma of smaller crystallites presumably comes from the pitch used as a cementing material in the process of graphitization.

Graphite of reactor grade contains a significant concentration of hydrogen and sulfur in addition to metallic impurities: a typical analysis showed 320 ppm of nonaqueous hydrogen and 175 ppm sulfur. Such concentration of impurity can be accommodated at the layer edges without interference with the normal graphite layer structure, just as must be assumed for natural graphite.

3. Discomposition in Graphite: A Preliminary View

3.1. Primary Effects

The initial step in neutron-induced discomposition of graphite is the ejection of a carbon atom from its lattice site by a fast neutron. In this process the fast neutron loses an amount of energy determined by its own velocity and the conditions of collision. The carbon atom gains the energy either as kinetic energy or as ionization or excitation energy of its electrons. The fraction of the neutron energy transferred into translational energy of the carbon atom was in the original, deliberately exaggerated calculations taken as unity. Later, it was appreciated that for high-energy neutrons a large fraction of the energy is involved in electronic processes. Seitz's conclusion⁽²⁾ that a 2-Mev neutron can be responsible for displacement of ca 2×10^3 carbon atoms takes into account the variation of amount of electronic excitation with energy of the impinging particle; it is based on the assumption that the activation energy for displacement of any atom from its lattice site is ca 25 ev.

A calculation of the number of carbon atoms displaced includes consideration not only of primary impinging particles (i.e., neutrons) but also of the cascade of secondaries. Carbon atoms ejected from their lattice positions by impinging neutrons themselves have sufficient energy to eject other carbon atoms. These secondaries in turn may eject others. The process repeats itself until the carbon atoms are reduced in energy below the minimum value required for ejection of a carbon atom from its lattice position. Some notion of the latter value may be obtained from the heat of sublimation of graphite to atoms variously given now as 141.7 and 170.6 kcal/mole.⁽⁹⁾ The energy required for ejection of an atom from the interior of a graphite lattice must be twice this amount, i.e., near 300 kcal/mole. On the average, a carbon atom will give up one half its kinetic energy as kinetic energy to another carbon atom. Consequently, on the average the carbon atoms will be slowed down to a kinetic energy of roughly 26 ev before they cease to displace other carbon atoms from the lattice. Seitz's value for this quantity would be about twice as great.

3.2 The Perfect Crystal of Infinite Extent

Consider, first, the changes producible on irradiation of a perfect graphite crystal of infinite extent. Initially, there are no irregularities, no vacancies, and no free carbon atoms. The impact of a single neutron on a carbon atom changes the picture. On the average about one-seventh of the energy is transferred from a neutron; the carbon atom, now partially ionized, hurtles through the lattice, displacing other carbon atoms which behave similarly, regaining their electrons and ultimately losing their components of momentum perpendicular to the planes. Depending upon the amount of energy each still holds, it continues to move somewhat freely between two of the planes.

In the region between the planes there are, of course, some transverse forces so that we may expect that even if no other traps are present the free atom would come to temperature equilibrium with the graphite and perhaps settle down as Mulliken⁽¹⁰⁾ has suggested, with the production of a "buttoning effect" between the planes.

Actually, once the crystal has been irradiated it is no longer perfect. The vacancies produced by the irradiation are themselves traps with a structure such as suggested in Fig. 2 (see section 2.2).

A vacancy is thus not the mere absence of a carbon atom; it is composed of the vacant lattice point itself, the dense region in the plane surrounding that point, and local distortions (ripples) in adjacent planes. Capture of a carbon atom by such a vacancy may not be an elementary process. The reversal of the formation process (ignoring the role of the impinging particle) is

However, the capture process need not be so simple as reaction (c1) implies. It may be

where reaction (c2) implies that the complex is thermodynamically unstable relative to the normal lattice and may be, in effect, a step en route thereto. In the ensuing discussion, the symbol c refers to combination processes, such as reactions (c1) and (c2), d to decomposition processes, and e to activation energies for single events. We may then write with certainty: $\epsilon_{c1} \gg \epsilon_{c2}$. It is not necessarily true that ϵ_{d2} for the reaction the inverse of (c2) is sufficiently greater than zero to confer significant stability on the vacancy-atom complex. More importantly, reaction (c2) may not be a simple step en route to the perfect lattice. Capture may occur one plane removed from the vacancy. Reference to possible varieties of vacancy-atom complexes is made to emphasize the multiplicity of even relatively simple ways in which a carbon atom may be trapped at a non-lattice point.

Yet another class of trap exists in the irradiated perfect crystal. Atoms trapped weakly between the planes are themselves rather effective as traps. For the addition of a second atom ϵ_c is probably low. On the other hand, the two atoms in the trap are now held more firmly than either would be alone⁽¹¹⁾ so that ϵ_d for the removal of either would probably be very high. The growth of a compound trap by accretion of free atoms would seem to be a highly probable process, because ϵ_c would be expected to remain small. On the other hand, ϵ_d for the exterior atoms might become somewhat smaller for a large clump than for a small one, because the forces are more and more of the van der Waals type in such cases.

3.3 The Perfect Crystal of Limited Extent

Consider now a crystal of limited extent. In a single crystallite there are about 50 planes and thus $50 \times 2.4 \times 10^3$ or 1.2×10^5 edge sites and about 2×10^6 exterior surface sites. Nevertheless, the latter appear to play no significant role in possible entrapment of carbon atoms. Apparently, ϵ_c for entrapment of a carbon atom at either kind of site will probably be zero, since there is a similarity to condensation from the gas phase onto a surface (cf section 5.3.1). On the other hand, ϵ_d for decomposition of the two classes of trapped atoms so formed will be quite different. For lattice ends, ϵ_d will be large; i.e., of the order of a few ev. The forces involved in the sitting-down of an atom on an exterior plane will be largely of van der Waals type and therefore extremely small; in this connection we note the interplanar distance in graphite, ca 3.35A, as compared with the interatomic distance, 1.42A, in the planes. To reach a surface an atom must possess sufficient transverse momentum to pierce a surface place; it is extremely improbable that it would then sit down on the plane. An atom coming from outside the crystal might sit down on the surface but ϵ_d would be so low that the most probable next event would be a diffusion of the atom along the plane to its edge where it would be trapped with a relatively large ϵ_d .

Just as atoms trapped interstitially within the crystal may serve to trap other atoms so may those trapped at the end of the lattice. Growth of such traps must occur by accretion of additional free atoms. The edges of planes are loaded with impurity atoms and flaws. Consequently we may expect edge clusters to grow inwards. (On the exterior-surface planes outward growth is possible.) For inward growth ϵ_c will be very small, as is ϵ_c for growth of interior clusters. We might expect that ϵ_d for edge clusters may be similar to that for interior clusters. However, since the linear extent of the edge is quite large, it is possible that atoms trapped at edges may act like clusters containing only a few atoms, in which ϵ_d is also large. In other words, ϵ_d is always relatively large for end traps but reaches a maximum for interior clusters when they contain a very small number of atoms (e.g., two or three).

3.4 Real Graphite

A real piece of graphite, whether natural or artificial, consists of many crystals. The ends of the crystals abut on other crystals and there may be some significant forces between them. Thus, ϵ_c for traps in such positions may be slightly above zero. There does not seem to be any reason, however, why ϵ_d should be sensibly reduced. An idea of the relative importance of such regions of contiguity is given by the notation that in the case of a plane 1000A across the number of atoms in the plane is ca 10^6 ; the number of edge atoms is about 2.4×10^3 .

A further characteristic of real crystals is the presence of impurities. If present in sufficient quantity, they will, as Mulliken points out, (10) affect the number of available end traps. Furthermore, they may not only change ϵ_c and ϵ_d in such regions, but they themselves may act as traps for the free C atoms. When they act as traps, ϵ_c will be small and ϵ_d will be large (cf the similarity to carbide formation). Impurity atoms trapped in the interior of graphite crystals would have similar properties. However, when clumps grow about such impurity centers the exterior portions would resemble other more usual carbon clumps.

A real crystal of graphite always contains vacancies. At the temperature of formation, a crystal of any substance would contain a number of vacancies determined by purely thermodynamic considerations. In general, as the temperature is lowered, the vacancies become frozen in, and their concentration far exceeds the equilibrium value characteristic of the temperature at which the crystal is studied (see section 2.2).

In section 2.2 it is indicated that the vacancies by themselves may create other traps: i.e., high concentration regions (see Fig. 2) and distortions of planes called ripples. Simple distortions may also exist for other reasons, e.g., transverse forces exerted by abutting crystals. Also, there may be traps in crystals resulting from the presence of unorganized carbon atoms. Thus, it follows that real graphite contains initially many of the types of traps which come into existence in a real crystal as a result of the process of neutron bombardment. Their properties have already been considered.

4. Observations to be Explained: A Brief Summary as of August, 1945

4.1 Effect of Neutron Bombardment on Elastic Modulus (12)

When graphite is exposed to fast neutron bombardment, either at a cyclotron or in a pile, the elastic modulus, E_f , (as measured by resonance frequency for longitudinal vibration) varies with exposure $\underline{L}$ (13) according to a law of the form: $(\partial E_f / \partial \underline{L})$ is positive; $(\partial^2 E_f / \partial \underline{L}^2)$ is negative. No simple expression for the function $E_f(\underline{L})$ has been found. Figure 3 includes a typical curve for variation of fractional increase in elastic modulus $(E_f - E_0)/E_0 = e_f$ with $\underline{L}$; e_f apparently approaches a steady state after sufficiently long exposure.

4.2 Effect of Neutron Bombardment on Electrical Resistance

Figure 3 shows that the fractional increase in electrical resistivity, r_f , of a collection of typical graphite samples increases with exposure to fast neutrons with a rate which decreases as the exposure continues. The law has the form

$$r_f^{-1} = AL^{-1} + r_{\infty}^{-1} \quad (1)$$

where A is a constant and r_{∞} is the fractional increase in resistivity at infinite exposure. As nearly as can be determined, the form of the law is the same within experimental error from the very beginning of exposure, i.e., $(\partial^2 r_f / \partial L^2)$ is always negative even at the lowest L values studied. Apparent deviations from such a relationship are probably to be traced to temperature uncertainties (cf section 4.5).

Fig. I. 3. Effect of neutron bombardment at about 35° on elastic modulus and electrical resistivity of artificial graphite.

4.3 Effect of Neutron Bombardment on Other Properties

Over a limited range of exposure of various pile graphites there is a roughly linear relationship between thermal resistance and electrical resistance, represented by the formula

$$\kappa^{-1} \simeq 3.2 \times 10^3 \rho \quad , \quad (2)$$

where κ is the thermal conductivity expressed in $\text{cal cm}^{-1} \text{deg}^{-1} \text{sec}^{-1}$ and ρ is in ohm-cm. Although the relationship is linear, the Wiedemann-Franz law is not followed. Since this equation holds roughly for all samples studied, irrespective of their history, it may be surmised that $1/\kappa$ is affected by neutron bombardment in much the same way as ρ .⁽¹⁴⁾

For various pile graphites exposed to radiation and also exposed to radiation and annealed at 1000°C , the fractional increase in cross-breaking strength is roughly the same as the fractional increase in elastic modulus.⁽¹⁵⁾

4.4 Effect of Subsequent Heating on Neutron-Induced Changes in Graphite⁽¹⁶⁾

For the most part, subsequent heating (annealing) decreases the neutron-induced effects on elastic modulus and electrical resistivity. Heating to any particular temperature tends to give a limiting resistance and a limiting elastic modulus lower than those induced by neutron bombardment at low temperature, but higher than the original values before exposure. Up to 1000°C , the higher the temperature of heating the greater is the effect on the asymptotic values of those quantities, defined as the value obtained after heating so prolonged that further changes in the quantities do not exceed the experimental errors. However, heating even to 1000°C does not restore elastic modulus or resistivity to initial values.

An interesting feature of the data is the dissimilarity of the curves relating residual fractional increase in elastic modulus, $\underline{e}_t$, and the corresponding parameter $\underline{r}_t$ to time of heating at a particular temperature (cf Fig. 4). The conclusion is inescapable that at least two types of disturbances are responsible for the effects observed. An analysis of activation energies for disappearance of these effects, according to the method of Vand,⁽¹⁷⁾ very definitely shows two general classes of disturbances with mean activation energies for their disappearance near 1.4 and 1.8 ev.

Fig. 1. 4

Dependence of residual fractional increase in elastic modulus and electrical resistivity on time of anneal at 260°C; the course of approach to asymptotic values.

4.6 Essential Difference Between Elastic Modulus Effects and Electrical Resistance Effects

For short exposures, the elastic modulus effect is substantially independent of temperature below 130°C whether the heating be during or after exposure. Under the same conditions the Wigner effect on electrical resistance is very dependent on temperature. Temperatures below 100°C serve markedly to decrease the Wigner effect on electrical resistance without any perceptible effect on elastic modulus. The conclusion is that there is a factor which enters into increase of electrical resistance which has no effect on elastic modulus. The latter conclusion receives additional support from another view of the data. As Eq. 1 indicates, the relationship between fractional increase in resistance and exposure is not linear. However, for exposures in which the ratio r/r_{∞} is small, the relationship is essentially linear. Such a linear relationship is not found for increase in elastic modulus. Furthermore, levelling-off of the fractional increase as a function of exposure occurs much earlier for elastic modulus than for electrical resistance.

4.6.1 - Approach to a Limiting Value - In asymptotic heating experiments (see section 4.4) samples are annealed at any one temperature until there is no significant change in the residual increase in elastic modulus and electrical resistivity. Figure 4 shows plots of two annealing curves at a single temperature; results at other temperatures are similar. In the work selected, the effect on electrical resistance was no longer perceptible after ca 500 minutes of heating; the effect on elastic modulus continues even beyond 5000 minutes. This result demonstrates that a type of decomposition which affects elastic modulus has no perceptible effect on electrical resistance.

4.7 High-Temperature Annealing

Figure 5 summarizes some data on asymptotic heating experiments (cf. section 4.4) extended to very high temperatures. The interesting feature here indicated is that samples whose residual fractional increase in electrical resistivity has been reduced to a relatively small value by prolonged heating below ca 1100°C experience marked increase in resistivity at about that temperature, passing through a maximum at ca 1300°C. On further annealing at even higher temperature the residual fractional increase is reduced almost to zero. The elastic modulus behaves differently. The residual fractional change decreases to smaller and smaller positive values with increased temperature and ultimately becomes extremely small and perhaps negative at temperatures exceeding ca 1500°C. The conclusion is that the type of discomposition involved is affected only by high-temperature heating and appears to be different from that implied by the other observations summarized in previous portions of section 4. Furthermore, the growth, followed by decrease, of electrical resistivity at ca 1300°C suggests that, in the process of destruction of this type of discomposition, still another variety of disturbance is produced.

Fig. I. 5. Effect of prolonged heating at various temperatures (asymptotic annealing) on residual fractional increase in electrical resistivity of neutron-bombarded artificial graphite.

5. Elaborations of the Model

5.1 Some Conclusions from the Facts

The results summarized in Section 4 seem to show that there are at least four different types of discomposition induced in graphite by neutron bombardment. One type has a major effect on electrical resistance and a minor effect on elastic modulus. For another type the converse is true. These two decomposition regions have different average activation energies for their destruction. Thus, each of the types may itself be composed of a continuous series of sub-varieties. In addition, there is a type already present at low exposure, characterized by its sensitivity to heating below 130°C, which appears to have an effect on electrical resistance without any perceptible effect on elastic modulus. The fourth type apparently has a very high activation energy for its destruction. In the course of its disappearance a new disturbance center (not necessarily present as a result of neutron bombardment itself) is produced. This latter type of disturbance also has a large activation energy for its destruction; it seems to have an effect on electrical resistance without a major influence on elastic modulus. Another class of phenomena must also be considered. Air-exposed and vacuum-exposed samples behave differently in their responses, both to bombardment and to subsequent heat treatment. This effect cannot be identified with a necessarily different class of disturbance; it does reflect the fact that a purely chemical effect may affect neutron-induced changes. Any satisfactory model must be consistent with the corresponding six groups of pertinent facts.

5.2 Fate of Displaced Atoms

Historically it is interesting to note that practically all details of possible occurrences during exposure of graphite were considered by Mulliken^(10, 18) even before he knew of the existence of temperature effects and of the speculations of the Radiation Chemistry Section. He indicated two important points. Carbon atoms ejected from normal lattice positions ultimately come to rest in interplanar positions and produce "buttoning effects"; such atoms are weakly held and may be freed from such positions by heating. Zachariasen later examined typical samples of heavily exposed graphite by X-ray technique⁽¹⁹⁾ and was able to show the existence of "blisters" induced in the carbon planes by neutron bombardment.⁽²⁰⁾ Zachariasen did not consider these blisters as evidence for a buttoning effect and indeed suggested that the planes might actually be pushed apart by interstitial atoms; an increase in crystallite volume, simultaneously reported,⁽²⁰⁾ supported this view. The previously found effect of temperature (in the range up to 500°C) on neutron-induced fractional changes in elastic modulus and electrical resistance were consistent with most of Mulliken's suggestions; however, they were not evidence per se for a buttoning, as opposed to a displacement, effect.

We may summarize the then-current concept of the mechanism of the Wigner effect in the following terms. Bombardment of graphite by neutrons causes several types of disturbance. Ejection of carbon atoms leaves vacancies. Such ejected atoms may come to rest in interstitial positions of stability determined by the relative positions of the nearest carbon atoms in the two adjacent planes. Some of the ejected carbon atoms come to rest at unoccupied sites at the edges of planes. The vacancies and the interstitial carbon atoms make important contribution to electrical resistance and elastic modulus changes. Their creation causes the displacement (either negatively or positively) of adjacent carbon atoms. Each elementary disturbance incites several surrounding disturbances. All of them make a contribution to the changes in properties.

5.3 Details about Traps

As indicated in section 3.2, a vacancy, no matter how produced is not the mere absence of a carbon atom. In a discomposition process the carbon atom is ejected so fast that the surrounding atoms are left in positions corresponding to the normal graphite structure. It is only reasonable to expect that the equilibrium structure will be different from this, and that within a few vibration periods the whole atmosphere of adjacent carbon atoms will shift relative to the vacancy to new positions (see Fig. 2). Energy is given up when such shifts occur. Conversely, in order for a carbon atom to annihilate a vacancy, activation energy is required.

A free carbon atom can travel about in the space between planes without giving up much energy. It loses energy very rapidly, however, when traveling perpendicular to the planes. For this reason the component of momentum perpendicular to the planes is rapidly lost, and the carbon atom oscillates in the region between planes until it is trapped. The free carbon atom can come to rest at a variety of traps. In general, that trap which requires the smallest activation energy for the entrapment process is preferentially occupied. If a trap is sufficiently shallow, the carbon atom there trapped will be released as a result of ordinary thermal vibration.

5.3.1 - Traps and their depths - In Mulliken's consideration⁽¹⁰⁾ of the nature of the entrapment process he suggested that the carbon atoms between planes are trapped by both planes, perhaps a little more weakly by one than by the other, the so-called "buttoning effect," Mulliken did not estimate the depth of the trap, i.e., the energy of activation of the process required to free the carbon atom from the trap. Regardless of whether the interstitial carbon atom is really involved in a buttoning effect (cf. Zachariasen⁽²⁰⁾), it would appear from consideration of lattice distances (i.e., $3.35\text{\AA}$ interplanar distance) and C-C valence bond lengths (i.e., $1.55\text{\AA}$ in C_2H_6 , $1.39\text{\AA}$ in C_6H_6) that the bonding to at least one of the carbon planes must be very weak indeed. The bonding to the other is also rather weak, the energy of the bonds depending on the number of carbon atoms in

the group of interstitial atoms as well as on their position relative to the nearest carbon atoms in the planes. Some of the bonds have a strength probably no greater than 0.8 ev. The evidence for this conclusion will be developed as we go along. It is sufficient to say that it is one aspect of the model here presented that all the increase in electrical resistance is attributed exclusively to vacancies and interstitial carbon atoms. Reference to Paper VII (cf. Section 4.4) indicates that some of the fast-neutron induced increase in electrical resistance is removed by heating even to relatively low temperatures; one fifth of the electrical resistance increase disappears on standing at room temperature for a year. This fact leads to the conclusion that the energy with which the weakest disturbances are bound does not exceed 0.8 ev. The graphitization processes in the manufacture of artificial graphite involve temperatures in excess of 2700°C. This fact suggests that vacancies are removed at very high temperatures. Thus, the 0.8-ev activation energy process probably pertains to displacement of interstitial carbon atoms. A corollary conclusion is that the annealing process occurring at 1000 to 1500°C (see Section 4.7) is in some way related to diffusion of vacancies; the temperature data suggest that the activation energy is greater than 3 ev. Thus, for the reactions

it follows that $\epsilon_{d3} < 0.8 \text{ ev}$ and $\epsilon_{d4} > 3 \text{ ev}$.

The last paragraph implies also that vacancies survive at temperatures adequate for removal of interstitially trapped carbon atoms; i.e., the rate r_{d4} is practically zero at temperatures at which reaction (d3) and all reactions of a similar class proceed vigorously. A logical conclusion, therefore, is that reaction (c1) (cf. Section 3.2) has an activation energy adequately high to prevent its occurrence in significant degree at those temperatures. Furthermore, this result makes it possible to make some statements concerning disturbances of the vacancy-atom complex type produced (as suggested in Section 3.2) by reaction (c2). The reaction

is a path for destruction of vacancies. On the basis of frequency-factor considerations it appears to be a far more probable process than reaction (c1), for we note that (d5) is unimolecular and (c1) is bimolecular. Thus, we are constrained to one of two conclusions: either the activation energy ϵ_{d5} is very high or reaction (d5) does occur readily, but only a relatively small number of carbon atoms are initially trapped by reaction (c2). The latter conclusion is by far the more simple and the more probable. It suggests both that the very low temperature annealing process by which

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electrical resistance is decreased without significant effect on elastic modulus is reaction (d5) and that there is an alternative path for disappearance of vacancy-atom complex disturbances. One such path is the acquisition of additional carbon atoms on prolonged exposure:

This conclusion is also consistent with the fact that sensitivity to low temperature annealing decreases with exposure (cf. Section 4.6.1 and Paper VII).

This last result has two-fold meaning: disturbances of the vacancy-atom complex type affect electrical resistance but are without effect on elastic modulus (and thus probably do not link planes together); disturbances of the vacancy-molecule complex type affect both electrical resistance and elastic modulus (and thus probably link planes together).

A major difficulty in the model, which we are not prepared to explain except with strictly ad hoc assumptions, is the curious variation of the ratio of fractional increases, e_f/r_f , with exposure. That number is at first greater than unity but drops to less than unity above the values $e_f = r_f \sim 0.75$. The only simple explanation which has occurred to the authors is that there are a small number of traps initially present, which represent discontinuities of structure where atoms can be captured and held firmly, strengthening the structure of the material but without local effect on electrical resistance because the situation was already disturbed. After these regions are filled up, the elastic modulus no longer increases so rapidly with exposure. The consequence of such a view is that the elastic modulus would vary with exposure according to the relation

$$E = E_0 + \int_0^L \frac{\partial E_1(L)}{\partial L} dL + \int_0^L \frac{\partial E_2(L)}{\partial L} dL$$

where we note that $\partial E_1/\partial L$ becomes zero for values of $L > L_1$. This statement has the minimum virtue that it fits the fact that no simple functional relationship exists between elastic modulus and exposure (cf. Section 4.1).

A typical class of trapping center which comes automatically to attention in this regard is the class of lattice edge traps. (18) For the reaction

the activation energy would appear to be small or nearly zero. (21) Disturbances of this class should be without effect on electrical resistance. However, if they serve to link planes together they might have some effect on

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elastic modulus. Neubert and Novick⁽²²⁾ did a series of experiments on the rate of bromine uptake in interplanar positions in graphite.⁽²³⁾ They found that the rate of uptake at a particular temperature was a function of the fractional increase of elastic modulus but not of electrical resistance. The phenomena of the diffusion involved the pushing - apart of adjacent planes. Thus, the bromine uptake results indicated that the elastic modulus is related to a factor which involves connection between planes and at the same time that such connection between planes has no special effect on electrical resistance. The only such connections which can be imagined to be devoid of effect on electrical resistance are those lying near already disturbed locales i.e., edge sites and regions of disturbance (dislocation) within the crystallites themselves.

In the simple Mulliken picture, carbon atoms may come to rest in interplanar positions where they are presumably held by weak forces. It is reasonable to suppose that analogously to reaction (c6), the simple Mulliken trap may also catch a second atom in a low-activation energy process to give a molecule complex:

It is important to note that one could expect somewhat different activation energies for the processes in which the two types of complexes would be destroyed by heating, i.e., for the two reverse reactions (d6) and (d8). Whether these activation energies are related to the values 1.4 ev and 1.8 ev discussed in Section 4.4 is difficult to establish.

Another class of disturbance is produced by the acquisition of additional free carbon atoms by trapped molecules (or other types of trapped atoms). Such additionally bound trapped atoms may contribute somewhat to increase in elastic modulus; it is difficult to see that they would contribute significantly to increase in electrical resistance. Levelling-off of modulus as a function of exposure eventually occurs.

The fact that electrical resistance continued to rise when elastic modulus had already levelled off emphasizes the continuing contribution of vacancies to electrical resistance. Such contribution, of course, decreases in significance as the crystal becomes more and more disordered.

5.3.2 - Heat of Formation of Traps - In general, the data show that the energy required to eject a carbon atom from its lattice position is high and from a trapped position relatively low. In the annealing process, in general, carbon atoms should be released from shallow traps and captured in deeper ones. Such a phenomenon should be reflected in energy release. Particularly, in heat capacity studies of bombarded graphite, this phenomenon should indicate an apparently low heat capacity. This phenomenon was suggested originally by Szilard⁽²⁴⁾ and observed by Maurer.⁽²⁵⁾

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5.4 Hall Coefficient

Maurer²⁶ found that the Hall coefficient of graphite changes signs on irradiation and again after annealing at sufficiently high temperature. Such a result indicates (a) that both positive holes and electrons contribute to electrical conductivity of graphite, (b) that the annealing process is effective in changing the number and type of electrical disturbance centers, (c) that both irradiation and annealing have an effect on the relative numbers of hole and electron conductors. Further studies and interpretation of this phenomenon will probably be described in forthcoming papers by Hennig.²⁷

5.5 Summary of the Model

The best graphite employed in this study was far from perfect because no real graphite can be. Before it was exposed to neutron bombardment it contained as possible irregularities originally present vacancies, ripples, minor displacements (e.g., submicroscopic mechanical breaks), lattice edges, impurities at edges, and intercrystalline material. All these have effects on elastic modulus and electrical resistance and any of them may function as more or less efficient trapping centers for displaced carbon atoms. Except for certain nuances regarding the vacancies themselves, activation energy for capture of displaced carbon atoms is probably low. The characteristics of the disturbances so produced have been described in previous sections. They are summarized in Table I.

6. Acknowledgements and Apologies

The present paper represents an imperfect distillation of ideas developed up to August 1945 and modified to some extent by information more recently developed. The authors express their appreciation specifically to a number of people, members neither of the Radiation Chemistry Section nor of the Solid Elements Group: Professor James Franck for the invaluable role already described; Professor E. P. Wigner for the original suggestions and continuing interest; Professors R. S. Mulliken, O. Stern, E. Teller, L. Szilard, W. H. Zachariasen, F. Seitz and his associates, Professors I. Estermann, M. Gensamer, J. S. Koehler, R. J. Maurer of the Radiation Physics Section; Doctors V. C. Hamister and H. G. MacPherson of the National Carbon Company, all of whom generously contributed original ideas in the course of repeated discussions; and also Professor I. Perlman and Doctors J. P. Howe and N. Hilberry who assisted generously in arrangements for special pile irradiations. Other acknowledgements for specific assistance appear in the individual papers. To all these people we express appreciation and apologies, the latter because we were not always certain of the source of ideas. If in any event in our zeal to give credit to one we have overlooked an equally important contribution to the same idea by another, we ask to be forgiven. Our excuse is that many of the ideas were current subjects of discussion before they were put in report form by an individual or group.

TABLE I

Summary of Characteristics of Neutron-Induced Disturbance in Graphite^(a)

Disturbance	Carbon capture		Dissociation		Effect on		Reference section
	Reaction	ϵ_c	Reaction	ϵ_d	e_f	e_r	
Additional vacancies	(<u>c</u> 1)	High	(<u>d</u> 4)	> 3 ev	No	Yes	4.7, 5.3.1
	(<u>c</u> 2)	Low					
Vacancy-atom complex	(<u>c</u> 6)	?	(<u>d</u> 3) or (<u>d</u> 5)	< 0.8 ev	No	Yes	4.6.1, 5.2, 5.3.1
Interstitial bound atom	(<u>c</u> 8)	?	(<u>d</u> 3)		No	Yes	
Vacancy molecule complex		Low	(<u>d</u> 6)	1.4 or 1.8 ev	Yes	Yes	4.4, 5.3.1
Interstitial bound molecule		Low	(<u>d</u> 8)		Yes	Yes	
Lattice edge	(c7)	Low	-				
Extended complexes:							
in interior		Low		< 1.4 ev	Yes	see 5.3.1	4.4, 5.3.1
at edge		Low		> 1.8 ev	Yes	No	4.6.2, 5.2

^aSymbols have significance as follows. ϵ_c , ϵ_d are activation energies for carbon atom capture and dissociation (or destruction by diffusion in the case of vacancies), respectively; e_f , e_r are fractional increases in elastic modulus and electrical resistivity respectively; "No" or "Yes" indicates whether the type of disturbance has an effect on such quantities. Reactions and reference sections are listed by their numbers in the text. In some cases only the c (i.e., combination) or d (i.e., destruction) reaction actually appears in the text; in such event the reaction listed in this table is merely the reverse of the corresponding reaction in the text. In other cases no reaction is written in the text; it is merely implied by the table.

Another apology refers to the content of this paper. We have attempted to be historically accurate about the ideas presented. We have also attempted to avoid inclusion of ideas which have not stood the test of time. On the other hand, we have tried not to include ideas which derive from more recent work, by other workers, which will doubtless be published shortly. We hope that we have succeeded in this effort without pre-emption of the positions of our more recently active colleagues.

The authorship of each of the papers in this series is limited to the few who had a major role in each of the tasks reported. On the other hand, it should be emphasized that all the members of the Solid Elements Group whose names appear as authors on any one of the papers made invaluable contributions to all of them. All deserve any credit which may derive from any one paper.

Finally, one of us (M. B.), for the entire Radiation Chemistry Section, and the other (T. J. N.), specifically for the Solid Elements Group, extend their great thanks to Dr. Oliver Simpson for encouragement, assistance, and pressure in breaking the log-jam of classification which blocked publication of this paper and the following group for so many years.

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II PRELIMINARY STUDIES OF ELASTIC MODULUS^{a,b}

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ABSTRACT

The effect of fast neutron bombardment on the longitudinal elastic modulus of artificial graphite has been investigated by the piezo-quartz resonator method. The elastic modulus of samples bombarded with cyclotron neutrons was found to increase with bombardment, rapidly at first and then less rapidly. For the longest bombardment the increase in elastic modulus was 46%. The heating of an irradiated sample to 3000°C caused a complete removal of the neutron-induced effect. Data are interpreted on the basis of interstitial disturbances and lattice vacancies produced during bombardment.

1. Introduction

During operation of a graphite pile, the process of neutron moderation dislodges carbon atoms from their initial positions in the artificial graphite structure by elastic collisions either between fast neutrons and carbon atoms or between recoil carbons and other carbon atoms.⁽¹⁻⁴⁾ Since artificial graphite is an aggregate of small, well-ordered graphite crystals⁽⁵⁾ with relatively very little intercrystalline bonding material, most neutron-induced processes were expected to involve expulsion of carbon atoms from crystallites, thus producing dislocated atoms and lattice vacancies. This discomposition phenomenon is called a Wigner effect.⁽¹⁾ The dislodged atoms can fall back into vacancies in the lattice, settle between the planes of the graphite lattice in metastable interstitial positions, or migrate to stable positions at the edges of the crystal.

The effects of residual lattice vacancies and interstitial disturbances on the mechanical properties of artificial graphite were investigated by a study of the elastic moduli of samples bombarded with fast neutrons. For

^aBased upon work done in the Radiation Chemistry Section, Metallurgical Laboratory, University of Chicago (now Argonne National Laboratory) during 1943. Participants in the work included M. G. Bowman, A. Novick, F. J. Safford and E. H. Phillips.

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this work a dynamic type of elastic modulus measurement was selected, since it was necessary to have a sensitive, reproducible, non-destructive test applicable to small specimens. In the technique employed stresses were, in general, small compared with the elastic limit. Consequently, creeping and elastic hysteresis effects were not troublesome.

2. Experimental Details

Various techniques for dynamic elastic modulus measurement are described in the literature.⁽⁶⁾ The procedure used in this work was that of Zacharias.^(6a, 7) A composite oscillator was formed by cementing the specimen to be measured to an X-cut piezo-quartz crystal. From the known resonance frequency of the quartz crystal and the observable resonance frequency of the composite oscillator, the resonance frequency of the specimen could be calculated.^(6a, f) The longitudinal elastic modulus, E , was then computed in the usual way, viz., $E = 4\rho f^2 \ell^2$, where ρ = density, f = resonance frequency, and ℓ = length of the specimen.

Specimens were right circular cylinders, ca 4 mm in diameter by 35 mm long. They were turned on a lathe and it was standard practice to take at least four cuts. Special care was taken to cut the ends flat and perpendicular to the cylinder axis in order that the specimen and the quartz resonator be coaxial when cemented together. The cementing was done with beeswax. Experiments in which the same sample was repeatedly recemented to the same quartz crystal showed that the observed resonance frequency was not seriously affected by the cementing operation. In the first experiments the samples were artificial graphite made from Whiting Refinery petroleum coke and coal tar pitch, designated as AGOT-W(T-15).^(5, 8, 9) The cylindrical axes of the samples were parallel to the extrusion axis of the stock bar. The average longitudinal elastic modulus was ca 10.8×10^{10} dynes cm^{-2} and the density was ca 1.62 g cm^{-3} .

After preparation and before measurements or irradiations were made, specimens were heated in a vacuum of 10^{-3} mm of Hg at 1000°C . In the preliminary experiments the heating lasted ten hours, but this technique was later revised to a 15-min heating in an atmosphere of helium at 1000°C . Weight losses in this annealing process averaged less than 0.1%. Samples were irradiated in soda glass ampules at an initial pressure of 10^{-3} mm Hg. Six successive bombardments were made and samples were remeasured after each exposure. As a result of various mishaps in the first three experiments, ampules occasionally would be found full of air after bombardment. Since no differences could be observed between samples irradiated in air or in vacuo the complication of sealed evacuated ampules was omitted in the last three experiments.

Samples were bombarded at the Washington University cyclotron. First neutrons (ca 16 Mev) were produced by deuteron bombardment (ca 12 Mev) of a water-cooled beryllium target and the graphite samples irradiated simply by fastening them against the back face of the target.⁽¹⁰⁾ The temperature of the samples during bombardment was estimated to have been $30 \pm 5^\circ\text{C}$. Relative numbers of neutrons were determined by measuring, in microampere-hours (μah), the total integrated deuteron current on the target. Deuteron currents, when the cyclotron operated at rated capacity, were ca 200 μa , which, assuming an efficiency of one neutron per 200 deuterons, amounts to a total production of ca 6.2×10^{12} neutrons/sec. In practice, however, it was difficult to obtain a precise correlation between μah and the number of neutrons traversing a specific sample. Neutron fluxes vary with the geometry and construction of the target, the instantaneous position of the deuteron beam, its energy, and the scattering angle. The total current on the target takes account of none of these variables. The most intense flux is in the region on a direct line with the original deuteron beam and closest to the beryllium target. An approximate neutron flux distribution⁽¹¹⁾ was measured by counting the Na^{24} activity induced by the (n, α) reaction in aluminum foils irradiated in various positions over the target face. From the resulting distribution it was roughly estimated that the most intense region had an area of ca 4.5 cm^2 and that the flux at 200 μa was ca 8×10^{10} fast neutrons/ $\text{cm}^2 \text{ sec}$. Because the samples extended out of this most intense region and because of wandering of the beam and of other fluctuations during the bombardment, specimens received 20% of the maximum flux on the average.

3. Experimental Results

Neutron-induced effects have been computed as fractional increases in elastic modulus, e_f ; i.e., $e_f = (E_f - E_0)/E_0$, where E_0 is the initial value of the elastic modulus of a particular specimen and E_f is its value after treatment.^(9, 11, 13-16) Table I summarizes the averaged fractional increases for all samples of the same history, the mean absolute deviations and the numbers of samples involved. Bombardment magnitudes are given in terms of μah of total deuteron current on the cyclotron target. The reality of the observed increases in elastic modulus is attested not only by the relatively systematic changes with neutron irradiation but also by the fact that other specimens handled in the same manner as those used, but not irradiated, showed no variations upon remeasurement. Samples measured with machinist's micrometers, before and after irradiation, showed no change in length. Masses of samples were unchanged. The small ring of beeswax left in the process of cementing the sample to the piezo-quartz crystal looked the same after the irradiation; on the basis of later work it was adjudged to play no significant role in the changes measured.

Figure 1 shows the manner in which elastic modulus of AGOT-W(T-15) changes with exposure to fast neutron irradiation. It should be noticed that there is large scattering about any curve which might be drawn through the points. The curve selected was drawn in such a way as to weight most heavily data from the two samples which had been in all six bombardments. The scattering has its origin in non-uniformity of the neutron flux over the target face and in the considerable sample-to-sample variations in physical properties, even of specimens cut from the same region of a single bar of graphite. It is clear, however, from the data in Table I, that increases in elastic modulus occur at a slower rate as the total exposure of samples increases. Thus e_f for the longest-exposed samples in the sixth bombardment increased from 0.34 to 0.46, while the new samples showed a change of 0.26. The changes observed indicate that interstitial disturbances and lattice vacancies produced by fast neutron bombardment do alter the physical properties of graphite as predicted by Wigner.⁽²⁾

TABLE I.

Effect of 16-Mev Neutrons on the Longitudinal Elastic
Modulus of Parallel-Cut Specimens
of AGOT-W(T-15) Artificial Graphite. (9, 11, 13-16)

Bombardment designation	Neutron exposure ($10^3 \mu$ ah)	e_f , Average fractional increase in elastic modulus	Number of samples
1	164	0.21 ± 0.01	3
2	108	0.10 ± 0.00	4
2, 1	272	0.26 ± 0.01	2
3	35	0.08 ± 0.02	7
3, 2	143	0.13 ± 0.01	4
3, 2, 1	308	0.28 ± 0.01	2
4	66	0.11 ± 0.02	14
5	37	0.06 ± 0.00	1
5, 3, 2, 1	344	0.34 ± 0.02	2
6	226	0.26 ± 0.04	3
6, 4	292	0.28 ± 0.04	7
6, 5, 3, 2, 1	570	0.46 ± 0.02	2

Fig. II. 1. Effect of cyclotron neutrons (16 Mev) on the longitudinal elastic modulus of AGOT-W(T-15) artificial graphite.

4. High Temperature Annealing Experiments

Irrespective of the mechanism for the neutron-induced changes in elastic modulus, annealing of bombarded samples at graphitizing temperatures, i.e., 3000°C , should to a large extent restore the original structure and the original elastic modulus. Such an experiment was done with one of the irradiated specimens from the first bombardment. That sample, together with several identical but unirradiated samples, was heated to 3000°C in an atmosphere of nitrogen. This heating was done for us by Dr. V. C. Hamister of the National Carbon Company in a furnace of the carbon resistor tube-type designed by J. W. Gartland.⁽¹²⁾ The elastic modulus of each sample was measured before and after heating. Table II summarizes the results.

Evidently annealing at very high temperatures had the anticipated effect. For unirradiated control samples the elastic modulus decreased slightly; for the irradiated specimen the elastic modulus healed to about the same value reached by the unirradiated samples in the heating process.

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TABLE II.

Effect of Heating to 3000°C on the Elastic Modulus of Irradiated
and Unirradiated AGOT-W(T-15) Artificial Graphite.⁽¹³⁾

	Irradiated (1 sample)	Unirradiated (7 samples)
E_0 , initial elastic modulus (10^{10} dynes/cm ²)	11.2	10.95 ± 0.25
E_f , elastic modulus after exposure (10^{10} dynes/cm ²)	13.47	---
$\frac{E_f - E_0}{E_0}$, fractional neutron-induced change	0.22	---
E_h , elastic modulus after 3000°C anneal (10^{10} dynes/cm ²)	9.94	9.82 ± 0.35
$\frac{E_h - E_0}{E_0}$, fractional change after heating	-0.11	-0.11 ± 0.02

5. Discussion of Results

The preliminary experiments showed that the longitudinal elastic modulus of artificial graphite was increased by fast neutron bombardment. The rate of increase was rapid in the first irradiation and became less rapid as the irradiations continued. The result suggested the possibility that the elastic modulus approaches a steady value after prolonged bombardment.

Artificial graphite consists of an agglomeration of nearly randomly oriented minute graphite crystals held together by a small amount of slag and disorganized carbon.⁽⁵⁾ During bombardment, fast neutrons (passing through the graphite) collide with carbon atoms of the crystal lattice and transfer to each struck atom, on the average, ca 1/7 of the neutron kinetic energy. This energy is more than sufficient to eject the struck atom from its original position in the graphite crystal lattice. The ejected recoil moves through the graphite until it has degraded its excess energy, either by interaction with the electronic systems of the carbon atoms or by elastic collisions. In the latter process it loses, on the average, ca 1/2 of its energy to the struck carbon atom. As long as these new recoils have sufficient energy they continue the discomposition process.

The dislocated atoms can either lodge in metastable positions between the planes of the graphite lattice, return to lattice vacancies or diffuse to stable positions at the edges of the crystallite. A more detailed view of the Wigner effect in graphite is given in the first paper of this series.

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III. PRELIMINARY STUDIES OF ELECTRICAL RESISTIVITY^{a,b}T. J. Neubert,^c M. G. Bowman,^d A. R. Van Dyken, and J. Royal^eABSTRACT

The electrical resistivity of artificial graphite bombarded with cyclotron neutrons increases approximately linearly with amount of neutron bombardment. The largest increase observed in this work was 42 per cent. Heating irradiated samples of artificial graphite to moderate temperatures (100 and 200°C) causes a partial reversal of the effect. In a sample of natural graphite, the magnitude of the effects, both upon bombardment and upon heating after bombardment, agreed with the data for artificial graphite. This result suggests that the disturbances are in the crystalline structure of the graphite and not in the "amorphous" intercrystalline material.

1. Introduction

In a preceding paper⁽¹⁾ an account has been given of the manner in which the longitudinal elastic modulus of artificial graphite was increased by bombardment with cyclotron neutrons. The present paper describes a similar investigation of the electrical resistivity of graphite. Electrical resistivity was chosen as a suitable property for study because of its sensitivity to both macro and micro structural changes in solids and because of the simplicity and precision of measurement. The fact that only small samples were required was also important.

^aBased upon work done in the Radiation Chemistry Section, Metallurgical Laboratory, University of Chicago (now Argonne National Laboratory) during the period 1943 - 1944. Participants in the work included R. C. Hirt, A. Novick, E. H. Phillips, and E. H. Smith.

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2. Experimental Details

In planning the initial experiments there was no way of knowing how large the changes were likely to be. It was necessary, therefore, to put more emphasis on precision than on convenience or speed of measurement. Samples had to be kept small because of the limited regions of high neutron flux at cyclotrons. Since a sample of acceptable size would have a resistance of less than 0.05 ohm, the technique of measurement had to be essentially potentiometric, so that contact resistances between the sample and the measuring circuit did not interfere. Such technique requires four electrical connections, two current leads and two potential leads.

The primary problem was, therefore, to devise a suitable type of specimen. Since there was a chance that the neutron-induced changes would be small, it was desirable that potential contacts used during initial prebombardment measurements be left attached to the sample, so that after bombardment an exactly equivalent remeasurement could be made. In this way any questions of ability to reproduce contact positions would be avoided, provided the contacts were so bonded to the graphite that they could withstand normal handling.

It was known that bismuth cast onto artificial graphite adheres quite well if the graphite is first cleaned in boiling carbon tetrachloride.⁽²⁾ Pieces of artificial graphite were, therefore, machined to cylindrical form with appropriate notches and grooves to receive bismuth end-caps and potential rings. The blanks were then cleaned in carbon tetrachloride, bismuth was cast on each end separately, and the excess bismuth machined away. Casting operations were carried out in vacuum (10^{-3} mm Hg) in a glass tube. A sudden quenching of the cast molten metal by plunging the glass container into ice water was used to produce a finer grain structure and thus facilitate the machining. Finished samples were cylinders of artificial graphite ca 4 mm in diameter, ca 6 cm long with a cap of bismuth at each end, and a ring of bismuth 2 mm wide and ca 0.3 mm thick at a distance of 5 mm from each end. Potential connections were made by means of short lengths of silver wire fused to the bismuth rings. Such samples were very satisfactory for electrical resistivity measurements, although they were quite delicate and were tedious to prepare.

Resistivities were measured by an essentially zero-current potentiometric technique. The measuring circuit is shown in Fig. 1. A steady current was passed through the specimen, R_x , with a reference resistance, R_r , connected in series, and the potential drops in each were compared by means of a galvanometer, G. For convenience a potential divider, S, was put across the fixed resistance R_f .⁽³⁾ A measurement was made by adjusting the deflection on the galvanometer when in the reference resistance circuit so that it duplicated the deflection observed with the same galvanometer across the potential contacts of the sample. Thus the resistance of the sample was simply

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the fraction of the reference resistance R_r indicated by the potential divider. A pinch-type, double-pole, double-throw knife switch, K , connected the galvanometer alternatively to the potential rings on the sample or to the reference resistance. The knife switch could be thrown so rapidly, relative to the period of the galvanometer, that the galvanometer moved smoothly from one position to another when the system was not in balance and did not move at all when the balance point was reached.

Fig. III 1.

Schematic diagram of circuit for electrical resistivity measurement.

Measurements were made at room temperature but, to prevent drafts on the sample and thus maintain a constant temperature during a measurement, the sample and its mounting were enclosed in a wooden cabinet. The temperature was read at the time of measurement on a thermometer mounted near the sample, and the resistance observed was corrected to 25°C. The temperature coefficient of resistivity was determined, in the region of room temperature, and found to be -0.0015 per degree centigrade for both unirradiated and (lightly) irradiated specimens. The normal procedure with the bismuth-contact resistance samples involved four separate measurements. After each measurement the sample was removed from its holder, turned end for end, replaced, and remeasured. A series of preliminary tests showed the average deviation from the mean of a set of readings to be less than 0.1% and to be unaffected by normal cautious handling.

After the first fast neutron bombardments were completed and the magnitudes of the neutron-induced changes in resistivity were known, it was clear that the complicated bismuth-contact type specimens were not necessary. Satisfactory precision could be obtained by use of plain right circular cylindrical samples with measurement of the potential drop between two

probes resting against the sample.⁽⁴⁾ It was, therefore, possible to construct a sample mount which would permit resistance measurements on the same specimens used in the elastic modulus measurements described in the previous paper.⁽¹⁾ The sample to be measured was supported horizontally between two brass contact screws, recessed slightly to receive the sample. The potential probes were steel phonograph needles, mounted at a constant distance apart in a Lucite bar, and pressed against the sample by two spring-bronze strips. The measuring circuit was the same as shown in Fig. 1.

Artificial graphite is generally very inhomogeneous; its properties vary considerably from one part of a sample to another. It was standard practice, therefore, to take at least six separate readings on each sample. Three readings were taken at different points on the circumference of the sample, by rotating the sample in the axis of the recessed brass screws. After this operation the sample was removed, turned end for end, replaced, and three similar additional readings were made. The six readings were averaged to give the sample resistances. The mean absolute deviation of separate readings was ca 0.4 per cent.

3. Neutron-Induced Resistivity Changes in Artificial Graphite

The first neutron-induced changes in the electrical resistivity of artificial graphite were observed with the bismuth-contact resistance samples. These were cut from AGOT-W (T-15) artificial graphite,⁽⁵⁾ with the sample axis parallel to the axis of extrusion of the stock bar. Samples had an average prebombardment resistivity of ca 8×10^{-4} ohm cm. Specimens were irradiated with 16-Mev neutrons at the Washington University cyclotron (at St. Louis) under the same conditions as were the elastic modulus samples discussed in the previous paper,⁽¹⁾ i.e., neutrons of ca 16 Mev were produced by deuteron bombardment of a water-cooled beryllium target. It was estimated that for a 200- μ a deuteron beam the fast neutron flux in an average specimen was ca 1.5×10^{10} fast neutrons/cm² sec.

Samples were irradiated in vacuo (10^{-3} mm Hg) in sealed soda-glass ampules attached to the outside face of the cyclotron target at temperatures estimated to be $30 \pm 5^\circ\text{C}$. Five bombardments were made.⁽⁶⁻⁹⁾ Sample resistances were measured before and after each bombardment at room temperature and corrected to 25°C .

Neutron-induced effects were computed in terms of the fractional increase in electrical resistivity, r_f ; i.e., $r_f = (R_f - R_0)/R_0$, where R_0 is the initial resistance of the unirradiated sample and R_f is the final resistance after a particular bombardment. Fractional changes for all samples of the same history in the various bombardments were averaged and average deviations from the means were calculated. Table I summarizes the values obtained. Bombardment magnitudes are given as μ ah of total deuteron current on the cyclotron target.

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TABLE I

Effect of 16-Mev Neutrons on Electrical Resistivity of Parallel-Cut,
AGOT-W (T-15), Bismuth-Contact Artificial Graphite Specimens

Bombardment Designation	Metric of Neutron Exposure,* $10^3 \mu\text{ah}$	r_f , Average Fractional Increase in Electrical Resistivity	Number of Samples
1	88	0.089 ± 0.012	4
2	35	0.036 ± 0.001	2
2,1	123	0.106 ± 0.006	3
3	37	0.090	1
3,2	72	0.086 ± 0.003	2
3,2,1	160	0.155 ± 0.016	3
4	226		0
4,3	263	0.296	1
4,3,2	298	0.300	1
4,3,2,1	386	0.354 ± 0.018	2
5	108	0.099 ± 0.28	4
5,3,2	180	0.133	1
5,4,3	371	0.296	1
5,4,3,2	407	0.382	1
5,4,3,2,1	494	0.419 ± 0.003	2

* The metric of neutron exposure is the number of micro-ampere hours (μah) of deuteron beam incident on the beryllium cyclotron target.

Figure 2 shows the manner in which the electrical resistivity of artificial graphite changed with neutron exposure. Fractional increases in electrical resistivity are plotted against the accumulated μah of bombardment. All five bombardments have been considered to be essentially equivalent and no attempt was made to correct for position of individual samples during bombardment. Such a simplifying assumption is justified by sample-to-sample variations in electrical properties of artificial graphite, by fluctuation of neutron flux distribution and by variation of cyclotron efficiency. These considerations explain, to a certain extent, the large scattering of experimental points plotted in Fig. 2. In addition, it is impossible to detect any orderly variations which show that conditions during any one bombardment differed systematically from conditions in other bombardments. The data indicate that the Wigner effect in artificial graphite caused the electrical resistivity to increase and that this increase in its early stages was essentially linear with neutron bombardment.⁽⁹⁾

Fig. III 2. Effect of cyclotron neutrons (16 Mev) on the electrical resistivity of AGOT-W (T-15) artificial graphite.

These first bombardments established the fact that resistance changes were sufficiently large to make unnecessary the use of samples with bismuth contacts. Accordingly, in subsequent work emphasis was put on resistivity measurements using the same small cylindrical samples employed in study of fast neutron-induced changes in longitudinal elastic modulus.⁽¹⁰⁾

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4. Thermal Annealing of Radiation Damage in Artificial Graphite

Irrespective of the particular nature of neutron-induced defects, prolonged heating at graphitizing temperatures should restore the irradiated material essentially to its original state. Actually, "annealing" an irradiated elastic modulus sample to 3000°C completely removed the neutron-induced change in modulus.⁽¹⁾ However, if the disturbances are interstitial atoms (or groups of atoms) and lattice vacancies,⁽¹¹⁾ it might be expected that at least a part of the effect can be healed at temperatures considerably lower than 3000°C.

To test these ideas, low temperature annealing experiments were made on two bismuth-contact resistivity specimens, both of which had been bombarded at $30 \pm 5^\circ\text{C}$ for $72 \times 10^3 \mu\text{ah}$ at the Washington University cyclotron. The fractional increase in resistivity, r_f , of sample #10 during bombardment was 0.086; of sample #11, 0.082. After preliminary measurements were completed, sample #11 was heated in an air oven at $100 \pm 5^\circ\text{C}$; sample #10 was similarly treated at $200 \pm 5^\circ\text{C}$. Higher temperatures could not be investigated because the bismuth would have melted. At intervals, samples were removed from the ovens, cooled to room temperature, measured and replaced in the ovens. Times of remeasurement varied between 17 min and 3785 min.⁽⁸⁾ Fractional changes remaining at each measurement [i.e., $r_t = (R_t - R_0)/R_0$] are shown in Table II.

TABLE II

Effect of Low Temperature Anneal on Neutron-Induced Changes in Electrical Resistivity of AGOT-W (T-15) Artificial Graphite

Sample 11 Heated at $100 \pm 5^\circ\text{C}$		Sample 10 Heated at $200 \pm 5^\circ\text{C}$	
Time of Heating, (min)	r_t^*	Time of Heating, (min)	r_t^*
0	0.082	0	0.086
30	0.076	17	0.058
150	0.074	32	0.051
335	0.070	60	0.049
1055	0.067	150	0.046
3755	0.062	365	0.045
		1085	0.045
		3785	0.047

* r_t is residual fractional increase in electrical resistivity.

100 50

The resistance of sample #11, heated at 100°C, continued to drop throughout the entire period of annealing, while "healing" in sample #10, heated at 200°C, was approximately complete after 150 min. All the changes after this time were within the limits of precision of the resistivity measurements. The fact that only about one-half of neutron-induced increase in resistivity is removed during a 200°C anneal suggests the presence of more than one type of disturbance. The preliminary nature of these data and the large experimental fractional error (0.002) relative to the neutron-induced fractional change (0.08) prevented any successful treatment by chemical kinetics methods.

5. Discomposition in Natural Graphite

The mechanism of the discomposition in artificial graphite is thought to involve disturbances in the minute crystallites. It was important, therefore, to study the behavior of natural graphite under fast neutron bombardment.⁽¹²⁾ Well-formed natural graphite is, however, very soft and not at all strong mechanically, and thus is not readily machined. Only one suitable sample⁽¹²⁾ resulted from all our machining attempts. This was a cylinder 1.37 in. long by ca 0.146 in. in diameter. The specimen was crude and not exactly cylindrical. It was cut from what appeared to be a single crystal. The angle between the normal to the graphite planes and the cylinder axis of the specimen was 75 to 80 deg.

The resistance of the sample was measured as has been described, using the phonograph needle potential contact setup. Measurements were very difficult to make because of extreme softness and fragility of the sample. The resistivity of this particular sample of natural graphite, before neutron irradiation, was 6.5×10^{-4} ohm cm. After initial measurements, the sample was bombarded three times with fast neutrons at the Washington University cyclotron. Table III summarizes resistivities observed after each irradiation. It is clear that fast neutron bombardment increases the electrical resistivity of natural graphite.

Comparison of data of Table III with those of Fig. 2 indicates that fractional changes observed in natural graphite are of approximately the same magnitude as changes observed in AGOT-W (T-15) artificial graphite. This fact indicates that the seat of the radiation damage effect responsible for electrical resistivity changes in artificial graphite is principally in the small, more or less perfect, crystallites and not in intergranular material. This conclusion is further supported by the fact that neutron-induced increase in resistivity of the natural graphite sample can be partially removed by heating at relatively low temperature. Approximately two-thirds of the accumulated change was healed by annealing the specimen for 6.5 hr at 155°C. The result is similar to those obtained on annealing of irradiated artificial graphite specimens.

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TABLE III

Effect of Fast Neutron Bombardment and Subsequent
Thermal Annealing on Electrical Resistivity of a
Specimen of Natural Graphite

Sample Treatment	R, Electrical Resistivity (10^{-4} ohm cm)	Total Neutron Exposure (units of $10^3 \mu\text{ah}$)
Initial Measurement	6.54 ± 0.32	0
Bombarded $27 \times 10^3 \mu\text{a hr}$	6.92 ± 0.20	27×10^3
Bombarded $226 \times 10^3 \mu\text{a hr}$	8.08 ± 0.13	253×10^3
Bombarded $110 \times 10^3 \mu\text{a hr}$	8.63 ± 0.20	361×10^3
Remeasured	8.48 ± 0.12	361×10^3
Annealed 6.5 hrs at 155°C	7.28 ± 0.18	361×10^3

6. Discussion

Fast neutrons, in the present experiments with energy of ca 16 Mev, passing through the graphite specimens can make collisions with carbon atoms and thus transfer to the struck atom, on the average, ca $1/7$ of the neutron energy. In this process the carbon atom is ejected from its normal position within the graphite and by virtue of its own kinetic energy has the ability to eject other atoms. This process can continue until the energies of all the primary and secondary recoils are below what is necessary to dislodge further atoms.

Accordingly, observed changes in properties of graphite are attributed to disturbances produced in the graphite structure by the fast-neutron-moderation process. The disturbances are thought to have the character of lattice vacancies and carbon atoms trapped in one form or another between or at edges of planes of the graphite crystallites. (11, 13) It is not expected, however, that all atoms initially displaced to interstitial positions will remain interstitial. During bombardment there can be a back reaction to lattice vacancies and also a diffusion of interstitial atoms to crystal edges. Furthermore, interstitial disturbances are not necessarily simple atoms.

The presently reported experiments do not indicate very much about the details of the mechanism. It is clear, however, that disturbances are formed and that the observed increases in resistivity are approximately linear. The hypothesis that the seat of disturbance measured by these methods is within the crystallites, and not in whatever small amount of intercrystalline

material may exist, is supported by agreement in the magnitudes of changes observed in artificial graphite samples and in the natural graphite "single-crystal" specimen. The tendency toward a low-temperature thermal annealing of the disturbances further supports the idea of interstitial atoms or atomic complexes, especially since natural graphite and artificial graphite are so similar in behavior on annealing.

Examination of the thermal-annealing data for artificial graphite apparently indicates that the curves for 100°C and for 200°C approach different limiting values. The suggestion is that the disturbances removed by the annealing treatment have different activation energies for thermal healing. The residuum left after a long-time anneal at 200°C would, according to this (1945) picture, be interstitial disturbances of higher activation energy and lattice vacancies. It is presumed that, both in back reactions during irradiation and in thermally-induced healing, at least part of the knocked-out atoms ultimately come to rest at the crystallite edges. Thus, there will always be some vacancies in the lattice. These will be healed only at very high temperatures.⁽¹¹⁾ An annealing experiment in which the elastic modulus change was studied showed that the process of vacancy diffusion was complete at 3000°C. Further experiments and data on these various problems are presented in accompanying papers.

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IV. FURTHER STUDIES OF ELASTIC MODULUS AND ELECTRICAL RESISTIVITY^{a, b}

M. G. Bowman,^c W. R. Burns,^d R. C. Hirt,^e T. J. Neubert,^f
A. Novick,^g J. Royal,^h and A. R. Van Dyken

ABSTRACT

Neutron exposures of a variety of artificial graphites were increased over the amounts previously reported and further fractional increases in elastic modulus (to ca 1.8) and electrical resistivity (to ca 2.8) were obtained for (type AGOT-K) artificial graphite. Both cyclotrons and reactors were used as neutron sources. The electrical resistivity increases approximately linearly for short exposures, but as exposures are prolonged the rate of increase diminishes and there is evidence that a steady state value would ultimately be attained. The initial rate of elastic modulus increase is large. The rate of change diminishes continuously with exposure, but in this case also a steady state was not attained for the longest exposure (83 L-units). The electrical resistivity effect is very temperature sensitive, the neutron-induced changes being in all cases less the higher the temperature of irradiation. The elastic modulus effect, however, is insensitive to irradiation temperatures up to ca 130°C for short irradiations, but for longer exposures changes are less the higher the temperature. Effects of neutron bombardment on different types of graphite differ in magnitude, being

^aBased upon work done in the Radiation Chemistry Section, Metallurgical Laboratory, University of Chicago (now Argonne National Laboratory) during the period 1943-1945. Participants in the work included S. G. Davis, S. Gordon, F. J. Safford, P. H. Yuster, R. C. Boe, R. M. Donegan, H. Petrzilka, E. H. Phillips, E. H. Smith, G. Steel, M. Stewart, and L. Weil.

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greatest for the best organized graphite and smallest for the least organized material. The fractional increase in the electrical resistivity or elastic modulus of any given type of graphite is in fixed ratio to the fractional increase in the same property of a standard type of graphite sample (type AGOT-K) exposed to the same degree irrespective of the amount of change up to exposures of at least 16 L-units.

1. Introduction

The research program to investigate the effect of fast neutron bombardment on the physical properties of artificial graphite⁽¹⁾ was begun at the end of 1942 shortly after Wigner⁽²⁾ had pointed out the interest of such work.

The first neutron irradiation was made at the Washington University cyclotron from February 17 to April 12, 1943. Experiments with this source were continued until March, 1944. During the period December 1943 to July 1944 similar experiments were under way at the 60-inch cyclotron of the University of California.

In the winter of 1943-44 the air-cooled, graphite-moderated pile at Clinton Laboratories, Oak Ridge, Tennessee, became available for experimental work; during the following summer the heavy-water-moderated pile at Argonne National Laboratory began operation at full power. Graphite specimens were exposed in each unit as soon as it became available. The existence of these experimental piles provided neutron fluxes considerably larger than those available at cyclotrons.

Preliminary experiments at the Washington University cyclotron indicated that reasonably short neutron bombardments, even with a source as weak as a cyclotron, readily produced changes of 10 to 40 percent in both the longitudinal elastic modulus⁽³⁾ and in the electrical resistivity⁽⁴⁾ of artificial graphite. In connection with electrical resistivity studies this result was very important, since it made unnecessary the complicated and fragile bismuth-contact type samples used in the earliest experiments and permitted satisfactory resistance measurements on the same samples as were used in the study of elastic modulus changes.⁽⁴⁾ This procedure cut the number of samples required approximately in half, thus permitting a more effective use of neutron bombardment facilities, and at the same time provided a direct correlation between changes in the two properties.

2. Experimental Details

The samples used throughout the present work were right-circular cylinders.⁽⁴⁾ Sample diameters were ca. 4 mm, but lengths were always adjusted so that the specimen had an initial resonance frequency of 36000 sec⁻¹. Lengths varied therefore, for samples of different graphites,

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depending upon their particular elastic modulus, between 2.7 and 4.0 cm. Before measurements were made specimens were given a 10-min preanneal at 1000°C in an atmosphere of tank helium. This treatment had no important effect on unirradiated samples. The elastic modulus tended to increase slightly (2.5%), and the electrical resistivity to decrease slightly (1%). Weight losses were less than 0.1%.

Elastic moduli were determined by means of the piezo-quartz resonator technique.⁽³⁾ The method involved forming a composite resonator, consisting of the sample and an appropriate piezo-quartz crystal cemented together, and determining the resonance frequency of the sample (and hence its longitudinal elastic modulus) by means of standard techniques. Each sample was measured on two separate quartz crystals. Initial pre-irradiation measurements (at 36000 sec⁻¹) were required to check within ca. 0.2%. Tolerances on post-irradiation measurements were, however, somewhat larger and depended upon the sample, the amount of handling, and the extent of irradiation. Quartz resonators of higher frequency were used, where necessary, in the post-irradiation measurements.⁽⁵⁾

Electrical resistivities were determined by passage of a constant direct current through the sample and observation of the potential drop between two steel potential contacts pressed firmly against the sample.⁽⁴⁾ Measurements were always made on the same apparatus. Initial resistances varied between ca. 0.01 and ca. 0.1 ohm depending upon the type of graphite; the potential contacts were 2.66 cm apart. All measurements were corrected for temperature to 25°C, using a temperature coefficient of -0.0015 per °C. Although this temperature coefficient changed in the course of continued neutron exposure to values of ca. -0.0010 per °C, the initial value was always used in temperature-correction computations. The ordinary precision of the measurement was ca. 0.5%, but such precision was not attainable for some of the special types of graphite studied.

Samples were prepared for irradiation by wrapping them, individually, in small pieces of 0.5-mil aluminum foil. Numbers impressed in the foils established the identity of the samples, themselves unmarked. Wrapped samples were then packaged in small containers appropriate to the neutron source. In early experiments samples were bombarded in vacuo in soda-glass or fused quartz ampules. It was found, however, that samples bombarded in vacuo could not be distinguished from samples bombarded in air. In later experiments the complication of sealing specimens in vacuo was abandoned. A more advantageous disposition of samples at the neutron source could thus be obtained.

Each sample was measured before and after bombardment and fractional increases in the appropriate property were calculated. Such fractional increases are designated by r_f and e_f for electrical resistivity (R) and elastic

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modulus (E), respectively. Thus

$$r_f = (R_f - R_0)/R_0, \quad e_f = (E_f - E_0)/E_0,$$

where the subscript, f , denotes the measurement after a particular bombardment, and the subscript, 0 , denotes the initial measurement on the sample before any neutron irradiation.

Amounts of neutron irradiation are reported in the units appropriate to the particular neutron source and in L-units.⁽⁶⁾ One L-unit is defined as that amount of neutron bombardment which at 35° C produces a 25% increase in the elastic modulus of a previously unirradiated, parallel-cut specimen of AGOT-K(II) graphite. (The meanings of the artificial graphite code names are given in Section 3.) This particular definition was selected for two reasons: (a) neutron-induced increases in elastic modulus, if less than ca. 50%, are independent of the temperature of irradiation for temperatures below ca. 130° C, and (b) neutron-induced increases in elastic modulus are insensitive against post-irradiation annealing for low amounts of bombardment.⁽⁷⁾

In most cases, samples were bombarded more than once. The usual practice was to include several unirradiated samples in each new bombardment so that self-consistent curves of elastic modulus change vs bombardment could be built up by a system of internal monitoring. This process, although logically sound, turned out, however, to be less precise than was anticipated but was necessary because variations of the neutron sources from one experiment to another, or even during a single experiment, were not adequately reflected in the "bombardment magnitude" as reported by the operators of the various neutron sources.

3. Types of Artificial Graphite Studied

The production of artificial graphite and the various graphites of interest are described elsewhere in considerable detail.⁽⁸⁾ A brief resume, however, is appropriate. Artificial graphites are manufactured from petroleum coke and coal tar pitch. Calcined powdered coke and pitch are mixed to form a plastic mass which is extruded with heat and pressure into bars. These bars are then baked to a minimum temperature of 750° C in a gas-fired oven to harden them, reimpregnated with pitch, and finally graphitized by heating at ca. 2700° C in an electric furnace. The resultant material is an aggregate of small "natural graphite" crystallites held in a matrix of slag and disorganized carbon. The crystallites are present in the original coke as a result of the coking process, and according to the best information available⁽⁹⁾ do not grow during the graphitization process by more than (if as much as) a factor of two. The function of the graphitization is to perfect crystallites, to decompose the bonding pitch, and to distill out the larger part of the impurities.⁽⁹⁾

Coke particles at the time of extrusion are in the form of flat flakes so that there is a tendency for them to become aligned in the extrusion process with their flat surfaces parallel to the axis of extrusion. The fact that the coke-powdering operation yields flat particles suggests, by reason of the anisotropy of graphite, that crystallites within flakes are aligned. Conversely, coke particles are flat because they consist of a few aligned crystallites. Preferential orientation in artificial graphite leads to different values for various physical properties depending upon the manner in which the test specimen was cut from the original stock bar. In the present work neutron-induced changes were investigated for samples cut with their own axis both parallel to and perpendicular to the axis of extrusion. Since parallel-cut samples were always more well-behaved, they were more frequently used. (Note added, November 10, 1955. The description of the coke particles given above does not conform exactly with the description given recently by the National Carbon Company; cf. "The Production and Properties of Graphite for Reactors" by L. M. Currie, V. C. Hamister and H. G. MacPherson, paper 534 presented at the International Conference on the Peaceful Uses of Atomic Energy, Geneva, August, 1955.)

3.1 Pile Graphites

The artificial graphites used in this work were manufactured by the National Carbon Company. The three of particular interest have been designated AGOT-K, AGOT-C, and AGOT-W. The specification AGOT indicates that the material is artificial graphite meeting certain purity standards. The letters K, C, and W designate the refinery which supplied the petroleum coke. The principal differences among these three types are chemical purity,⁽¹⁰⁾ density,⁽¹⁰⁾ crystallite size and extent of crystallite orientation relative to the axis of extrusion.⁽⁸⁾ AGOT-K is purest, densest, has the largest crystallites and exhibits the largest degree of preferential crystallite orientation. Samples of each of these three pile graphites were used in the Wigner effect research, but the principal emphasis was given to AGOT-K. It was attempted to do all measurements and bombardments on samples machined from the central region of a single bar. This procedure was, however, not always possible. Consequently, in certain cases the designation of a particular graphite type includes a Roman numeral indicating the accession number of the bar used. (Note added, November 10, 1955. The specific cokes mentioned above are not all available now, and after the elapse of eleven years those that are available under the same names are somewhat different in their characteristics as a result of changes in oil refinery processing and in the sources of crude petroleum used.)

3.2 Specially Graphitized Materials

Three graphites of different degrees of graphitization were prepared especially for this research by the National Carbon Company at the instance of V. C. Hamister and H. G. MacPherson. These were produced on a laboratory scale by reimpregnation of a standard bar of gas-baked

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stock with pitch, followed by gas-baking and graphitization in a high temperature laboratory tube furnace. The final temperatures of graphitization were 2100°C, 2400°C, and 3000°C. The 3000°C product resembled plant-produced AGOT-W, as closely as a laboratory product can correspond to material produced under actual plant conditions. The 2100°C material represented a product in which practically no "graphitization" had taken place. The 2400°C material had intermediate properties. These graphites, for convenience, have been designated Sp 2100, Sp 2400, and Sp 3000.

3.3 Specially Prepared Pseudo-Graphites

Two materials of widely different particle size were also supplied by the National Carbon Company. The one, pbL, was made from lampblack bonded with coal tar pitch; the other, pbNG, was made by bonding natural graphite flour with pitch. Each material was "graphitized" at 3000°C. In neither case was a study made of possible preferential orientation of crystallites. The particle-size in lampblack is too small to exhibit any preferential orientation.⁽⁸⁾ In the case of the pitch-bonded natural graphite there undoubtedly was some preferential orientation, even though so far as is known the material was not extruded.⁽⁸⁾

4. Cyclotron Experiments

In addition to preliminary work on AGOT-W(T-15) already reported,^(3,4) two bombardments⁽¹¹⁾ with ca 16 Mev neutrons were made on AGOT-K(I), AGOT-C, and AGOT-W graphites⁽¹²⁾ at the Washington University cyclotron. Samples were exposed simply by fastening them to the outside of the target. Sample temperature is estimated to have been $30 \pm 5^\circ\text{C}$. Table I gives the averaged fractional increases in electrical resistivity, r_f , and in elastic modulus, e_f , for each set of samples. Mean absolute deviations are given with each entry to indicate the experimental scattering.

The bombardment magnitudes are given both in μah of integrated deuteron current on the beryllium cyclotron target and in L-units. The conversion factor used for the first experiment was $2.1 \times 10^5 \mu\text{ah/L-unit}$; the factor used for the second experiment was $6.4 \times 10^4 \mu\text{ah/L-unit}$. This difference arose from an improvement in the design of the beryllium target between the first and the second experiments. The data in Table I indicate that the electrical resistivity of artificial graphite increases more or less linearly with neutron bombardment while the elastic modulus increases with a diminishing rate.

The 60-inch cyclotron of the University of California at Berkeley also was used in the study of the Wigner effect in graphite. Neutrons were again produced by deuteron bombardment of a beryllium target but their maximum energy was ca 20 Mev. If the efficiency of neutron production were taken to be one neutron per 250 deuterons, the calculated total flux for a 200- μa deuteron beam was ca 3.6×10^{14} neutrons per minute. The

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target face was monitored by means of the (n- α) reaction on aluminum and, from the results obtained, it was estimated that approximately 1/3 of all the neutrons produced pass forward through a 5-cm² area of the target face.

TABLE I.

Fast Neutron-Induced Changes in Electrical Resistivity and Elastic Modulus of Parallel-Cut Artificial Graphite Specimens
Irradiated at The Washington University Cyclotron
(Temperature: $30 \pm 5^\circ\text{C}$)

Bombardment number	Nominal exposure ($10^3 \mu\text{ah}$)	Exposure (L-units)	e_f	r_f	Number of samples
AGOT-K(I) Graphite					
1	170	0.8	0.21 ± 0.03	0.11 ± 0.01	5
2	108	1.6	0.33 ± 0.02	0.21 ± 0.02	4
2,1		2.4	0.39 ± 0.02	0.29 ± 0.02	4
AGOT-C Graphite					
1	170	0.8	0.19 ± 0.03	0.12 ± 0.02	5
2	108	1.6	0.33 ± 0.03	0.23 ± 0.03	4
2,1		2.4	0.42 ± 0.01	0.33 ± 0.01	4
AGOT-W Graphite					
1	170	0.8	0.13 ± 0.02	0.10 ± 0.02	5
2	108	1.6	0.26 ± 0.04	0.21 ± 0.03	4
2,1		2.4	0.31 ± 0.02	0.26 ± 0.03	4

Because the neutron flux through a sample is very dependent upon position of the sample, target geometry and transient conditions in the cyclotron, it was desirable to devise a technique by which each graphite sample could be individually monitored. Bombardments usually lasted 30 to 50 days, so the half-life for the monitoring product would have to be at least longer than that. The reaction selected was the (n-2n) reaction on tungsten with 77-day half-life. The threshold for this reaction is above 2 Mev. The same activity can also be produced with slow neutrons by (n- γ) reaction. Consequently, in the bombardments at Berkeley slow neutrons were screened away from the monitors by the Pyrex ampules in which samples and monitors were enclosed.

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The tungsten was in the form of 16-mil wires, 3-cm long. After bombardment the activity of each wire was measured; thus, after extrapolation to the time of shutdown and with corrections for periods during which the cyclotron was not operating, it was possible to determine relative exposures of all samples. Furthermore, by making use of the monitoring of the target face and the estimate of total flux, it was possible to convert these relative exposures to total fast-neutron flux, n_t , through the sample.

Three bombardments were made: (1) 10,689 μah ,⁽¹³⁾ (2) 50,806 μah , and (3) 81,965 μah .⁽¹⁴⁾ The specimens used were parallel-cut samples of AGOT-K(I), AGOT-C, and AGOT-W. Table II gives the fractional increases in electrical resistivity, r_f , and elastic modulus, e_f , corresponding to various amounts of irradiation. The values listed were read from graphs on which were plotted all the data for each sample in every bombardment. Figure 1 illustrates the type of curve and the scattering of points for AGOT-K(I). Bombardment magnitudes have been given in terms of the total neutrons per cm^2 traversing the sample, n_t , and in L-units, where the factor of conversion is 0.45×10^{17} neutrons per cm^2 per L-unit.

TABLE II

Neutron-Induced Changes in Elastic Modulus and Electrical Resistivity of Artificial Graphite Irradiated with ca. 20-Mev Neutrons at the 60-in. Cyclotron at The University of California

Total exposure, 10^{17} neutrons (20 Mev)	Total exposure, L-units	AGOT-K(I)		AGOT-C		AGOT-W	
		e_f	r_f	e_f	r_f	e_f	r_f
0.5	1.1	0.26	0.22	0.24	0.20	0.23	0.28
1.0	2.2	0.40	0.38	0.38	0.36	0.35	0.43
2.0	4.5	0.61	0.64	0.59	0.64	0.52	0.63
3.0	6.7	0.77	0.86	0.76	0.87	0.64	0.78
4.0	8.9	0.90	1.04	0.90	1.07	0.72	0.91
5.0	11.1	1.02	1.20	1.04	1.26	0.80	1.03

^aIn general, e_f represents fractional increase in elastic modulus, r_f represents fractional increase in resistivity.

Fig. IV. 1. Effect of cyclotron neutrons (20 Mev) on electrical resistivity and elastic modulus of parallel-cut AGOT-K(I) artificial graphite.

Trends apparent in the earlier data (3, 4) were duplicated and extended. The elastic modulus increased rapidly in early stages of bombardment, but as bombardment continued the rate of change decreased. Electrical resistivities increased in a somewhat linear fashion only in early stages of bombardment; definite departure from linearity was apparent as the exposure progressed. There was no sign of a "steady state" for changes in longitudinal elastic modulus as high as 100% and corresponding changes in electrical resistivity as great as 120%.

5. Experiments in the Graphite Pile at Oak Ridge

The Oak Ridge pile is a 24-ft cube of graphite containing uranium loaded into a lattice of horizontal charging channels. In addition to the charging channels there are a number of other special holes for monitoring instruments and experimental work. Graphite samples were irradiated in three different positions which are described below. In the early stages of operation, pile power levels were ca 0.5 megawatt but were gradually raised above 3 megawatts as the amount of air-cooling was increased. Bombardment magnitudes were reported by the pile operation group in megawatt days, Mwd, of total energy developed by the whole pile during the period of exposure. This practice, however, turned out to be quite troublesome, since in addition to the variation of neutron flux with position in the

pile, there were many changes in loading from time to time which were not describable in a quantitative manner. For this reason, in the present work, bombardments are recorded in L-units (cf. Section 2).

5.1 Irradiations Inside Doughnuts in Hole 1867.

Uranium tubes, in which graphite samples could be bombarded, were designed to take advantage of the higher fast neutron fluxes in the immediate vicinity of uranium in a going pile.⁽¹⁵⁾ A typical tube was 24-in. long and was formed from six aluminum-clad uranium slugs in the shape of hollow cylinders, 4-in. long, 1.75-in. o.d. and 1-in. i.d. These slugs, called doughnuts, were located near the transverse center-line in hole No. 1867, one of the central charging channels. The doughnuts were thus very near the center of activity of the pile. A long aluminum tube extended from the front face of the pile through the doughnuts so that samples in appropriate aluminum containers could be pushed to various positions either inside or outside the doughnuts. Since hole No. 1867 was specially enlarged to accommodate the doughnuts a relatively greater-than-normal air flow was available for cooling, and it was found on this account that the temperature of samples inside the doughnuts was only a few degrees above inlet air temperature, i.e., sample temperatures were of the order of $35 \pm 5^\circ\text{C}$.

Figure 2 summarizes the averaged fractional increases in elastic modulus, e_f , and in electrical resistivity, r_f , of samples of parallel-cut AGOT-K graphite irradiated inside doughnuts in hole 1867 of the Oak Ridge pile. Samples of both AGOT-K(I) and AGOT-K(II) were used, but scattering was so great as to obscure any differences in behavior of specimens from these two bars. The amount of fast neutron bombardment is given in L-units; the factors used for converting Mwd to L-units varied between 4 and 8 Mwd per L-unit.

Although the data of Fig. 2 extend to higher values, the observed trends are the same as shown in Fig. 1. The scattering of points has two principal origins: (a) uncertainty in amount of neutron bombardment, and (b) uncertainty of temperature during irradiation. In instances where the temperature of irradiation was higher than usual, electrical resistivity changes (circles) are lower than expected, whereas elastic modulus changes (squares) are relatively unaffected, cf. the points near 20 L-units in Fig. 2. In instances when only the reported amount of irradiation is in error, pairs of points (i.e., both squares and circles) deviate from the curves, cf. the points at 3 L-units and at 51 L-units. As a means for removal of at least one element of imperfection from the data, viz. the bombardment magnitude, it is useful to plot the change in electrical resistivity against the change in elastic modulus for the same samples. Such a curve, for all sets of samples bombarded at temperatures nominally close to 35°C , is given in Fig. 3. Points representing samples in which, for one reason or another, temperatures were higher than usual fall below the "best line." The lines in Fig. 2 and other figures were drawn so as to be consistent with the actual data and at the same time consistent with the modulus-resistance graph, Fig. 3.

Fig. IV. 2.

Effect of exposure inside the "doughnuts" in hole 1867 of the Oak Ridge graphite pile, temperature ca 35°C.

Fig. IV. 3.

Relation between fractional increases in electrical resistivity and elastic modulus for samples exposed at temperatures close to 30°C. (Squares: Oak Ridge pile - doughnuts; triangles: Oak Ridge pile - hole No. 1867-NNU; circles: Argonne pile - central thimble).

5.2 Irradiations in Hole No. 1867. Eight Inches from Uranium

It was also possible to bombard graphite samples in the outer portions of the aluminum tube leading from the front face of the pile to the doughnuts. Since the lattice spacing of the uranium-bearing holes was 8 in. and since hole No. 1867 was unloaded except for the uranium doughnuts at its mid-section, samples exposed in this position (designated 1867-NNU) were 8 in. from the nearest uranium. For this reason, rate of bombardment was approximately one-half^(16, 17) that of samples irradiated inside the doughnuts.

During exposure, samples were disposed 24 in. to 55 in. from the center line of the pile (12 in. to 43 in. from the front end of the doughnuts). Consequently, nominal bombardments, as reported by the pile-operating group, were corrected to equivalent bombardments at the center of the pile. This correction was made under the assumption that the flux along the axis of the pile showed a cosine dependence.^(17, 18)

A special series of bombardments⁽¹⁹⁾ was carried out in this position (1867-NNU) in order to establish as precisely as possible the shape of the curves for increase of electrical resistivity and elastic modulus vs neutron exposure for short exposures and to provide irradiated samples for subsequent annealing experiments.⁽⁷⁾ Thirty carefully measured, standard-sized, parallel-cut samples of AGOT-K(I) artificial graphite were put in the pile at one time. Eight sets of samples were withdrawn after varying amounts of exposure. Sets of samples were larger and the intervals of bombardment smaller in the early stages of the experiment and smaller and longer, respectively, in the later stages. The power level at the time of this experiment was ca 1 Mw; sample temperatures were $32 \pm 5^\circ\text{C}$.

For each of the eight sets of samples, Table III gives the averaged results and mean absolute deviations of fractional increases in electrical resistivity, r_f , and elastic modulus, e_f . Bombardment magnitudes are stated in Mwd, corrected for sample position, and in L-units, computed using the factor 11.5 Mwd/L-unit. Figure 4 shows both sets of data. The curves have again been drawn so as to be consistent with a graph of e_f vs r_f (cf. Fig. 3).

Analysis of electrical resistivity data obtained in this group of experiments showed that to a good approximation they could be represented by a hyperbola. If $\underline{L}$ be the amount of neutron exposure (in L-units), r_f the neutron-induced fractional increase in electrical resistivity, and $\underline{A}$ and r_∞ are constants, the appropriate hyperbola has the form

$$\underline{A} \underline{L}^{-1} = r_f^{-1} - r_\infty^{-1} \quad (1)$$

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TABLE III.

Neutron-Induced Changes in Electrical Resistivity and Elastic Modulus of Samples of Parallel-Cut AGOT-K(I) Artificial Graphite, Irradiated in Hole No. 1867 in the Oak Ridge Graphite Pile, 8 in. from Uranium Metal
(Temperature: $32 \pm 5^\circ\text{C}$)

Set number	Neutron exposure (Mwd)	Neutron exposure (L-units)	e_f	r_f	Number of samples
1	3.12	0.27	0.096 ± 0.006	0.052 ± 0.004	6
2	5.09	0.44	0.143 ± 0.007	0.080 ± 0.003	5
3	9.03	0.78	0.209 ± 0.005	0.143 ± 0.005	4
4	14.11	1.23	0.298 ± 0.003	0.202 ± 0.009	3
5	24.45	2.13	0.405 ± 0.018	0.321 ± 0.007	3
6	32.85	2.86	0.496 ± 0.028	0.397 ± 0.002	3
7	42.39	3.69	0.546 ± 0.013	0.484 ± 0.011	3
8	56.35	4.90	0.613 ± 0.014	0.573 ± 0.018	3

Fig. IV. 4. Effect of exposure "not near uranium" in hole No. 1867-NNU in the Oak Ridge pile, temperature ca 32°C .

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A plot of the reciprocal of the resistivity change against the reciprocal of the bombardment gives a straight line, which indicates that the data are satisfactorily represented by such a hyperbola. In the present case the relationship is

$$r^{-1} = 5.9 L^{-1} + (1.44)^{-1} \quad (2)$$

This equation suggests that the resistivity would exhibit a "steady-state" (i.e., maximum) increase of 1.44 (obviously considerably less than actually found for prolonged bombardment, as shown in Fig. 2). Evidently, for small bombardments, in which the increase in resistivity is small compared to 1.44, the increase is an approximately linear function of the amount of neutron exposure. For the present such a hyperbola should be considered as nothing more than an empirical description of the observed neutron-induced increases in electrical resistivity in these experiments. No similar simple representation of the elastic modulus data has been discovered.

5.3 Irradiations in Experimental Hole 21

The Oak Ridge pile has several experimental holes which run horizontally through the pile transverse to the charging channels. These holes are 4 in. x 4 in. square and are ordinarily filled with graphite stringers which can be pushed in and out to install or remove samples. Graphite samples were irradiated in aluminum cans placed in a stringer near the center of the pile in hole 21 (2.67 ft. to the front of center and 1.3 ft. below center). During exposure samples were located 3 in. to 10 in. from uranium, but the essential difference between exposures here and in hole No. 1867-NNU was the temperature. Since the region of hole 21 is not directly cooled, samples located there are at the same temperature as the graphite moderator of the pile. This temperature rose from 75°C to ca 130°C in the course of the experiments.

A number of neutron bombardments were made using parallel-cut samples of AGOT-K graphite. The qualitative nature of the changes in electrical resistivity and elastic modulus was the same as observed in other experiments. The quantitative differences which did exist were the result of the higher bombardment temperature. From other experiments in which samples were irradiated in electric furnaces maintained at various temperatures, it is known that for small bombardments, less than 3 L-units, the elastic modulus change is relatively insensitive to temperature in the range between room temperature and 130°C. This fact permits calculation of L-unit values for samples irradiated in hole No. 21. Figure 5 demonstrates the temperature dependence of neutron-induced increases in electrical resistivity and elastic modulus. The curves shown are, however, very arbitrary, since the data at hand were few and the uncertainties in bombardment magnitudes and temperatures were large. For purposes of comparison, curves for changes observed with samples irradiated inside the doughnuts have been included. Figure 5, except for the 35° curves, must be taken only as an indication of gross trends.

Fig. IV. 5. Effect of exposure temperature on fractional increases in elastic modulus and electrical resistivity of parallel-cut AGOT-K artificial graphite.

6. Experiments in the D₂O-Moderated Pile at Argonne Laboratory

The Argonne pile (CP-3) consisted of an array of aluminum-clad natural uranium rods suspended vertically in a tank of heavy water. The tank was 6 ft in diameter and ca 7 ft tall; the uranium rods were 6 ft. long; and the lattice spacing was 5.375 inches. Heat was removed from the moderator by circulating it through an external cooling system, and the progress of the chain reaction was regulated by appropriate control mechanisms and safety devices. The power level during normal operation was 0.25 to 0.30 Mw. Thermal neutron fluxes at 0.30 Mw were estimated to be ca 10^{12} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ at the center of the pile.

Experimental work was performed in a centrally located test thimble ca 4 in. in diameter, extending downward, parallel to the uranium rods, to ca 1 ft. from the bottom of the tank. A special assembly of smaller tubes fitted into the large tube so that specimens in aluminum

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containers (1 in. diam. and several inches long) could be inserted into the pile. Sample temperatures were controlled by either water or air cooling to $25 \pm 5^\circ\text{C}$.

An experiment was performed to investigate the distribution of fast neutron flux along the length of the test thimble. Graphite samples were irradiated at various distances from the bottom of the thimble and the changes in electrical resistivity and elastic modulus were measured. The data indicated that the fast neutron flux had a maximum relative value of 1.0 at ca 12 in. from the bottom of the thimble (ca 24 in. from the bottom of the tank). From this maximum the flux decreased with approximate cosine dependence, having the value 0.92 at the bottom of the thimble and 25 in. above the bottom, and the value 0.8 at ca 33 in. from the bottom. In practice, samples were always irradiated in the region 0 to 18 in. from the bottom of the thimble and, because of uncertainty of position of individual samples, no attempt was made to correct for variation of fast flux with position.

Neutron exposures were recorded in terms of megawatt hours, Mwh, of total integrated power developed by the pile. Because it was practically impossible to change the distribution of uranium, the neutron production per Mw remained relatively constant during the course of the experiments. Only two conversion factors were required to convert nominal Mwh to L-units: (a) 25 Mwh/L-unit for experiments 1, 2, and 3, in which the thimble assembly was water-cooled, and (b) 20 Mwh/L-unit for experiments 4, 5, and 6 in which a different air-cooled assembly was used. The cause of this difference is uncertain but may be the result of the fact that, with the air-cooled assembly, there was less moderator between samples and uranium metal.

Samples of each of the types of graphite described in section 3 were irradiated. Both parallel-cut and perpendicular-cut specimens were used, except in the cases of pbL and pbNG. The techniques of sample preparation and measurement were the same as described earlier. Six bombardments were made. Four of these were relatively long bombardments in which each new bombardment involved samples from all previous bombardments. The remaining two bombardments were shorter and were incidental to other work.

Table IV summarizes the averaged fractional increases, r_f and e_f , for all sets of parallel-cut AGOT-K(II) samples.⁽²⁰⁾ Mean absolute deviations and the number of samples used are also included. Bombardments have been assigned consecutive numbers so that the history of any set of samples can be traced. Figure 6 shows the results in graphical form. The lines through the experimental points have been drawn in such a way as to be consistent with a plot of resistance change vs elastic modulus change for all the samples measured (e.g., see Fig. 3).

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TABLE IV.

Neutron-Induced Changes in Electrical Resistivity and Elastic Modulus of
Samples of Parallel-Cut AGOT-K(II) Artificial Graphite Irradiated in
the Central Thimble of the Argonne Heavy-Water Pile

(Temp: $25 \pm 5^\circ\text{C}$)

Bombardment designation	Neutron exposure (Mwh)	Neutron exposure (L-units)	e_f	r_f	Number of samples
1	49.2	1.97	0.370 ± 0.015	0.289 ± 0.008	15
2	76.6	3.07	0.482 ± 0.015	0.438 ± 0.007	6
2, 1	125.8	5.05	0.649 ± 0.016	0.627 ± 0.013	15
3	89.0	3.56	0.528 ± 0.010	0.497 ± 0.016	4
3, 2	165.6	6.62	0.756 ± 0.021	0.809 ± 0.012	6
3, 2, 1	214.8	8.59	0.892 ± 0.017	0.946 ± 0.015	13
4	144.1	7.21	0.729 ± 0.054	0.836 ± 0.040	5
4, 3	233.1	10.76	0.939 ± 0.003	1.128 ± 0.017	4
4, 3, 2	309.7	13.83	1.068 ± 0.023	1.326 ± 0.014	6
4, 3, 2, 1	358.9	15.80	1.181 ± 0.011	1.427 ± 0.016	8
5	27.7	1.38	0.331 ± 0.009	0.245 ± 0.005	5
6	31.7	1.58	0.296 ± 0.011	0.226 ± 0.007	4

Fig. IV. 6. Effect of neutron exposure in the central thimble of the Argonne heavy-water pile on the electrical resistivity and elastic modulus of parallel-cut AGOT-K(II) artificial graphite, temperature ca 25°C .

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The electrical resistivity data fit the hyperbola of Eq. (1) with a constant r_{∞} which implies an ultimate increase of ca 320 percent, i. e.,

$$r_f^{-1} = 6.18 L^{-1} + (3.22)^{-1} \quad . \quad (3)$$

In the case of samples irradiated in hole No. 1867 of the graphite pile at Oak Ridge, the corresponding ultimate increase predicted was 144 percent. Analysis of electrical resistivity data for samples irradiated at ca 30° C at each of the sources used showed that there was indication of a tendency for the ultimate increase (i. e., r_{∞}) to be larger the higher the rate of bombardment.

The results for samples of other types of graphite are similar to those for parallel-cut AGOT-K(II) specimens. It has been observed, however, that for each bombardment or combination of bombardments the ratio of the average change in electrical resistivity or elastic modulus for any given kind of specimen to the corresponding change for AGOT-K(II) graphite was constant within the experimental scattering. For this reason it was unnecessary to record explicitly the individual data for the various specimen types studied. All the results can be represented by the curves in Fig. 6, provided the proper proportioning ratio be included. These are summarized in Table V. The ratios given are of the form p_i/p_k , where p_i represents the fractional increase in electrical resistivity or in elastic modulus for a given type of specimen in any bombardment and p_k represents the fractional increase in the same property exhibited by parallel-cut AGOT-K(II) specimens in the same bombardment. The entries in Table V are the averages of such ratios calculated for each bombardment. Average initial values of electrical resistivity and elastic modulus are also included.

The series Sp2100, Sp2400, and Sp3000 indicate that neutron-induced changes are greater the higher the temperature of graphitization. It is interesting to note that for Sp2100, a material in which practically no graphitization has occurred, there was no increase in electrical resistivity on neutron exposure. The dependence of elastic modulus changes on crystallite size is shown by the series pbNG, AGOT (any type), pbL. The same correlation of large elastic modulus change with large crystallite size is also exhibited within the series AGOT-K, AGOT-C, and AGOT-W. Parallel-cut samples seem to show smaller elastic modulus increases than perpendicular-cut samples.

DISCUSSION

The disordering of solids by the action of fast massive particles has been treated by Seitz. ⁽²¹⁾ Neutrons in collisions with carbon atoms in graphite transfer on the average about one seventh of their energy to the struck atom. On moving through the graphite the recoil thus produced dissipates its energy practically exclusively by electronic excitation until the energy

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TABLE V.

Relative Effect of Neutron Bombardment in the Argonne Heavy Water Pile on Elastic Modulus and Electrical Resistivity of Various Graphites Compared to Parallel-Cut AGOT-K(II) as a Standard. (Parallel-Cut, ||; Perpendicular-Cut, $\perp$)

Type of graphite	E_0 (10^{10} dynes/cm ²)	e_i/e_k	R_0 (10^{-4} ohm cm)	r_i/r_k
AGOT-K(II)	13.9	1.00	5.79	1.00
$\perp$	5.78	1.24 ± 0.05	10.49	0.96 ± 0.03
AGOT-K(I)	13.1	0.96 ± 0.03	6.45	0.89 ± 0.02
AGOT-C	10.6	0.91 ± 0.04	7.65	0.92 ± 0.03
$\perp$	6.44	0.92 ± 0.04	11.93	0.75 ± 0.04
AGOT-W	10.0	0.79 ± 0.04	8.41	0.86 ± 0.03
$\perp$	6.63	0.79 ± 0.03	11.81	0.78 ± 0.02
Sp 3000	7.1	1.03 ± 0.04	9.4	0.85 ± 0.03
$\perp$	5.5	1.09 ± 0.04	11.4	0.83 ± 0.03
Sp 2400	6.6	0.50 ± 0.04	22.	0.25 ± 0.02
$\perp$	5.5	0.61 ± 0.04	22.	0.35 ± 0.02
Sp 2100	6.4	0.23 ± 0.03	38.	0.00 ± 0.01
$\perp$	4.9	0.24 ± 0.04	45.	0.00 ± 0.01
pbL	5.8	0.24 ± 0.04	65.	0.07 ± 0.01
pbNG	15.6	1.16 ± 0.10	9.7	0.61 ± 0.03

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approaches a critical value which, calculated according to equations given by Seitz,⁽²¹⁾ is ca. 11 kev for graphite. Below this energy practically all of the remaining energy is lost in elastic encounters with carbon atoms. It is assumed that a stationary carbon atom must receive at least 25 ev in order to be knocked free of the graphite lattice, and that about one half the energy expended by a moving carbon atom below 11 kev is useful in causing permanent displacements. Each neutron produces several primary carbon recoils which, in turn, produce secondary recoils, etc. On being slowed to thermal energies, one 2-Mev fission neutron will generate a cascade of recoil atoms and cause approximately 2000 displacements.⁽²¹⁾

Uncertain knowledge of fast neutron fluxes through samples in pile exposures make calculations difficult. It is possible, however, to estimate numbers of displaced atoms using the Berkeley cyclotron exposures of section 2. The data indicate that one L-unit corresponds to a flux of 4.5×10^{16} fast neutrons per square centimeter. Recognizing that the range of fast neutrons is very large relative to the dimensions of the graphite specimens used and taking the scattering cross section to be $4 \times 10^{-24} \text{ cm}^2$, the number of primary carbon recoils per cm^3 can be calculated. Thus $(4 \times 10^{-24} \text{ cm}^2) \times (4.5 \times 10^{16} \text{ neutrons/L-unit}) \times (8.5 \times 10^{22} \text{ carbon atoms/cm}^3)$ gives 1.5×10^{16} primary recoils/ cm^3 per L-unit.

The total number of atoms displaced by a single primary fast carbon recoil calculated according to Seitz (reference 21, Eq. 21) is approximately ninety. One L-unit of exposure, therefore, generates ca. 1.4×10^{18} displacements per cm^3 or about 1.6×10^{-5} displaced atoms per carbon atom in graphite. (Note. November 17, 1955, W. Primak has pointed out that recent theoretical calculations by Seitz and Koehler, Snyder and Newfeld, and Harrison and Seitz indicate that the numbers 2000 displacements per thermal neutron and 90 displacements per carbon recoil are about a factor of three too low. He further has pointed out that the scattering cross section ($4 \times 10^{-24} \text{ cm}^2$) of carbon used was too high by a factor of about three. Fortuitous cancellation of errors thus permits the value 1.4×10^{18} displacements per cm^3 per L-unit to remain unchanged.)

Most of the carbon of artificial graphite is in the form of "natural graphite" crystallites embedded in a magma of slag and disorganized carbon. On the basis of manufacturing details,⁽⁸⁾ it can be estimated that the non-crystalline material, which comes predominantly from the coal tar pitch, does not contribute more than one quarter of the bulk of artificial graphite. It is reasonable to assume, therefore, in the absence of any contrary information, that the neutron-induced changes in electrical resistivity and elastic modulus are a result of disturbances in crystallites. In a single graphite plane, hexagonal in shape and 1000 Å in extent, there are approximately 10^6 carbon atoms. Thus an exposure of one L-unit produces about 16 displaced carbon atoms per plane. An exposure of ca. 6 L-units, which causes an increase in both electrical resistivity and elastic modulus of ca. 70%, produces about 100 displaced carbon atoms per graphite plane.

Displaced carbon atoms have several fates: (1) they may return to a lattice vacancy, (2) they may move to an edge or inner fissure of the crystal, (3) they may remain as single interstitial carbon atoms, (4) they may form interstitial molecules, (5) they may combine to form larger aggregates. The observed changes in electrical resistivity and elastic modulus confirm the existence of permanently displaced carbon atoms and lattice vacancies in neutron bombarded graphite. The increase in electrical resistivity for short bombardments is understandable in terms of scattering of electrons (or positive holes) by the interstitial disturbances and lattice vacancies.

The behavior of the elastic modulus can be understood to some extent by presuming that interstitial disturbances increase the rigidity of the individual "natural graphite" crystals, thus causing the increase in elastic modulus. The steep initial rise and the early tendency towards a "saturation" indicate that this rigidity effect must have a large effective radius per disturbance and involve a kind of disturbance formed early in the disordering process. A more extensive discussion of neutron-induced disordering is given in the first paper of this series.⁽¹⁾

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V. THERMAL CONDUCTIVITY MEASUREMENTS^{a,b}

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ABSTRACT

The thermal conductivity of artificial graphite is decreased by fast neutron bombardment. In a typical sample which received a neutron bombardment of 24 L-units at a maximum temperature of ca 125°C, the increase in thermal resistivity was about 200 per cent. For exposures of less than 3 L-units the increases in thermal resistivity and electrical resistivity are equal; for greater exposures the increase in thermal resistivity is larger. Very much as for electrical resistivity, about 94 per cent of the thermal resistivity effect can be removed ("healed") by heating to 800°C. Most of this healing is complete at about 300°C. Increased thermal resistivity of graphite after irradiation is attributed to disturbances in the lattice structure of the crystallites, e.g., lattice vacancies and interstitial carbon atoms or molecules. Annealing causes a removal of a portion of these disturbances and the thermal resistivity is decreased.

1. Introduction

Preceding papers of this series have shown that Wigner's prediction⁽¹⁾ of the fast neutron-induced disarrangement of the lattice structure of graphite was amply verified in studies of its elastic modulus^(2,4) and electrical resistivity.^(3,4)

^aBased upon work done at the Metallurgical Laboratory, University of Chicago (now Argonne National Laboratory) during 1943 by the authors and others including W. R. Burns, R. C. Hirt, J. Royal and R. T. Schenck.

^bThis article was originally intended for publication as paper 3.8 of Vol. 10B, Radiation Chemistry, of the National Nuclear Energy Series (Plutonium Project Record) under the editorship of Milton Burton.

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Since neutron bombardment caused changes in electrical resistivity of the graphite, changes in its thermal conductivity were expected. This paper reports the initial study of the effect of neutron bombardment on the thermal conductivity of artificial graphite.

2. Experimental

2.1 Details of Apparatus

The heat flow, dQ/dt , in the direction $\underline{x}$, across an area, $\underline{A}$, normal to $\underline{x}$, is described by the equation

$$dQ/dt = -\underline{K} \underline{A}(dT/dx) \quad , \quad (1)$$

where $\underline{K}$ is thermal conductivity and dT/dx is the thermal gradient along the direction of heat flow. The thermal conductivity can therefore be calculated from data on steady-state flow of heat down a cylindrical rod of known dimensions and temperature difference between two fixed points along the length of the rod.

Figure 1 is a diagram of the apparatus used. A steady flow of heat along the sample (b) was maintained by an electric heater (c). The heat which passed down the length of the sample was transferred to a (0.5 in. diameter) copper rod. The system, heat source-sample-heat sink, was surrounded by a glass jacket as shown in Figure 1 and the entire assembly submerged in a water thermostat to a depth sufficient to cover the sample chamber. The thermostat water temperature was in the neighborhood of 25°C and was regulated to $\pm 0.005^\circ\text{C}$. The copper rod (a) passed through the glass jacket and extended into the water. It was cemented into place with Apiezon "W" wax (f) which held it rigid and made the joint tight. The end of the sample was machined so that it fitted snugly into a hole in the end of the copper rod. This arrangement provided a satisfactory method of heat removal at constant temperature and, in addition, supported the sample and its accessories in the middle of the chamber. It is considered an important aspect of the apparatus that there was no other point of contact with the interior of the jacket. During measurement, conduction and convection losses from the sample to the water bath (other than along the length of the sample through the copper block) were eliminated by maintaining the sample in an "insulating" vacuum, 5×10^{-6} mm Hg or better.

The heating element (c) was made of ca 30 cm of 10-mil platinum wire wound on an alundum core, insulated by a coat of clear Glyptal resin and mounted in a graphite sleeve 0.25 in. i.d., 0.5 in. o.d., and 1.5 in. long. The end of the graphite sleeve through which the lead wires passed was sealed with Insulute cement. The other end fitted firmly onto the sample. Four electrical leads (e) were required: two current leads and two potential leads.

Heating currents were supplied by a 6-volt storage battery with suitable series resistor. Power inputs were determined by measurement of the heater current with a precision ammeter and the voltage drop across the heater with a potentiometer. Heater temperatures were observed by means of a thermocouple (d) imbedded in the graphite casing.

Fig. V. 1 Thermal Conductivity Apparatus.

The temperature difference between two points in the sample was determined by using two single-junction copper-constantan thermocouples, each referred to an ice-water mixture. The individual temperatures were measured by successive and separate readings of the two thermocouples with a Leeds and Northrup type K-II potentiometer. This procedure was preferred to the use of a differential thermocouple, since, in such a case, the thermocouple junctions would have to be electrically insulated from the graphite. Furthermore, the emf-temperature relationship for copper-constantan is not linear, so that the information thus obtained would not yield the actual temperature data and accurate temperature differences required. The couples were constructed of B and S 32 gauge wire, with silver-soldered junctions. During measurement the thermocouples were inserted into 0.25 in. deep, 0.019 in. diameter holes in the graphite sample. The fit between couples and holes was just as tight as possible in order to insure good thermal contact.

The ten wires required (six thermocouple wires, two heater power leads and two potential leads from the heater coil) were brought into the system through a vacuum-tight seal. The vacuum-tight insulating seal was made by running the wires through a spacer and sealing it into the male part of a ground glass joint with Apiezon "W" wax. This joint fitted into a sidearm of the tube leading to the vacuum system and provided a simple way of introducing or removing the electrical parts of the apparatus.

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2.2 Technique of Measurement

The first step in the use of the apparatus was a determination of power loss, P_L , from the heater as a function of its temperature. This involved measurement of the power necessary to maintain the heater alone (i.e., with no sample in the apparatus) at various temperatures, T_H , relative to the bath temperature, T_B . The power loss was $P_L = 0.01244 (T_H - T_B)$ watts. Thus the heat flow, P_S , from the heater through the sample to the copper block per unit time could be obtained by subtracting the extraneous power loss, P_L , from the total power input, P_T .

Dimensions were measured prior to introduction of the sample into the apparatus. The samples were all ca 1 cm in diameter and were right cylinders to within 0.01 mm. The center-to-center distance between thermocouples varied between 7 and 9 cm and was known to ± 0.01 cm. For measurement of its thermal conductivity a sample was mounted on the copper rod, the thermocouples inserted, the heater placed in position, the vacuum jacket closed, the assembly put in the regulated water bath and the evacuating system started. While the system was pumping down, the thermocouples were read in order to check that each gave the same temperature. After an insulating vacuum was obtained, the heater current was turned on and adjusted. It usually required about 20 minutes for a steady state to be reached. At this time the three thermocouples were read, and the voltage drop and current in the heater were measured. Usually two or three sets of readings were made. Currents were accurate to ca 0.5%, voltage drops to $< 0.1\%$. This calibration of copper-constantan used was that given in the International Critical Tables.⁽⁵⁾

The thermal conductivity, K , in units of $\text{cal cm}^{-1} \text{sec}^{-1} \text{deg}^{-1}$, was calculated by substituting in the formula.

$$K = 0.239 \frac{(P_T - P_L)\Delta x}{A\Delta T}, \quad (2)$$

where $0.239 (P_T - P_L)$ is the heat conducted along the sample per unit time, ΔT the temperature difference between two points along the length of the sample Δx cm apart, and A the cross-sectional area of the sample.

The method and the apparatus were checked by measurement of 2S aluminum and brass (0.70 Cu, 0.30 Zn). The values obtained for 2S aluminum at 27°C averaged to $0.543 \text{ cal cm}^{-1} \text{sec}^{-1} \text{deg}^{-1}$. The Alcoa handbook⁽⁶⁾ gives $0.54 \text{ cal cm}^{-1} \text{sec}^{-1} \text{deg}^{-1}$ for 2S annealed Al at 100°C. The value for the brass sample was $0.245 \text{ cal cm}^{-1} \text{sec}^{-1} \text{deg}^{-1}$ at 27°C, as compared with $0.250 \text{ cal cm}^{-1} \text{sec}^{-1} \text{deg}^{-1}$ for a sample of the same brass mentioned above but measured with a different apparatus in another laboratory.⁽⁷⁾

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Six measurements on a sample of parallel-cut AGOT-W (II) graphite gave the value $0.386 \pm 0.003 \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ deg}^{-1}$ at 25°C . Table I shows the specific data for those six measurements and illustrates the process of calculation of the thermal conductivity.

TABLE I

Calculation of the Thermal Conductivity at 25°C for
One Specimen of AGOT-W (II) Graphite.^a

P_T (watts)	$T_H - T_B$ ($^\circ\text{C}$)	P_L (watts)	$P_T - P_L$ (watts)	ΔT ($^\circ\text{C}$)	K ($\text{cal cm}^{-1} \text{ sec}^{-1} \text{ deg}^{-1}$)
0.346	3.30	0.041	0.305	2.18	0.382
0.474	4.65	0.058	0.416	2.98	0.381
0.568	5.36	0.067	0.501	3.55	0.385
0.350	3.29	0.041	0.309	2.16	0.389
0.438	4.20	0.052	0.386	2.76	0.390
0.580	5.55	0.069	0.511	3.58	0.389

^aAfter the first three measurements the specimen was dismounted and other samples measured. The last three measurements were made one week later.

2.3 Thermal Conductivity of Unirradiated Graphite

Measurements were made on six types of artificial graphite: AGOT-K (Bars I, II and III), AGOT-C (Bars II and III), AGOT-W (Bars I and II), Sp 2100, Sp 2400, Sp 3000. The first three graphites differed among themselves only in the source of the raw coke used in the manufacturing process. The remaining three were experimental graphites prepared by the National Carbon Company. They were essentially AGOT-W stock that had been graphitized at three different temperatures, *viz*, 2100°C , 2400°C and 3000°C . The preparation and properties^(4,8) of these graphites and the neutron-induced changes in elastic modulus and electrical resistivity have been discussed in earlier papers.^(2,3,4)

Table II summarizes the average thermal conductivities of the various types of graphite. The values given are averages for all the samples measured; figures in parentheses indicate the number of samples; mean absolute deviations are also included. Orientations of samples are indicated in Table II by || for samples whose axis is parallel to the extrusion axis and by $\perp$ for perpendicular-cut samples. The coke particles at the time of extrusion are of such a form that the extrusion process causes a preferential orientation of graphite crystallites relative to the extrusion direction.⁽⁸⁾ Thus, the thermal conductivities of specimens cut parallel to the extrusion axis and perpendicular to the extrusion axis are different.

TABLE II

Thermal Conductivity at 25°C of AGOT Artificial Graphite and of Specially Graphitized Materials (Unirradiated)

Type of Graphite	K, Thermal Conductivity, $\text{cal cm}^{-1} \text{sec}^{-1} \text{deg}^{-1}$	Type of Graphite	K, Thermal Conductivity, $\text{cal cm}^{-1} \text{sec}^{-1} \text{deg}^{-1}$
AGOT-K(I)	0.546 (1)	AGOT-W(I)	0.397 (1)
AGOT-K(II)	0.560 ± 0.002 (3)	AGOT-W(II)	0.398 ± 0.013 (2)
AGOT-K(III) $\perp$	0.291 ± 0.002 (3)	AGOT-W(II) $\perp$	0.303 ± 0.002 (2)
AGOT-C(II)	0.428 ± 0.001 (2)	Sp 3000	0.344 (1)
AGOT-C(III)	0.455 ± 0.003 (3)	Sp 2400	0.187 (1)
AGOT-C(III) $\perp$	0.320 ± 0.004 (2)	Sp 2100	0.073 (1)

2.4 Changes in Thermal Conductivity with Fast Neutron Bombardment

The effect of neutron bombardment on thermal conductivity of artificial graphite was studied using the graphite pile at Oak Ridge Laboratory and the heavy water pile at the Argonne Laboratory. Details of the bombardments were the same as described in earlier papers.^(2,3,4)

The thermal conductivity of each sample was measured before and after every irradiation. Corresponding electrical resistivities of each sample were determined using a Kelvin bridge. Table III summarizes the

TABLE III

Neutron-Induced Fractional Increases in Thermal Resistivity (k_f) and Electrical Resistivity (r_f) of Samples of Artificial Graphite.
 K_0 and R_0 Are the Prebombardment Thermal Conductivity and Electrical Resistivity, Respectively.

Type of Sample	Total ^a Irradiation (L-units)	Estimated Exposure Temperature (°C)	K_0 (cal cm ⁻¹ sec ⁻¹ deg ⁻¹)	k_f Fractional Increase in Thermal Resistivity	R_0 (10 ⁻⁴ ohm cm)	r_f Fractional Increase in Electrical Resistivity
AGOT-K,	2.6(A)	30	0.563	0.47	5.50	0.47
	5.3(A)	30	0.563	0.78	5.50	0.74
	7.6(A)	30	0.563	1.02	5.50	0.96
AGOT-K,	16 (X)	125	0.546	0.87	5.81	0.74
AGOT-K, ⊥	16 (X)	125	0.292	0.83	11.80	0.68
AGOT-W,	2.6(X)	125	0.404	0.34	8.18	0.28
	16 (X)	125	0.404	0.92	8.18	0.67
AGOT-W, ⊥	16 (X)	125	0.304	0.86	11.04	0.64
AGOT-C,	2.3(A)	30	0.450	0.29	7.36	0.29
AGOT-C,	16 (X)	125	0.457	0.87	7.35	0.65
AGOT-C, ⊥	16 (X)	125	0.321	0.87	10.85	0.64

^a(A) indicates Argonne Heavy Water pile; (X) indicates Oak Ridge graphite pile.

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data for several bombardments. The fractional increases in thermal resistivity, k , are defined in terms of the thermal conductivity, K , by

$$k_f = (K_f^{-1} - K_0^{-1})/K_0^{-1} = (K_0 - K_f)/K_f \quad (3)$$

where the subscript $_0$ denotes initial properties and subscript $_f$ final properties. Fractional increases in electrical resistivity, $r_f = (R_f - R_0)/R_0$, have been included so that thermal resistivity can be correlated with electrical resistivity and with other physical properties. Bombardment magnitudes are listed in L-units⁽⁴⁾ and estimates of the temperature of bombardment are given. The place of bombardment is indicated by a letter in parentheses adjacent to the bombardment magnitude, (A) for the pile at Argonne Laboratory, (X) for the pile at Oak Ridge Laboratory.

Figure 2 shows the increase in thermal resistivity and electrical resistivity as a function of the amount of neutron bombardment at ca 30°C. The figure and other data in Table III indicate that the fractional increase in thermal resistivity is approximately the same as that in electrical resistivity for samples bombarded with less than 3 L-units at a temperature of ca 30°C. Beyond that exposure the thermal resistivity appears to increase faster than does electrical resistivity. For samples irradiated at higher temperatures, changes in thermal resistivity are less than would have been produced in an equivalent bombardment at a lower temperature.

Fig. V. 2

Increase of thermal resistivity and electrical resistivity for AGOT-K graphite (parallel-cut) irradiated with fast neutrons at 30°C.

An interesting aspect of the data is the approximate linearity of thermal resistivity, K^{-1} , with electrical resistivity R , as given by the relationship

$$K^{-1} = 3.2 \times 10^3 R \quad (4)$$

The initial properties of all of the various graphites studied obey equation (4) with a precision of approximately 5 per cent for AGOT type graphites and approximately 10 per cent for the specially graphitized materials (Sp 2100 etc.). This is true both for parallel-cut and perpendicular-cut specimens. Thermal resistivities and electrical resistivities of neutron-irradiated specimens and the corresponding values after annealing at 800°C also satisfy equation (4) with a precision of about 5 per cent. It is important to emphasize, however, that this simple relationship between K^{-1} and R exists only for relatively short bombardments. As is clear from Fig. 2 deviations are already becoming apparent at exposures of 3 L-units.

2.5 Thermal Healing of Neutron Induced Changes

A second series of thermal conductivity measurements was made on samples of irradiated AGOT-W graphite. These were cut from graphite bars which had been part of the structure of the Oak Ridge pile since startup. The bars were removed from the pile at different times and new graphite inserted. The samples cut from these different bars thus had different bombardments, but it was possible, by use of elastic modulus data for samples cut from each bar, to determine the approximate exposure in terms of L-units.

Thermal conductivities were measured on six samples. Fractional increases in thermal resistivity, k_f , could be estimated by assumption of average initial thermal conductivities consistent with those for AGOT-W, listed in Table II. Because of rather large bar-to-bar variations such estimates are, of course, rather uncertain. After the first measurements were completed the samples were heated and remeasured. From other experiments on the electrical resistivity and elastic modulus it was known that the neutron-induced effects could be "healed" (i.e., more or less removed) by heating at moderate temperatures.^(4,9) A large part of the resistance increase is removed by heating for one-half hour at 800°C and so this temperature was used as a basis for the "annealing" of specimens employed for thermal conductivity studies.

Table IV summarizes thermal conductivity data (given as fractional increases in thermal resistivity) for samples from each bar, before and after annealing. The letters χ , γ , ϵ and δ identify the various bars. The values of the initial thermal conductivities assumed in the calculations for Table IV are $0.38 \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ deg}^{-1}$ for parallel-cut samples and $0.28 \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ deg}^{-1}$ for perpendicular-cut samples. Evidently, thermal resistivity increases with bombardment at least as far as 200 per cent at ca 24 L-units. This change in thermal properties is healed to a large extent by heating to 800°C. The unhealable (at 800°) residual effect also increases as the amount of neutron bombardment is increased. The considerable extent of thermal annealing during bombardment at higher temperatures is evident upon consideration of samples ϵ and δ .

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TABLE IV

Fractional Increase in Thermal Resistivity of
Irradiated AGOT-W Graphite

Designation of Sample	Estimated Exposure (L-units)	Approximate Exposure Temperature (°C)	k_f , Increase After Neutron Exposure	k_h , Residual Increase After 800°C Anneal
χ -bar,	6	70	0.48	0.02
χ -bar, $\perp$	6	70	0.46	0.04
γ -bar,	9	90	0.61	0.06
γ -bar, $\perp$	9	90	0.58	0.08
ϵ -bar,	24	125	2.02	0.24
δ -bar,	48	175	0.86	0.22

The healing of neutron-induced effects was investigated also in other annealing experiments. Before being heated to 800°C, the parallel-cut γ -bar sample was heated to 194°C (16 hours) and 250°C (6 hours). Thermal conductivity and electrical resistivity were measured after each heating. Figure 3 summarizes the results. Thermal conductivity change was found to heal to different extents depending upon the temperature of annealing. Thermal resistivity closely paralleled the electrical resistivity, but the agreement exhibited in Fig. 3 must not be too highly regarded since it is dependent upon the initial properties of the specimen. These initial properties were unknown and reasonable values had to be assumed for purposes of calculation. Examination of the data does show, however, that neutron-induced changes in thermal conductivity are very easily healed by heating, and that most of the annealing which will occur at 800°C is already accomplished before 300°C.

Fig. V. 3

Thermal healing of neutron-induced changes in thermal resistivity and electrical resistivity for a sample of AGOT-W graphite.

3. Discussion

The principal mechanism of thermal conduction in graphite is not electronic in nature. This can be shown by consideration of the Wiedemann-Franz law:

$$K/\sigma T = 5.87 \times 10^{-9} \text{ cal ohm sec}^{-1}/\text{deg}^{-2},$$

where K is the thermal conductivity ($\text{cal cm}^{-1} \text{ sec}^{-1} \text{ deg}^{-1}$), σ the electrical conductivity ($\text{ohm}^{-1} \text{ cm}^{-1}$) and T the absolute temperature in degrees Kelvin. On the basis of the electrical resistivity actually observed for graphite, the Wiedemann-Franz law predicts a thermal conductivity ca 200 times too small. Consequently, heat conduction would appear to be by lattice vibrations of some sort. There will, of course, be some contribution of an electronic nature, but this must be minor. In addition the intergranular resistance to heat flow across crystallite boundaries must be considered. This last term may be very important.

As an approximation, however, it seems reasonable to suppose that the intergranular resistance might not be affected by small amounts of neutron irradiation. The bombardment is a disordering process. Since the intergranular material (unlike the crystallites) is not very highly organized it would not react very rapidly to further disorganization. Consequently, an acceptable conclusion is that the principal effect of fast neutrons on the thermal conductivity of graphite involves some kind of interference with the lattice vibrations of the crystallites themselves. The decrease in thermal conductivity which would correspond to the observed neutron-induced increase in electrical resistivity will be present but relatively rather small in magnitude.

Neutron bombardment of graphite produces interstitial disturbances and lattice vacancies within the crystallite and also causes further disorganization of non-ordered material.⁽¹⁰⁾ The lattice vacancies and interstitial carbon particles (i.e., atoms or atom groups) are the disturbing factors which change the thermal conductivity via their effect on the lattice vibrations. Interstitial disturbances are probably bound fairly loosely between the planes of graphite crystallites and may accordingly be expected to move on annealing at moderate temperatures. This healing process was observed.

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VI. RATE OF HEALING EXPERIMENTS^{a, b}T. J. Neubert,^c and A. Novick^dABSTRACT

The distribution spectra for the thermal annealing of disturbances produced in artificial graphite by fast neutron bombardment suggest that the interstitial disturbances which anneal out below 1000°C fall into two broad classes, with mean characteristic activation energies of 1.4 and 1.8 electron volts. Disturbances with characteristic energy 1.4 ev seem to be predominantly responsible for electrical resistivity effects, while those with energy 1.8 ev seem to be most important so far as elastic modulus effects are concerned. Secondary maxima in the distribution curves indicate the extent to which disturbances characteristic of the electrical resistivity changes affect the elastic modulus and vice versa.

1. Introduction

Fast neutron-induced changes in the physical properties of artificial graphite⁽¹⁻⁴⁾ are considered to be the result of disturbances in the artificial graphite structure produced by the neutron moderation process.⁽⁵⁾ If the disturbances are carbon atoms or groupings of carbon atoms, either trapped interstitially or at inner fissures in the graphite crystallites, it might be expected that at least a part of the effect could be healed at relatively low temperatures. Annealing experiments performed on cyclotron-irradiated samples indicated that there was significant healing of neutron-induced increase in electrical resistivity at 100°C and at 200°C.⁽³⁾

^aBased upon work done at the Metallurgical Laboratory, University of Chicago (now Argonne National Laboratory) during the period 1943 - 1946, and summarized in ANL-4369, November 18, 1949.

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Healing rates were high in the early stages of annealing, decreasing as the annealing was carried further, and ultimately dropping to values so low as to be within the precision of the resistivity measurements.

When rate data from these and other preliminary experiments⁽⁶⁾ were examined, in order to determine whether the annealing process could be described by a first-order rate equation having a single activation energy, it was found that no such simple interpretation could be given to the results. Furthermore, the fact that the limiting value to which the resistance changes dropped after a long-time anneal at 200°C was lower than the corresponding limiting value for annealing at 100°C, suggested that a distribution of activation energies would probably be necessary to describe the results of annealing experiments.

2. Analysis of Thermal Annealing Data

A method for calculating distribution spectra of activation energies for thermal healing processes has been outlined by Vand,⁽⁷⁾ who discussed two separate types of experiments by which such activation energy spectra can be determined: (a) the method of ageing, and (b) the method of tempering. In the method of ageing, healing of a given physical property in a set of specimens is studied as a function of time at a series of constant temperatures. In the method of tempering, healing is studied under the condition that the specimen temperature is constrained to rise uniformly in time and observations are made either as a function of time or as a function of temperature. The kinds of assumptions and approximations involved in the Vand technique of analysis can be seen from a brief survey of his treatment of ageing data. Data from ageing experiments at fixed temperatures are of the form indicated in Figs. 1 and 2.

If it is assumed that each disturbance in neutron-bombarded graphite has a higher energy content than is characteristic of the nondisturbed lattice, then by a local fluctuation it can receive the critical activation energy, E , necessary to bring it over the energy barrier which prevents its spontaneous healing. The disturbances can then be thought of as ordered according to their characteristic activation energies for thermal annealing, and the total number of disturbances, n_0 , at time $t = 0$ and the total number, n_t , at any subsequent time, t , can be written as:

$$n_0 = \int_{-\infty}^{+\infty} H_0(E) dE \text{ and } n_t = \int_{-\infty}^{+\infty} N(E, t) dE, \quad (1)$$

where $N(E, t)$ is the number of disturbances having energies in the range $E + dE$ at time t ; and $N_0(E)$ is a corresponding quantity for time $t = 0$. It is next assumed that the mechanism for thermal annealing is describable in terms of a first-order rate process. This leads readily to an expression for n_t of the following form:

Fig. VI. 1. Annealing of the neutron-induced change in elastic modulus of samples heated at various constant temperatures.

Fig. VI. 2. Annealing of the neutron-induced change in electrical resistivity of samples heated at various constant temperatures.

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$$n_t = \int_{-\infty}^{+\infty} N_0(E) \exp[-At \exp(-E/kT)] dE = \int_{-\infty}^{+\infty} N_0(E) \phi dE. \quad (2)$$

The function $\phi = \exp[-At \exp(-E/kT)]$ is essentially zero at $E = 0$ and approaches unity as E approaches infinity. In some intermediate region ϕ undergoes a somewhat rapid transition from values near zero to values near unity. A point of inflection occurs at

$$E' = kT \ln At. \quad (3)$$

In order to render Eq. (2) more amenable to mathematical manipulation, Vand suggested that the function ϕ be approximated by taking it to have the value zero for $E < E'$ and the value unity for $E > E'$. Eq. (2) thereby reduced to

$$n_t = \int_{E'}^{+\infty} N_0(E) dE. \quad (4)$$

The inflection point, E' , defined by Eq. (3), is interpreted as describing the activation energy characteristic of disturbances healing at time t . The various assumptions imply that disturbances of energy E_i will not heal at a given temperature until such a time has elapsed that $E' = E_i$, [see Eq. (3)] and then, at that time, all disturbances of energy, E_i , will heal instantaneously. This is hardly an ideal approximation, but it does seem to be necessary. By differentiation of Eq. (4) with respect to time, Vand then completes his analysis by reducing it to an experimentally applicable form.

Thus

$$\frac{d}{dt} n_t = \frac{d}{dt} \int_{E'}^{+\infty} N_0(E) dE = -N_0(E) \frac{kT}{t}, \quad (5)$$

and

$$N_0(E) = \frac{-t}{kT} \frac{d}{dt} n_t. \quad (6)$$

Equation (6) seems, therefore, to provide a means for calculating the number of disturbances $N_0(E)$ as a function of a characteristic activation energy, E , defined by Eq. (3). There is, however, no simple technique for the observation of n_t ; instead, what is observed is a combination of the number of disturbances of a given activation energy and the importance of that kind of disturbance in changing some physical property. In the annealing experiments to be described in this paper, measurements were made of the healing as a function of time of the neutron-induced increases in electrical resistivity and elastic modulus. Thus Eq. (4) must be rewritten as follows:

$$r'_t = \int_{E'}^{\infty} I_R(E) N_0(E) dE = \int_E^{\infty} R_0(E) dE, \quad (\text{for electrical resistivity}) \quad (7a)$$

$$e'_t = \int_{E'}^{\infty} I_E(E) N_0(E) dE = \int_E^{\infty} E_0(E) dE. \quad (\text{for elastic modulus}) \quad (7b)$$

In Eqs. (7a) and (7b), r'_t and e'_t are, respectively, the residual fractional increase in electrical resistivity and the residual fractional increase in elastic modulus left in samples at time t . The new factors $I_R(E)$ and $I_E(E)$ are functions (importance factors) which describe the effect of one disturbance of energy E on the electrical resistivity and the elastic modulus. The product of an importance factor, $I(E)$, and a number of disturbances, $N_0(E)$, can then be redefined as in the right-hand members of Eqs. (7a) and (7b). The forms of Eq. (6) which will be used are, therefore,

$$R_0(E) = \frac{-t}{kT} \frac{d}{dt} r'_t; \quad E_0(E) = \frac{-t}{kT} \frac{d}{dt} e'_t. \quad (8)$$

For tempering experiments in which measurements are made while the temperature is rising linearly in time, Vand has made a similar, although necessarily somewhat more complicated, analysis involving the same assumptions and approximations as in the case of ageing experiments. His computations show that $R_0(E)$ and $E_0(E)$ are given essentially by the slope of the curves of electrical resistivity vs temperature and elastic modulus vs temperature. The exact equations as well as the relationships which relate activation energy and temperature must be sought in Vand's paper.⁽⁷⁾

3. Ageing Experiments

A set of samples of irradiated graphite were heated at various constant temperatures, and annealing of the neutron-induced electrical resistivity increase and the elastic modulus increase was studied as a function of time. The samples were all parallel-cut AGOT-K(II) artificial graphite⁽⁸⁾ irradiated for 73 Mwd (10 L-units) in the Oak Ridge pile, $T = 35 \pm 5^\circ\text{C}$. The techniques of measurement of electrical resistivity and elastic modulus were the same as have been previously described.^(2,3,6) Samples were heated by placing them in a closely fitting metal tube, closed at its lower end. The tube and sample were plunged into a bath of liquid boiling at an appropriate temperature and, after the heating had progressed as far as desired, were removed and cooled by quenching in ice water. The electrical resistivity and elastic modulus of the sample were then measured at room temperature and the heating process continued.

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Rates of annealing were studied at temperatures ranging from 100°C to 303°C, and for times up to ca 10^5 min. In order that all healing curves should start from a common value, the neutron-induced change remaining at each time of measurement was divided by the change for zero time of heating. Thus the electrical resistivity and elastic modulus parameters to be used were calculated as follows:

$$r'_t = [(R_{f,t}/R_0) - 1] \quad [(R_{f,0}/R_0) - 1] \quad (9a)$$

and

$$e'_t = [(E_{f,t}/E_0) - 1] \quad [(E_{f,0}/E_0) - 1] \quad (9b)$$

Here r'_t and e'_t denote the relative amount of neutron-induced increase in electrical resistivity and elastic modulus remaining at time t . Upper case letters refer to the property measured. The subscript, f , indicates that the measurement was made after neutron irradiation; the second subscript indicates the time of heating after which the measurement was made; and the single subscript, 0, indicates that the measurement was made prior to irradiation. For the samples used the average value of $[(R_{f,0}/R_0) - 1]$ was 1.063 ± 0.025 ; the average value of $[E_{f,0}/E_0] - 1$ was 0.968 ± 0.020 . Some of the data are shown in Figs. 1 and 2.* It will be noticed that the healing data exhibit the behavior discussed earlier.

The healing of the neutron-induced increase in electrical resistivity was investigated at temperatures in the neighborhood of room temperature. A series of five samples, three bombarded at the University of California (60-inch) cyclotron ($11 \times 10^4 \mu\text{ah}$, 5.7 L-units) and two bombarded in the "doughnuts" in the Oak Ridge pile (34 Mwd, 5.7 L-units), were measured after bombardment and then at various times after standing at room temperature, for times up to 366 days. Table I summarizes the results. Of the samples used, three were AGOT-K graphite and two were AGOT-C graphite, but there seems to be no significant differences between samples, either by reason of the kind of graphite or technique of neutron irradiation. The temperature of irradiation was probably in the neighborhood of 30°C for both neutron sources. It will be noticed that in each of the five samples the electrical resistivity change decreased in 366 days to about 80% of its value at the time the experiment was begun. Analysis of the measurements for times less than 200 days indicate activation energies, for the thermal healing of disturbances, of approximately 1 ev. A first-order rate process was assumed and the frequency factor was taken to be 10^{13} sec^{-1} . Similar assumptions have been made in all the calculations to be described.

*Table IV in the Appendix gives the experimental values on which Figs. 1 and 2 and subsequent calculations are based.

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TABLE I

Amounts of Neutron-Induced Electrical Resistivity Change Remaining in Irradiated Samples (5.7 L-units) after Various Times of Standing at 25°C

Description	AGOT-K			AGOT-C	
Sample n-source	K-196 cyc.	K-198 pile	K-201 cyc.	C-223 pile	C-227 cyc.
0 days	0.82	0.82	0.74	0.85	0.76
53 days	0.76	0.79	0.68	0.79	0.70
104 days	0.71	0.75	0.62	0.75	0.64
137 days	0.69	0.72	0.59	0.72	0.63
165 days	0.67	0.72	0.61	0.73	0.63
261 days	0.66	0.71	0.59	0.71	0.62
366 days	0.64	0.69	0.58	0.69	0.60
$\frac{r_0}{r_{366}}$	0.78	0.84	0.79	0.82	0.80

4. Tempering Experiments

Tempering experiments were performed on four samples of irradiated graphite. Samples were heated in such a way that the temperature changed approximately linearly in time, and the electrical resistivity was observed as a function of temperature. Electrical resistivities were measured by determination of the potential drop, between two brass clamp contacts on the sample, when a constant known direct current was flowing. A thermocouple attached to one end of the sample indicated the temperature. The sample and its accessories were mounted in a small Alundum tube which was enclosed in a graphite sleeve. The entire assembly fitted snugly into an electric furnace. The graphite sleeve and the adequate length of the furnace guaranteed a reasonably even temperature along the length of the sample. Samples were heated in an atmosphere of nitrogen. Measurements were made at half-minute intervals during the heating period, and several readings were made during the cooling period. The irradiation histories of the samples are as follows:

(a) Sample No. W-208, AGOT-W graphite, was irradiated in the "doughnuts" of the Oak Ridge pile for 34 Mwd (5.7 L-units) at a temperature of 25 to 30°C. The resultant fractional increase of electrical resistivity was 0.76; of the elastic modulus, 0.62.

(b) Sample No. W-214, AGOT-W graphite, was irradiated at the University of California cyclotron for ca $10^5 \mu\text{ah}$ (4.7 L-units) at a temperature of 25 to 30°C. The resultant fractional increase of the electrical resistivity was 0.62; of the elastic modulus, 0.46.

(c) Samples No. X-11 and No. X-17, were cut from a bar of AGOT-W graphite which had been part of the structure of the Oak Ridge pile. The bar received an irradiation of 54 Mwd (6 to 7 L-units). Irradiation temperatures were approximately 75°C except for a period of 36 hours near the end of the irradiation during which temperatures were slightly above 100°C. The resultant fractional increase in electrical resistivity and elastic modulus of these samples is not known since initial pre-irradiation measurements could not be made.

Results of the tempering experiments are shown in Fig. 3. It has been necessary to recompute the experimental values in such a way that the ordinary temperature dependence of the electrical resistivity of graphite is eliminated. The technique used was to calculate the fractional excess resistivity, r_T , at each temperature, as follows:

$$r_T = (R_{hT} - R_{cT})/R_{cT} \quad (10)$$

where R_{hT} is the electrical resistivity (in arbitrary units) at temperature T during the heating run and R_{cT} is the corresponding quantity during the cooling run. The data for samples W-208 and W-214 computed as described, and shown in Fig. 3, exhibit a small decrease in electrical resistivity effect at low temperatures, but as the temperature rises a point is reached, in the neighborhood of 100°C, at which the values begin to decrease quite markedly. The steepest region of healing is between 200°C and 300°C and as the temperature approaches 500°C the rate of change decreases to zero. The changes in the neighborhood of 200°C are construed as evidence for the disappearance of interstitial disturbances, which are assumed to be completely healed when the temperature has reached 500°C. The data for samples X-11 and X-17 are somewhat different, but in a way which is consistent with the irradiation histories of the samples. The differences between the results for samples X-11 and X-17 are caused by the different heating rates, 0.2 deg sec⁻¹ and 0.3 deg sec⁻¹, respectively.

Fig. VI. 3. Tempering data for neutron irradiated AGOT-W graphite.

5. Discussion of Ageing Experiments

The ageing data of the first experiments described in Section 3 were analyzed by the technique outlined by Vand⁽⁷⁾ and summarized in Section 2. Since calculation of the distribution functions $R_0(E)$ and $E_0(E)$ necessarily involves computation of time rates of healing of the electrical

resistivity and elastic modulus effects, i.e., Eq. (8), values of r_t^1 and e_t^1 were interpolated from graphs of experimental data in such a way as to provide tables of secondary data more amenable to calculation. These secondary data were determined by plotting the experimental data (against t and against $t^{1/2}$) and interpolating values for a uniform set of times, from carefully drawn curves. The times taken extended from 1 min to 15000 min in approximately geometric progression. Interpolated values for each time and for each sample were then plotted against temperature and a uniform systematically varying family of curves was drawn, showing the extent of healing in a given time as a function of temperature. Values were then read from these curves at 25°C intervals between 100°C and 300°C. That such interpolated values provide a reasonably satisfactory representation for the fundamental data is indicated by Figs. 1 and 2, in which the lines through the experimental points were drawn in accordance with the technique just described.* The only case in which there is a serious disagreement is for the electrical resistivity changes occurring at 303°C. The disagreement could have been removed by remaking all of the intermediate graphs.

The derivatives necessary for computing $R_0(E)$ and $E_0(E)$ according to Eq. (8) were calculated by taking differences between adjacent time values in the tables of secondary data and dividing by the time interval. Activation energies were calculated by Eq. (3). The time parameter used was the average time for the interval taken. The frequency factor, A , was taken to be $10^{13.03} \text{ sec}^{-1}$; i.e., $\ln A = 30.0$; and the value of k used was $8.62 \times 10^{-5} \text{ ev deg}^{-1}$.

The distribution spectrum and the results of the individual calculations for the elastic modulus data are shown in Fig. 4. It will be noticed that the distribution curve drawn is quite arbitrary and that there is a considerable scattering of points. This scattering has several possible origins: (a) The precision of the measurements is such that relative changes as a function of time are known, at best, to 1%. (b) One sample was used for each temperature, and sample-to-sample variations are to be expected. (c) The timing measurements in the early stages of annealing experiments were complicated by the time required to heat the sample to the proper temperature and to cool it after the heating period was completed. (d) The temperatures of boiling liquid baths were subject to some uncertainties by reason of occasional superheating and heater-power fluctuations. (e) The interpolation process, necessary to render the experimental data more readily calculable, may have introduced systematic spurious trends in the final results.

The scattering of the first points in the various series of values for higher temperatures (connected by dashed lines in Fig. 4) is probably best explained by (c) and (e) above. The elastic modulus points (Fig. 2) scatter

*Tables V and VI in the Appendix give the interpolated values which were used in calculations.

less than the corresponding electrical resistivity points (not shown) because of a somewhat better precision of elastic modulus measurements and because the rates of change of elastic modulus during heating are more uniform than the rates of change of electrical resistivity (cf. Figs. 1 and 2). It is thought to be unlikely, however, that any of the foregoing imperfections of measurement or calculation has changed the broad aspects of the distribution curves.

Fig. VI. 4. Distribution function, $E_0(E)$, for thermal annealing of the elastic modulus effect in irradiated (10 L-units) AGOT-K, by the method of ageing.

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The distribution spectra for elastic modulus and electrical resistivity annealing have been superposed and are shown in Fig. 5. Each set of curves has been decomposed into two secondary curves, indicated with dashed lines, the sum of which reproduces the primary curve. In drawing the primary curves, the ultimate decomposition into secondary curves was an important consideration. Table II summarizes the various parameters useful in the description of the distribution spectra. The four components have been labelled R_R , R_E , E_R , and E_E .

Fig. VI. 5. Distribution spectra for the thermal annealing of disturbances in irradiated AGOT-K artificial graphite (10 L-units). $\underline{R}$ denotes electrical resistivity, $\underline{E}$ denotes elastic modulus.

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TABLE II

Characteristics of the Four Secondary Maxima in the
Distribution Curves of Figure 5

	R_R	R_E	E_R	E_E
position (ev)	1.38	1.81	1.34	1.81
maximum	2.87	0.40	0.60	1.45
half-width (ev)	0.25	0.48	0.28	0.53

It would be convenient to represent the four secondary distribution curves of Fig. 5 by ordinary Gaussian distributions and thus to make the integrations of Eq. (8) by the use of standard error function tables. Such cannot be done with the present data because the discrepancy in the positions of the maximum of R_R and E_R is too great to allow a satisfactory fitting of the results. Furthermore the "resolving power" of the present experiments is too poor to exclude the possibility of "fine structure." If, however, the integrations are made by simply summing the products of heights by widths at half height, reasonable values for the total annealing are obtained, viz.,

$$r_{\infty}' = \int_{1.0}^{2.5} R_0(E) dE \cong 2.87 \times 0.25 + 0.40 \times 0.48 = 0.91 \quad (11)$$

$$e_{\infty}' = \int_{1.0}^{2.5} E_0(E) dE \cong 0.60 \times 0.28 + 1.45 \times 0.53 = 0.94 \quad (12)$$

The values $(1-r_{\infty}') = 0.09$ and $(1-e_{\infty}') = 0.06$ are to be compared with the values $r_M' = 0.09$ and $e_M' = 0.04$ for the amount of neutron-induced change remaining after a 1000°C anneal. Presumably, there are no disturbances with activation energies for thermal annealing between 2.5 and ca 4 ev (1000°C).

No extensive discussion of the 25°C annealing experiments is proposed, other than to point out the general agreement of the activation energy calculated and the distribution spectra of Fig. 5. The value of ca 1 ev for the 25°C experiments is consistent with a healing of the low temperature corner of the R_R "bump." The difference in intensity of R_R and E_R is also consistent with the fact that elastic modulus changes at room temperature were small.

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6. Discussion of Tempering Experiments

The tempering data of Section 4 have been used to calculate activation energy spectra. The formulae appropriate to those calculations have been given by Vand.⁽⁷⁾ The derivatives, dr_T/dT , were computed from the experimental data by reading values of r_T at points spaced uniformly in temperature, taking differences and dividing by the size of the temperature interval. Figure 6 shows the distribution function, $R_0(E)$, so obtained.

Fig. VI. 6. Distribution functions, $R_0(E)$, for the thermal annealing of disturbances in irradiated AGOT-W artificial graphite; by the method of tempering.

The curves resemble the $R_0(E)$ curve of Fig. 5. Table III summarizes the characteristic properties of the $R_0(E)$ distribution curves for samples W-208 and W-214. The approximate areas under the curves are 0.5 and 0.4 for samples W-208 and W-214, whereas the preheating neutron-induced changes were 0.76 and 0.62, respectively. The discrepancies in these figures indicate that not all interstitial disturbances were healed by the time the samples reached 500°C, i.e., residuals of 0.05 to 0.07 are to be expected, rather than the ca 0.2 value found above.

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TABLE III

Characteristics of the $R_0(E)$ Distribution Curves for
Samples W-208 and W-214

Sample	$R_R(E)$		$R_E(E)$	
	W-208	W-214	W-208	W-214
position (ev)	1.41	1.40	ca 1.9	ca 1.9
maximum	1.26	0.90	ca 0.17	ca 0.13
half-width (ev)	0.36	0.38	ca 0.36	ca 0.34

It will be noticed in Table III that the widths at half height for the R_R components are significantly greater than those of Table II. This can result either from the differences in the technique of observing $R_0(E)$ or from the fact that the samples of the present experiments were of AGOT-W graphite. The exact differences between AGOT-W artificial graphite and AGOT-K graphite are not known, but it is fairly certain that the crystallite size in AGOT-W is smaller than that in AGOT-K.⁽⁸⁾ In such a case it would not seem unreasonable to expect a graphite with larger and probably "more perfect" crystallites to exhibit sharper maxima.

The calculations pertinent to Fig. 6 involved computing average derivatives (dr_T/dT) for temperature intervals of 40°C. It is clear from the figure that this technique was unable to reveal any fine structure. Some calculations were made in which the derivatives were taken over 10°C intervals. Figure 7 shows the results of these calculations and it is evident that a certain amount of fine structure has appeared. No opinion will be ventured in regard to the reality of the various peaks. It is curious, however, that there should be so many points of similarity between the curves. For comparison with previous curves, the low resolution curve for sample W-208 (dashed line) has been included in Fig. 7.

The results of the measurements on sample X-11 are shown in Fig. 6. Sample X-11, in the course of its irradiation in the Clinton pile, experienced an annealing period of 36 hours at about 100°C as compared with a temperature of about 75°C throughout the rest of its irradiation. The effect of this heat treatment is clearly indicated by Fig. 6. The low energy part of the distribution curve has been annealed away and the peak lowered and moved towards higher temperatures.

Fig. VI. 7. Distribution functions, $R_0(E)$, for the thermal annealing of the electrical resistivity effect in irradiated AGOT-W artificial graphite, by the method of tempering.

It was hoped, that, by a method described by Leaf and Novick,⁽⁹⁾ it would be possible to estimate the frequency factor A by comparison of the temperatures at which the rate of healing was a maximum for identical samples tempered at significantly different rates. Both sample X-11 and X-17, however, being among the first samples run, yielded data not sufficiently precise for such estimates. Qualitatively the results for sample X-17 are in agreement with those of sample X-12 and the maximum rate of healing does occur at a higher temperature.

7. Concluding Remarks

The distribution spectra for thermal annealing of the disturbances produced in artificial graphite by fast neutron bombardment, suggest that interstitial disturbances which anneal below 1000°C fall into two broad classes, with mean characteristic activation energies of 1.4 and 1.8 ev. Disturbances with characteristic energy 1.4 ev seem to be predominantly responsible for electrical resistivity effects, while those with energy

1.8 eV seem to be the most important disturbances so far as elastic modulus effects are concerned. The secondary maxima in the distribution curves (e.g., Fig. 5) indicate the extent to which disturbances characteristic of the electrical resistivity changes affect the elastic modulus changes and vice versa. The resolving power of the experimental techniques, herein employed, is not adequate to permit exclusion of possible "fine structure" in the distribution spectra. Indeed, the tendency of calculated points to scatter and the curves of Fig. 7 suggest that such fine structure exists and that improved experimental techniques would cause it to become observable. Lattice vacancies are expected to be observed by a peak in each curve at ca 4.0 eV, but are, of course, not found in the present data because to observe them would require experiments at temperatures in excess of 1300°C.⁽¹⁰⁾

In discussion of the fates of knocked-out atoms it is usually assumed that the interstitial disturbances, which remain after fast neutron bombardment, may exist between the planes of the graphite crystallites as single C-atoms and/or molecules, and possibly also as clusters of C-atoms and/or molecules. It is to be expected that, if such species exist, each will exhibit a characteristic activation energy for thermal annealing, viz., the peaks in the distributions of Figs. 6 and 7. Thus it may be possible at some time to assign each observed maximum to a specific type of disturbance. This would be a reasonably hopeful prospect if ever it were possible to evaluate the importance functions of Eqs. (7).

It must constantly be kept in mind, however, that the annealing process has been assumed to be governed by a first-order rate law. This together with the various approximations in the Vand analysis will make the problem of interpretation difficult. Calculated distribution spectra will nonetheless provide a succinct means of recording the general aspects of annealing studies in radiation-damaged materials.

8. Acknowledgements

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M. G. Bowman and A. R. Van Dyken performed many experiments preliminary to the present experiments and were very helpful in planning, initiating, and discussing the present experiments.

9. Appendix

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Table IV

Relative fractional neutron-induced changes in electrical resistivity, r_t' , and elastic modulus, e_t' , remaining after annealing for time, t , (in minutes) at various temperatures. Sample resistivities before and after irradiation (R_0 and R_x) are in units of 10^{-4} ohm cm; moduli (E_0 and E_x) are in units of 10^{10} dyne cm^{-2} .

t	r _t '	e _t '	t	r _t '	e _t '	t	r _t '	e _t '
Sample KP-206 R ₀ = 5.68; R _x = 11.78 E ₀ =13.94; E _x = 27.69 T = 100°C			5760	0.362	0.741	1987	0.271	0.546
			8695	0.354	0.734	6300	0.260	0.490
			11705	0.353	0.709	20170	0.239	0.425
			15545	0.343	0.704	33130	0.236	0.396
Sample KP-177 R ₀ = 5.63; R _x = 11.69 E ₀ =14.08; E _x = 27.86 T = 131°C			Sample KP-183 R ₀ = 5.75; R _x = 11.98 E ₀ =13.77; E _x = 27.35 T = 180°C			Sample KP-187 R ₀ = 5.82; R _x = 11.74 E ₀ =14.31; E _x = 27.57 T = 260°C		
0	1.000	1.000	0	1.000	1.000	0	1.000	1.000
120	0.928	0.956	111	0.413	0.819	1	0.484	0.813
1045	0.798	0.923	355	0.381	0.760	3	0.370	0.732
2485	0.724	0.903	985	0.352	0.723	6	0.337	0.684
5515	0.653	0.884	2550	0.339	0.663	12	0.308	0.640
15500	0.580	0.872	7890	0.315	0.625	24	0.287	0.592
37025	0.536	0.879	10805	0.302	0.608	50	0.274	0.547
80200	0.489	0.874	14000	0.296	0.599	116	0.264	0.494
107350	0.473	---	Sample KP-224 R ₀ = 5.82; R _x = 25.78 E ₀ =14.04; E _x = 27.17 T = 210°C			267	0.248	0.437
			0	1.000	1.000	747	0.238	0.393
			2	0.597	0.861	1682	0.227	0.340
			6	0.495	0.816	2942	0.219	0.299
			20	0.412	0.771	5430	0.214	0.267
			104	0.354	0.716	9795	0.207	0.232
			235	0.323	0.670	17235	0.199	0.198
			770	0.318	0.603	23015	0.202	0.184
			1700	0.287	0.520	Sample KP-189 R ₀ = 5.82; R _x = 11.82 E ₀ =14.16; E _x = 27.62 T = 303°C		
			8800	0.269	0.463	0	1.000	1.000
			18350	0.269	0.430	0.5	0.508	0.819
			28295	0.260	0.411	1.5	0.331	0.662
			41255	0.255	0.391	3	0.275	0.586
Sample KP-178 R ₀ = 5.82; R _x = 12.16 E ₀ =13.74; E _x = 27.24 T = 155°C			Sample KP-271 R ₀ = 5.97; R _x = 12.17 E ₀ =13.32; E _x = 26.50 T = 230°C			6	0.243	0.464
0	1.000	1.000	0	1.000	1.000	13	0.230	0.398
5	0.834	0.918	30	0.353	0.789	30	0.221	0.365
11	0.836	0.924	200	0.316	0.702	60	0.206	0.284
31	0.706	0.878	487	0.292	0.633	151	0.193	0.207
61	---	0.861				519	0.167	0.130
173	0.516	0.831				1420	0.159	0.096
1210	0.403	0.774				2685	0.152	0.085
2960	0.372	0.757				3755	0.149	0.074
						6725	0.146	0.075

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Table V.

Interpolated electrical resistivity healing data

Number	1	2	3	4	5	6	7	8	9
Temperature (°C)	100	125	150	175	200	225	250	275	300
time (min.)	residual fractional electrical resistivity effect, r_t								
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
1	0.995	0.980	0.955	0.890	0.750	0.600	0.505	0.440	0.385
2	0.988	0.965	0.925	0.818	0.650	0.510	0.430	0.374	0.326
4	0.981	0.946	0.888	0.743	0.570	0.448	0.378	0.323	0.282
8	0.974	0.923	0.848	0.668	0.510	0.410	0.345	0.297	0.260
15	0.968	0.894	0.804	0.603	0.463	0.380	0.322	0.276	0.242
30	0.960	0.867	0.738	0.538	0.418	0.353	0.303	0.262	0.230
60	0.947	0.820	0.664	0.478	0.383	0.334	0.288	0.250	0.216
130	0.923	0.765	0.584	0.435	0.358	0.313	0.275	0.240	0.205
250	0.897	0.710	0.530	0.408	0.345	0.301	0.263	0.228	0.197
500	0.860	0.645	0.480	0.384	0.325	0.285	0.250	0.218	0.188
1000	0.810	0.584	0.436	0.363	0.314	0.275	0.241	0.211	0.182
2000	0.750	0.533	0.405	0.347	0.304	0.267	0.234	0.205	0.177
4000	0.683	0.490	0.385	0.333	0.290	0.256	0.226	0.198	0.173
8000	0.620	0.453	0.368	0.320	0.280	0.248	0.218	0.192	0.169
15000	0.575	0.429	0.355	0.308	0.271	0.240	0.212	0.186	0.163

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Table VI.

Interpolated elastic modulus healing data

Number	1	2	3	4	5	6	7	8	9
Temperature (°C)	100	125	150	175	200	225	250	275	300
time (min.)	residual fractional elastic modulus effect, e_t								
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
1	0.995	0.987	0.973	0.946	0.913	0.873	0.830	0.778	0.695
2	0.993	0.981	0.961	0.932	0.897	0.852	0.788	0.719	0.614
4	0.990	0.973	0.948	0.916	0.879	0.829	0.747	0.660	0.539
8	0.986	0.963	0.933	0.898	0.859	0.803	0.707	0.602	0.467
15	0.981	0.954	0.919	0.881	0.840	0.777	0.670	0.552	0.410
30	0.974	0.942	0.902	0.860	0.815	0.746	0.630	0.497	0.350
60	0.966	0.928	0.884	0.838	0.789	0.715	0.589	0.445	0.294
130	0.956	0.913	0.863	0.812	0.757	0.676	0.544	0.390	0.238
250	0.947	0.900	0.845	0.790	0.729	0.642	0.506	0.346	0.197
500	0.936	0.884	0.825	0.764	0.696	0.605	0.465	0.302	0.159
1000	0.924	0.869	0.806	0.738	0.663	0.566	0.425	0.262	0.127
2000	0.911	0.854	0.785	0.712	0.628	0.526	0.384	0.225	0.102
4000	0.896	0.838	0.764	0.685	0.593	0.486	0.344	0.191	0.081
8000	0.881	0.822	0.744	0.659	0.556	0.444	0.303	0.161	0.063
15000	0.866	0.807	0.724	0.633	0.522	0.407	0.267	0.137	0.049

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VII. ASYMPTOTIC ANNEALING EXPERIMENTS^{a,b}A. Novick,^c T. J. Neubert^d and A. R. VanDykenABSTRACT

The thermal annealing of neutron-induced decomposition of graphite was investigated by means of experiments in which irradiated specimens were heated for long periods at successively higher temperatures. The properties studied were electrical resistivity and elastic modulus. The measurements were designed to show (a) effect of the amount of irradiation, (b) differences between the various types of artificial graphite, (c) dependence upon the extrusion-produced crystallite orientation, and (d) dependence upon degree of graphitization and crystallite size.

Extension of annealing experiments to 2000°C is described. It was found that whereas annealing at temperatures less than 1000°C caused the electrical resistivity effect and the elastic modulus effect to decrease, annealing in the region 1100° to 1330°C caused the electrical resistivity effect to increase. Annealing above 1350°C caused the electrical resistivity effect to decrease again until at ca 2000°C the specimens exhibited their prebombardment resistivities. No such phenomenon was observed for the elastic modulus effect in the region above 1000°C.

^aBased upon work done at the Metallurgical Laboratory, University of Chicago (now Argonne National Laboratory) during the period 1943-1945, and summarized in U.S. Atomic Energy Commission ANL-4477, July 7, 1950.

^bThis article was originally intended for publication as paper 3.12 of Vol. 10B, Radiation Chemistry, of the National Nuclear Energy Series (Plutonium Project Record) under the editorship of Milton Burton.

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1. Introduction

The previous paper has discussed thermal annealing of the fast neutron-induced changes in graphite from the viewpoint of rate of annealing experiments.⁽¹⁾ In most cases, when irradiated graphite samples are heated at temperatures higher than the irradiation temperature, the neutron-induced increases in electrical resistivity⁽²⁾ and elastic modulus⁽³⁾ are seen to decrease. The changes, upon heating at constant temperature, are rapid in the early stages of heating, but as the heating is continued the rate of decrease diminishes until times are reached after which further changes are difficult to measure. The rapid initial decrease and the long slow decrease are seen each time the heating is repeated at a new higher temperature.

In order to be able to make quick appraisals of the character of the neutron-induced disturbances many annealing experiments were performed in which the limiting residual neutron-induced change, after a long-time anneal at constant temperature, was investigated as a function of temperature. These experiments have been called "asymptotic annealing experiments." Strictly speaking, neutron-induced changes should be expected to anneal completely at any temperature, but practical experimental problems of precision of measurement and time of heating make asymptotic experiments necessary.

2. Description of Experimental Techniques

In all experiments to be discussed (in this paper) the residual neutron-induced effects were determined by measurements at room temperature. Such measurements, of electrical resistivity and elastic modulus, have been described in earlier papers,^(2,3)

For temperatures up to 303°C samples were heated, in groups of approximately thirty, in a graphite magazine which slipped into a tightly fitting nickel tube (ca 2 in. o.d. x 1/32 in. wall x 20 in. long) closed at the lower end. The assembly was heated by immersing in a boiling liquid bath which was heated electrically. Glass wool was packed into the nickel tube above the sample magazine to decrease heat loss by convection and a closure and pumping system at the outer upper end was provided so that, for heating at temperatures of 230°C and above, the system could be evacuated and filled with helium. Table I lists the boiling baths used for the various temperatures and gives the approximate time of heating at each temperature. The entries for the anneal at 37°C have been included for orientation purposes only. No annealing experiments at room temperature will be described in this paper (see, however, the preceding paper of this series).⁽¹⁾

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For temperatures above 303°C samples were heated in two smaller graphite magazines in an electric furnace in an atmosphere of helium. The temperatures and approximate annealing times are listed in Table I. For temperatures above 1000°C a completely different heating technique was employed. This will be described in Section 7.

TABLE I

Summary of Asymptotic Annealing Procedures

Temp. (°C)	Approx. heating time	E' (ev)	Heating arrangement	Atmosphere
(37)	(400 days)	(1.27)	(room temperature)	(air)
131	230 hr	1.52	boiling isoamyl alcohol	air
156	130 hr	1.59	boiling bromobenzene	air
183	85 hr	1.67	boiling o-dichloro- benzene	air
207	75 hr	1.76	boiling tetralin	air
230	50 hr	1.83	boiling butyl carbitol	helium
260	50 hr	1.93	boiling Dowtherm	helium
303	30 hr	2.07	boiling diphenylamine	helium
450	3 hr	2.45	electric furnace	helium
1000	20 min	4.07	electric furnace	helium

3. Discussion of Annealing Experiments

Samples were heated at each annealing temperature for such times that the rate of healing was practically insignificant at the time heating was discontinued. Times of heating were chosen in accordance with the rate of annealing experiments described in the previous paper.⁽¹⁾ Figure 1 displays typical data for two samples of approximately the same amount of irradiation (ca 3.7 L-units). The abscissa gives the annealing temperature; the ordinate gives the residual fractional increase in electrical resistivity, r_T , and elastic modulus, e_T , i.e.,

$$r_T = (R_T - R_0)/R_0 \quad \text{and} \quad e_T = (E_T - E_0)/E_0, \quad (1)$$

where the subscript T indicates that the value has been obtained by measurement after a long time anneal at temperature T, and the subscript 0 indicates the initial pre-irradiation value of the appropriate physical property.

Figure 1 is typical of all the asymptotic data to be reported. It can be seen that the electrical resistivity effect is particularly sensitive to annealing at low temperature whereas the principal decreases in the elastic modulus effect occur at relatively higher temperatures. After about 400°C there is little further change in either electrical resistivity or elastic modulus. The significant decreases in the region of temperatures up to 400°C usually have been considered to be related to the removal by healing to edges, cracks, or lattice vacancies of the interstitial disturbances produced during neutron irradiation. According to such a model, the residual effects at 1000°C would be the result of lattice vacancies. It is not necessary, however, to presume that only vacancies remain after a 1000°C anneal. It is reasonable that neutron-induced disturbances are C atoms and molecules, existing singly and in clusters and trapped interstitially or at edges or inner fissures of graphite crystallites.⁽⁷⁾ Thus, many "mechanisms" can be conceived, some of which might imply kinds of centers stable at 1000°C.

Fig. VII. I. Typical asymptotic annealing data for two samples of parallel-cut AGOT-K artificial graphite, irradiated ca 3.7 L-units at $32 \pm 5^\circ\text{C}$.

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Further examination of Fig. 1 indicates reasonably good agreement between the results for the two samples shown. The way in which the points for each sample are distributed suggests that sample KP-367 was irradiated somewhat more than sample KP-316 and at a slightly higher temperature. Considering either set of points it is seen that the electrical resistivity curve (solid line) and the elastic modulus curve (dashed line) could be drawn with bends and kinks such that the lines would pass through all points. There would, furthermore, be quite good correlation between the positions of the wiggles in the curves for both electrical resistivity and elastic modulus. In reporting the present data, however, all such effects have been disavowed because of the lack of precision of measurement of physical properties, the temperature fluctuations during annealing, the dependence of results on time of heating, and the sample-to-sample variation always troublesome in graphite work. The precision of measurement of electrical resistivity and elastic modulus is such that the residual fractional increases are considered to be reliable to ± 0.01 in most cases, leaving deviations larger than this to be explained otherwise.

From study of the rates of annealing of neutron-induced changes in irradiated graphite,⁽¹⁾ it has been possible to compute distribution functions $R_0(E)$ and $E_0(E)$ for the electrical resistivity and elastic modulus effects which describe the concentration and importance of disturbances in changing the properties of graphite as a function of their activation energy for thermal annealing. The computations involve several crude approximations, principally that of a first order-rate equation for the healing process, but nonetheless the distribution spectra are useful for recording some of the differences between the electrical resistivity and elastic modulus effects.

Figure 2 shows the distribution spectra for the thermal annealing of disturbances in AGOT-K graphite irradiated 10 L-units at about 35°C. The solid curves $R_0(E)$ and $E_0(E)$ are shown decomposed into two curves each (dotted curves). The disturbances appear to fall into two principal classes, with characteristic activation energies 1.4 ev and 1.8 ev. Each of the principal kinds of disturbance, cf. curves R_R and E_E , has a certain effect on the other property of which it is not most characteristic, cf. curves R_E and E_R .

Asymptotic annealing experiments give integrals of the distribution functions shown in Fig. 2. Thus

$$r_T = \int_{E'}^{\infty} R_0(E) dE \quad \text{and} \quad e_T = \int_{E'}^{\infty} E_0(E) dE, \quad (2)$$

where

$$E' = kT \ln At \quad . \quad (3)$$

Fig. VII. 2. Distribution spectra of activation energies for thermal annealing of disturbances in neutron bombarded AGOT-K graphite (10 L-units).

These relationships state that as a specimen is annealed the disturbances heal in order of their characteristic activation energies so that after an anneal for t seconds at $T^\circ\text{K}$ all disturbances of energy less than E' ev have disappeared. (k is Boltzmann's constant, $8.62 \times 10^{-5} \text{ ev deg}^{-1}$, and A is a frequency factor taken to be $\text{ca } 10^{13} \text{ sec}^{-1}$.)

Using the distribution functions of Fig. 2 and the times and temperatures of heating listed in Table I, the integrals of Eq. (2) were calculated. Values of E' , the lower integration limit, are included in Table I. The results, shown in Fig. 3, have been plotted against annealing temperature in order to emphasize the analogical equivalence to the data and curves of Fig. 1.

Fig. VII. 3. Form of asymptotic annealing curves computed by integration of $R_0(E)$ and $E_0(E)$ distribution functions of Fig. 2.

4. Dependence of Neutron-Induced Effects on the Amount of Irradiation

Figures 4 and 5 summarize the data of asymptotic annealing experiments on samples of parallel-cut AGOT-K graphite with varying amounts of neutron irradiation.* The samples used were bombarded either in the Oak Ridge graphite pile or in the Argonne heavy water pile. Samples were, for the most part, irradiated at temperatures close to room temperature. However, in order to take maximum advantage of the data at hand, it was necessary to include (with adequate corrections) some samples for which the irradiation temperature was above the usual temperature for a part of the irradiation. Irradiation magnitudes, in L-units, were assigned by means of the curve for elastic modulus change vs bombardment for parallel-cut AGOT-K samples irradiated in the Argonne pile.⁽⁴⁾ Figures 6 and 7 indicate the results of the annealing experiments plotted as functions of the amount of neutron irradiation. Plotted points are not shown because of insurmountable difficulties in

* Table III in the Appendix gives these data explicitly; Table IX gives the irradiation histories of the samples.

designating the points for various samples and because there is a considerable scattering. Instead, an attempt was made to prepare self-consistent curves which would depict the trends and at the same time would not violate the experimental numbers too seriously. Figures 4, 5, 6, and 7 are such curves. The estimated precision in the residual fractional increase is about ± 0.01 , and the lines shown are for the most part consistent with this standard of precision. The data for some samples show larger deviations for the electrical resistance effect at the lower temperatures, indicating that the irradiation temperature was higher than usual.

Fig. VII. 4. Dependence of the residual fractional increase in elastic modulus, e_T , upon annealing temperature, for parallel-cut AGOT-K artificial graphite with various amounts of irradiation.

Fig. VII. 5 Dependence of the residual fractional increase in electrical resistivity, r_T , upon annealing temperature, for parallel-cut AGOT-K artificial graphite with various amounts of irradiation.

Fig. VII. 6 Dependence of the residual fractional increase in elastic modulus, e_T , upon the amount of neutron irradiation for various annealing temperatures.

Fig. VII. 7. Dependence of the residual fractional increase in electrical resistivity, r_T , upon the amount of neutron irradiation, for various annealing temperatures.

The trends in the asymptotic curves in Figs. 4 and 5 are the same as those in Fig. 1. In fact, Fig. 1 and curve 6 of Figs. 4 and 5 are equivalent. Examination of the figures shows that while the elastic modulus effect in samples with low bombardments is quite unaffected by annealing temperatures below 200°C, the electrical resistivity effect is very nearly completely removed by the time that temperature is reached. As the amount of irradiation is increased, however, the elastic modulus effect becomes more sensitive with respect to low-temperature annealing and the electrical resistivity effect becomes less sensitive.

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It should be noted that the curves of residual electrical resistivity effect vs bombardment, Fig. 7, exhibit a slight concavity in the region of small bombardment. The available data are, however, not of sufficient precision to make this concavity certain, but, if true, it would not be unreasonable to suggest that some of the disturbances responsible for the electrical resistivity effect are complex disturbances, involving more than one carbon atom. Correspondingly, the shape of the e_T curves, Fig. 6, in the region of small bombardments might indicate that the elastic modulus effect is caused by the primary disturbances produced by neutron impacts, i. e., C atoms. It is also possible to presume that whereas the effect of disturbances on elastic modulus is always such as to increase the elastic modulus, different kinds of disturbances affect the electrical resistivity either positively or negatively. Thus, for a suitably devised model, if the rates and activation energies of thermal annealing were properly chosen, bombardment and annealing curves could be calculated which would be concave for small bombardments.

5. Dependence of Neutron-Induced Effects on the Type of Artificial Graphite and upon the Orientation of the Specimen Axis Relative to the Axis of Extrusion

Asymptotic annealing experiments have been performed with samples of each of the three pile graphites, AGOT-K, AGOT-C, and AGOT-W, the preparation and properties of which have been described.^(4,5) Examination of the data* has revealed no particularly significant differences among these graphites, other than those which can be dismissed on the basis of the known differences in behavior under irradiation. It has been found that, to within the precision with which observations can be made, the neutron-induced effect for any graphite is related to the effect in AGOT-K graphite by a multiplicative constant.⁽⁴⁾ Table II summarizes these multiplicative constants and the initial elastic modulus and electrical resistivity for various graphites. In the present annealing experiments the curves obtained for AGOT-K, AGOT-C, and AGOT-W graphite seem to be superposable if first properly normalized using the factors given in Table II.

The differences in behavior under annealing between parallel-cut and perpendicular-cut specimens of irradiated AGOT-K graphite are also describable in terms of the multiplicative constants of Table II. Figure 8 shows the results for two AGOT-K samples, one parallel-cut and one perpendicular-cut, irradiated for 3.8 L-units at about 35° C.

*Table IV in the Appendix gives the data.

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TABLE II

Summary of Relative Neutron-Induced Changes in Various Graphites
(Irradiated at ca 30°C)

Designation	E_0 (a)	e_i/e_k (c)	R_0 (b)	r_i/r_k (d)
AGOT-K	13.7	1.000	7.8	1.000
⊥	5.7	1.24 ± 0.05	10.5	0.96 ± 0.02
AGOT-C	10.6	0.91 ± 0.03	7.6	0.92 ± 0.02
⊥	6.4	0.92 ± 0.03	11.9	0.75 ± 0.04
AGOT-W	10.0	0.79 ± 0.03	8.4	0.86 ± 0.02
⊥	6.6	0.79 ± 0.02	11.8	0.78 ± 0.01
Sp-3000	7.0	1.03 ± 0.03	9.4	0.85 ± 0.03
⊥	5.4	1.09 ± 0.01	11.4	0.83 ± 0.02
Sp-2400	6.6	0.50 ± 0.02	21.8	0.25 ± 0.01
⊥	5.5	0.61 ± 0.03	21.7	0.35 ± 0.02
Sp-2100	6.4	0.23 ± 0.03	37.7	0.00 ± 0.01
⊥	4.9	0.24 ± 0.03	44.9	0.00 ± 0.01
pbNG	15.6	1.16 ± 0.09	9.7	0.61 ± 0.02
pbL	5.8	0.24 ± 0.03	65.3	0.83 ± 0.02

(a) E_0 = initial elastic modulus (units of 10^{10} dynes cm^2)

(b) R_0 = initial electrical resistivity (units of 10^{-4} ohm cm)

(c) $e_i = \Delta E/E_0$ } for any graphite; the subscript k denotes that
 (d) $r_i = \Delta R/R_0$ } the change is that for AGOT-K graphite.

Fig. VII. 8. Asymptotic annealing data for one sample of parallel-cut and one sample of perpendicular-cut AGOT-K artificial graphite, irradiated ca 3.8 L-units at ca 35°C.

6. Dependence of Neutron-Induced Effects on the Degree of Graphitization and upon Crystallite Size

Figures 9 and 10 summarize the data* for asymptotic annealing experiments on irradiated special graphites and pseudo-graphites which differ in degree of graphitization and in crystallite size. The various samples are as follows:

- (a) Sp-3000, AGOT-W stock graphitized at 3000°C.
- (b) Sp-2400, AGOT-W stock fired at 2400°C.
- (c) Sp-2100, AGOT-W stock fired at 2100°C.

* Table V in the Appendix gives the data.

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- (d) pbNG, pseudo-graphite made of natural graphite bonded with pitch and fired at 3000°C.
- (e) pbL, pseudo-graphite made of lampblack bonded with pitch and fired at 3000°C.

The special graphites (Sp-3000, Sp-2400, Sp-2100) differ in the degree of graphitization; the differences in asymptotic annealing curves for perpendicular-cut specimens irradiated 3.1 L-units at $25 \pm 5^\circ\text{C}$ are shown in Fig. 9. The curves are similar to equivalent curves for AGOT-K graphite. Sp-2100, the material with the lowest degree of graphitization, shows no change in electrical resistivity on neutron irradiation and also no changes on subsequent annealing. Sp-3000, the best graphitized material behaves in the manner to be expected of a well-graphitized AGOT-W specimen. The pseudo-graphites, pbNG and pbL, differ in crystallite size; the differences in behavior under asymptotic annealing are shown in Fig. 10.

Fig. VII. 9. Asymptotic annealing curves for perpendicular-cut samples of special graphites of differing degrees of graphitization irradiated 3.1 L-units at ca. 25°C.

Fig. VII. 10. Asymptotic annealing data for irradiated samples of pitch-bonded natural graphite (pbNG), pitch-bonded lampblack (pbL), and pile graphite (AGOT-K).

7. Description of High Temperature Experiments

In discussion of annealing experiments it was suggested that, if in healing to a crystallite edge, an interstitial C atom required a smaller activation energy than would be required for it to force an entry into a lattice vacancy, different 1000°C residuums would obtain for samples heated slowly to 1000°C and for samples heated quickly to 1000°C. To test this idea an apparatus was constructed in which one of the ordinary graphite specimens (4 mm diam x 40 mm long) could be heated to 1000°C in ca 1/3 sec. Comparisons of samples heated to 1000°C in the course of about 45 min with samples heated to 1000°C in ca 1/3 sec showed, however, no differences beyond the usual scattering of results. This experiment was, therefore, inconclusive, but the apparatus had been designed also to provide means for investigation of healing in temperature regions above those attainable with ordinary electric furnaces.

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For heating samples either quickly, or to high temperatures, the specimen was mounted between two clamps and heated by suitable direct currents from a bank of storage batteries. The clamps were made of graphite and had small recessions accurately machined to fit firmly over the end of the specimen to be heated. The ends of the clamps were copper plated and then silver soldered into large threaded pieces of copper which were fastened with good thermal and electrical contact to water-cooled current leads. An attempt was made to decrease heat losses along the clamps by having the clamp diameter only about three-fourths of the specimen diameter for a distance of about 1 cm between the cup which fitted the sample and the silver-soldered joint to the threaded copper bar. A platinum radiation shield, 1 cm in diameter, was provided to decrease radiative losses. The entire heating assembly was designed to fit freely into a cylindrical Pyrex envelope (3 in. in diameter, 20 in. in length) which could be flushed with helium and then evacuated to about 10^{-4} mm Hg.

The storage batteries were connected and disconnected by means of an automobile starter switch. Currents were adjusted by a water-cooled variable resistor made of 4 ft of 1/8 in. o.d. stainless steel tubing. Variability was attained via sliding metal clamps. An ammeter was included in the circuit. The technique in heating a specimen was to adjust the variable resistor to a value commensurate with the voltage and internal resistance of the storage batteries and with the sample temperature desired. The activator switch for the starter was then closed and as the heating occurred the sample temperature was observed with an optical pyrometer. When the temperature reached the desired value, the activator switch was opened. In this way annealings of several seconds were accomplished. Longer times could, of course, be obtained by repetitions.

In the construction of the high-temperature apparatus it was discovered that, unless one of the sample clamps was spring loaded, differential expansions would be such as to bend the samples. Unfortunately no records are available of what the temperatures were in these preliminary experiments. In the final apparatus, a simple spring mechanism was included and samples could be heated very nicely without bending.

8. Results of High-Temperature Annealing Experiments

Measurements of electrical resistivity and elastic modulus were made on a number of irradiated and unirradiated samples of parallel-cut AGOT-W graphite. The data were reduced to fractional changes calculated as described previously, e.g., for electrical resistivity, $r_T = (R_T - R_0)/R_0$. As irradiated samples were heated, the residual fractional increase in electrical resistivity changed as shown in Fig. 1. When annealing temperatures were raised above 1000°C the electrical resistivity passed through a maximum and dropped back close to its prebombardment value only when

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the annealing temperatures exceed 1600°C.* Unirradiated graphite increased slightly in electrical resistivity (ca 1%) upon heating to 2000°C. Figure 11 shows the complete asymptotic annealing curve for AGOT-W graphite samples irradiated for 20 L-units.

Fig. VII. 11. Asymptotic annealing data for samples of AGOT-W artificial graphite, irradiated for ca 20 L-units as part of the structure of the Oak Ridge pile.

No such interesting phenomenon is seen in the elastic modulus data. The elastic modulus of samples decreases continuously as temperatures are raised above 1000°C.** Unirradiated specimens on heating to

* Table VI in the Appendix gives the data.

** Table VII in the Appendix gives the data.

2000°C decrease to ca 5% below the 1000°C value; for specimens irradiated 20 L-units, the corresponding decrease is ca 10%. The 5% difference accounts for the last remnant of the original neutron-induced change, 5% of which remains in the elastic modulus after a 1000°C anneal. Whatever disturbances cause the electrical resistivity change to increase upon high temperature annealing seem to have little or no effect on the elastic modulus.

Figure 12 indicates the manner in which the asymptotic high-temperature resistivity effect depends upon the amount of irradiation.* The maximum at ca 1330°C is seen to increase with irradiation but no further conclusions are justifiable with the present data.

Fig. VII. 12. High temperature asymptotic annealing data for AGOT-W artificial graphite with different amounts of neutron irradiation.

9. Concluding Remarks

It has not been the intention of this paper to make any definite statements about possible mechanisms for the radiation-damage effects in graphite. The data presented are those taken in the course of experimentation which it was hoped might lead unequivocally to simple model.

*Table VIII in the Appendix gives the data.

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Such hopes went unrealized. There seem, however, to be a few salient facts which are clearly established by asymptotic experiments. Some of these may be summarized as follows.

1. The electrical resistivity effect is very sensitive with respect to annealing for low-bombarded samples, but becomes progressively less sensitive as the amount of bombardment is increased (Fig. 5).

2. The elastic modulus effect is very insensitive with respect to annealing for low-bombarded samples, but becomes progressively more sensitive as the amount of bombardment is increased (Fig. 4).

3. The electrical resistivity effect remaining after a 1000°C anneal is relatively large and appears to be increasing approximately linearly with bombardment (Fig. 7), while the elastic modulus effect after a 1000°C anneal is relatively small and gives some evidences of approaching a "saturation value" for highest bombardments reported (Fig. 6).

4. The initial slopes of elastic modulus effect vs bombardment (Fig. 6) are large and quite independent of temperature, while the initial slopes of the corresponding curves for the electrical resistivity effect (Fig. 7) are smaller and very temperature dependent. The concavity of the initial portions of the electrical resistivity curves may be very important.

5. The differences between parallel-cut and perpendicular-cut samples (Fig. 8) might provide hints as to which kinds of disturbances in irradiated graphite cause positive changes in properties measured and which kinds cause negative changes.

6. The high temperature annealing results (Fig. 12) suggest that some kinds of disturbances may cause changes in electrical resistivity with negative coefficients.

This summary is primarily a series of questions from which it can be seen that further work is necessary in which it will be important to place heavy emphasis on precision of measurement, on numbers of samples used, on control of bombardment variables and on the choice of the properties to be studied. The present work has indicated the gross annealing behavior of irradiated graphite so far as the electrical resistivity and elastic modulus effects are concerned and that there are no large differences between the three types of pile graphites. The differences between graphites having varying degrees of graphitization (Fig. 9) and varying crystallite sizes (Fig. 10) are large but at the moment do little toward suggesting a suitable model for the radiation damage. The "nature" of artificial graphite is not an insignificant factor in the difficulty of constructing an over-all picture of the effects of fast neutron bombardment of graphite.

10. Acknowledgments

The low temperature heatings were carried out by R. C. Boe and E. H. Phillips, and the many measurements of electrical resistivity and elastic modulus were made by R. C. Boe, R. Donegan, H. Petrzilka, E. H. Smith, M. Stewart, G. Steel, and L. Weil. J. Royal performed many of the high temperature experiments. Some of the high temperature experiments were continued by L. O. Beaman.

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11. Appendix

Table III

Asymptotic annealing data for parallel-cut AGOT-K graphite samples with various amounts of fast neutron irradiation

($\bar{r}$ and $\bar{e}$ denote the residual fractional increases in electrical resistivity and elastic modulus. The entries, $\bar{a}$, are the experimental results, the entries, $\bar{b}$, are values self-consistent with Figures 4, 5, 6, and 7.)

Sample	Irrad. L-units		As rec'd		131°C		156°C		183°C		207°C		230°C		260°C		303°C		450°C		1000°C	
			r	e	r	e	r	e	r	e	r	e	r	e	r	e	r	e	r	e	r	e
KP-273	0.35	a	0.052	0.098	0.014	0.100	0.011	0.102	0.007	0.098	0.006	0.096	0.008	0.087	0.005	0.080	0.006	0.055	0.006	0.029	0.012	0.014
		b	0.060	0.100	0.013	0.100	0.010	0.100	0.007	0.100	0.006	0.099	0.005	0.095	0.004	0.084	0.004	0.048	0.004	0.019	0.004	0.007
KP-257	0.47	a	0.081	0.137	0.019	0.139	0.019	0.139	0.015	0.129	0.004	0.121	0.010	0.100	0.006	0.092	0.005	0.060	0.002	0.023	0.006	0.002
		b	0.080	0.137	0.019	0.134	0.015	0.132	0.012	0.129	0.010	0.124	0.009	0.116	0.007	0.097	0.006	0.060	0.006	0.020	0.006	0.008
KP-219	0.80	a	0.141	0.214	0.036	0.186	0.035	0.188	0.033	0.172	0.011	0.153	0.016	0.129	0.027	0.106	0.011	0.064	0.017	0.021	0.016	0.012
		b	0.130	0.214	0.039	0.198	0.028	0.190	0.021	0.175	0.017	0.156	0.016	0.136	0.013	0.110	0.012	0.066	0.011	0.026	0.011	0.010
KP-240	1.33	a	0.212	0.302	0.089	0.258	0.055	0.247	0.044	0.228	0.033	0.195	0.036	0.167	0.036	0.139	0.023	0.081	0.021	0.032	0.025	0.016
		b	0.204	0.302	0.068	0.263	0.054	0.247	0.042	0.225	0.036	0.196	0.030	0.165	0.026	0.133	0.022	0.079	0.020	0.032	0.020	0.013
KP-305	2.00	a	0.322	0.383	0.103	0.314	0.085	0.295	0.075	0.267	0.055	0.228	0.054	0.184	0.052	0.147	0.040	0.088	0.036	0.036	0.041	0.012
		b	0.292	0.383	0.103	0.327	0.084	0.306	0.070	0.275	0.060	0.238	0.052	0.300	0.047	0.152	0.030	0.086	0.029	0.039	0.028	0.016
KP-185	3.13	a	0.398	0.494	0.132	0.406	0.111	0.385	0.094	0.351	0.080	0.270	0.069	0.220	0.072	0.138	0.048	0.062	0.032	0.020	0.031	0.013
		b	0.425	0.494	0.156	0.412	0.132	0.380	0.114	0.343	0.098	0.282	0.086	0.234	0.076	0.176	0.062	0.093	0.057	0.045	0.055	0.021
KP-316	3.70	a	0.491	0.544	0.163	0.464	0.148	0.431	0.123	0.379	0.104	0.295	0.098	0.238	0.087	0.180	0.069	0.087	0.056	0.045	0.056	0.025
		b	0.490	0.544	0.180	0.451	0.153	0.415	0.131	0.356	0.115	0.305	0.098	0.246	0.089	0.177	0.073	0.099	0.066	0.047	0.062	0.022
KP-367	3.75	a	0.465	0.547	0.192	0.480	0.164	0.439	0.143	0.398	0.119	0.328	0.116	0.259	0.103	0.205	0.083	0.108	0.066	0.059	0.068	0.029
		b	0.494	0.547	0.183	0.452	0.155	0.416	0.133	0.357	0.116	0.306	0.099	0.247	0.090	0.178	0.074	0.099	0.066	0.047	0.062	0.022
KP-212	4.33	a	0.545	0.594	0.177	0.475	0.151	0.434	0.132	0.389	0.110	0.316	0.087	0.262	0.094	0.198	0.061	0.102	0.043	0.051	0.038	0.026
		b	0.555	0.594	0.206	0.489	0.176	0.450	0.153	0.402	0.130	0.327	0.116	0.268	0.106	0.197	0.088	0.102	0.074	0.051	0.069	0.025
KP-380	5.30	a	0.647	0.662	0.222	0.556	0.201	0.498	0.175	0.446	0.142	0.352	0.138	0.282	0.134	0.218	0.129	0.108	0.111	---	0.099	0.030
		b	0.652	0.662	0.250	0.548	0.214	0.503	0.182	0.446	0.160	0.358	0.143	0.290	0.125	0.213	0.107	0.107	0.089	0.057	0.080	0.029
KP-222	5.30	a	0.632	0.662	0.248	0.544	0.217	0.494	0.192	0.438	0.153	0.337	0.142	0.285	0.138	0.215	0.097	0.100	0.084	0.057	0.076	0.031
		b	0.652	0.662	0.250	0.548	0.214	0.503	0.182	0.446	0.160	0.358	0.143	0.290	0.125	0.213	0.107	0.107	0.089	0.057	0.080	0.029
KP-263	6.35	a	0.688	0.730	0.278	0.602	0.244	0.552	0.213	0.484	0.174	0.377	0.157	0.313	0.149	0.235	0.117	0.113	0.094	0.065	0.079	0.030
		b	0.752	0.730	0.289	0.605	0.247	0.555	0.213	0.489	0.191	0.390	0.167	0.314	0.148	0.226	0.126	0.113	0.102	0.060	0.088	0.031
KP-171	7.55	a	0.778	0.801	0.324	0.665	0.277	0.600	0.242	0.532	0.196	0.402	0.183	0.328	0.172	0.241	0.130	0.107	0.100	0.058	0.082	0.035
		b	0.861	0.801	0.338	0.665	0.289	0.609	0.249	0.534	0.219	0.424	0.195	0.339	0.172	0.240	0.148	0.120	0.117	0.067	0.102	0.034
KP-419	8.00	a	0.853	0.823	0.370	0.709	0.320	0.640	0.280	0.580	0.239	0.451	0.215	0.351	0.202	0.262	0.167	0.130	0.134	0.074	0.123	0.038
		b	0.900	0.823	0.356	0.686	0.304	0.628	0.262	0.550	0.231	0.437	0.205	0.348	0.182	0.245	0.156	0.122	0.123	0.070	0.107	0.036
KP-428	11.8	a	1.013	1.006	0.480	0.835	0.418	0.775	0.379	0.685	0.306	0.498	0.291	0.406	0.269	0.281	0.215	0.124	0.170	0.084	0.136	0.071
		b	1.180	1.006	0.509	0.843	0.434	0.779	0.376	0.685	0.326	0.540	0.287	0.425	0.263	0.287	0.225	0.143	0.174	0.086	0.145	0.047
KP-184	13.7	a	1.116	1.086	0.581	0.945	0.506	0.849	0.449	0.751	0.370	0.596	0.335	0.465	0.316	0.350	0.264	0.206	0.204	0.146	0.177	0.078
		b	1.306	1.086	0.587	0.926	0.503	0.855	0.437	0.758	0.372	0.596	0.322	0.468	0.304	0.310	0.262	0.155	0.198	0.095	0.165	0.053

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Table IV

Summary of asymptotic annealing data for irradiated samples of AGOT-K, AGOT-C and AGOT-W artificial graphite

(Sample designations K, C, or W denote the kind of graphite, and P or N denotes the orientation of the specimen axis relative to the axis of extrusion, i.e., parallel-cut and perpendicular-cut, respectively.)

Sample	Irrad. L-units	Irrad. Temp.	As rec'd		131°C		156°C		183°C		207°C		230°C		260°C		303°C		450°C		1000°C	
			r	e	r	e	r	e	r	e	r	e	r	e	r	e	r	e	r	e	r	e
KP-428	12	~100°C	1.013	1.006	0.480	0.835	0.418	0.775	0.379	0.685	0.306	0.498	0.129	0.406	0.269	0.281	0.215	0.124	0.170	0.084	0.136	0.071
CP-130	12	~100°C	0.930	0.964	0.585	0.851	0.513	0.772	0.465	0.654	0.397	0.485	0.368	0.440	0.353	0.311	0.280	0.161	0.227	0.110	0.190	0.079
WP-150	12	~100°C	0.939	0.818	0.557	0.717	0.497	0.651	0.447	0.558	0.380	0.451	0.343	0.371	0.333	0.269	0.271	0.137	0.222	0.102	0.200	---
KP-380	5.3	~ 25°C	0.647	0.662	0.222	0.556	0.201	0.498	0.175	0.446	0.142	0.352	0.138	0.228	0.134	0.218	0.129	0.108	---	---	0.063	0.030
CP-117	5.3	~ 25°C	0.604	0.581	0.213	0.465	0.192	0.441	0.176	0.393	0.145	0.300	0.134	0.250	0.131	0.187	0.098	0.098	0.084	0.050	0.072	0.033
WP-133	5.3	~ 25°C	0.578	0.534	0.209	0.451	0.175	0.420	0.157	0.378	0.135	0.287	0.118	0.237	0.118	0.180	0.087	0.104	0.070	0.072	0.065	0.041
KP-300	5.0	~115°C	0.341	0.672	0.252	0.652	0.216	0.610	0.177	0.527	0.156	0.403	0.148	0.378	0.129	0.285	0.102	0.150	0.070	0.097	0.051	0.072
CP-108	5.0	~115°C	0.332	0.585	0.279	0.557	0.240	0.513	0.219	0.452	0.186	0.341	0.169	0.296	0.161	0.217	0.122	0.112	0.106	0.074	0.091	0.039
WP-128	5.0	~115°C	0.312	0.507	0.260	0.467	0.227	0.446	0.202	0.401	0.173	0.301	0.157	0.252	0.155	0.184	0.122	0.100	0.095	0.068	0.091	0.038
KM-459	3.1	~ 25°C	0.399	0.584	0.126	0.492	0.102	0.461	0.090	0.410	0.074	0.332	0.073	0.267	0.072	0.200	0.058	0.105	0.043	0.058	0.032	0.067
CN-211	3.1	~ 25°C	0.348	0.433	0.114	0.360	0.088	0.346	0.081	0.301	0.065	0.234	0.072	0.193	0.064	0.151	0.047	0.083	0.030	0.046	0.028	0.035
WN-181	3.1	~ 25°C	0.339	0.382	0.122	0.322	0.093	0.312	0.087	0.299	0.083	0.212	0.087	0.165	0.076	0.152	0.061	0.112	0.038	0.071	0.034	0.031
KP-367	3.8	~ 35°C	0.465	0.547	0.192	0.480	0.164	0.439	0.143	0.398	0.119	0.328	0.116	0.259	0.103	0.205	0.083	0.108	0.066	0.059	0.068	0.029
KN-166	3.8	~ 35°C	0.462	0.681	0.179	0.590	0.168	0.531	0.148	0.482	0.114	0.392	0.117	0.302	0.114	0.236	0.085	0.123	0.068	0.066	0.073	0.042

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Table V

Asymptotic annealing data for irradiated special graphites and pseudo-graphites

(Sample designations: Q = graphitized at 3000°C, P = fired at 2400°C, J = fired at 2100°C; the second letters denote whether the sample is parallel-cut (P) or perpendicular-cut (N); PENG = pitch bonded natural graphite, PBL = pitch bonded lampblack.)

Sample	Irrad. L-units	As rec'd		131°C		156°C		183°C		207°C		230°C		260°C		303°C		450°C		1000°C	
		r	e	r	e	r	e	r	e	r	e	r	e	r	e	r	e	r	e	r	e
QP-12	3.1	0.377	0.483	0.109	0.437	0.099	0.433	0.083	0.398	0.087	0.381	0.072	0.333	0.068	0.259	0.057	0.155	0.058	0.111	0.033	0.094
QN-23	3.1	0.362	0.552	0.124	0.471	0.095	0.439	0.107	0.401	0.088	0.324	0.092	0.271	0.076	0.216	0.058	0.126	0.057	0.082	0.045	0.065
PP-11	3.1	0.122	0.237	0.051	0.211	0.043	0.200	0.046	0.194	0.038	0.149	0.034	0.125	0.026	0.110	0.021	0.085	0.022	0.057	0.019	0.032
PN-22	3.1	0.139	0.265	0.052	0.221	0.032	0.200	0.039	0.209	0.036	0.155	0.040	0.135	0.028	0.014	0.022	0.083	0.022	0.062	0.018	0.025
JP-10	3.1	0.000	0.078	0.000	0.066	0.000	0.066	0.000	0.063	0.000	0.061	0.000	0.055	0.000	0.053	0.000	0.047	0.000	0.035	0.000	0.030
JN-23	3.1	0.000	0.094	0.000	0.079	0.000	0.075	0.000	0.075	0.000	0.061	0.000	0.047	0.000	0.041	0.000	0.057	0.000	0.043	0.000	0.028
PENG-116	~18	0.873	1.284	0.436	1.114	0.380	1.031	0.335	0.919	0.290	0.707	0.287	0.639	0.275	0.570	0.228	0.470	0.197	0.349	0.108	0.227
PBL-103	~25	0.080	0.361	0.071	0.332	0.067	0.307	0.060	0.288	0.051	0.246	0.054	0.207	0.048	0.165	0.036	0.150	0.031	0.138	0.010	0.130

Effect of high temperature annealing on the elastic modulus of AGOT-W graphite

(The elastic modulus, E , is given in units of 10^{10} dynes cm^{-2} .)

Sample	WP-206	WP-174	EP-11	EP-12	EP-21	EP-22	EP-23	WP-209	WP-286	WP-126	WP-150
L-units irradiation $E_M(1000^\circ\text{C})$	none 10.81	none 10.19	~ 20 9.99	~ 20 9.95	~ 20 9.80	~ 20 10.04	~ 20 9.77	~ 40 11.40	~ 35 10.30	~ 30 10.63	~ 10 10.14
E_T (E_T/E_M) T ($^\circ\text{C}$)	10.60 0.981 1400	10.16 0.997 1630	9.68 0.969 1440	9.51 0.956 1480	9.53 0.972 1530	9.73 0.969 1650	8.68 0.888 2180	10.92 0.958 1360	9.74 0.946 1580	9.63 0.906 1850	10.21 1.007 1400
E_T (E_T/E_M) T ($^\circ\text{C}$)	10.62 0.982 1600	9.51 0.933 2150	9.60 0.961 1460	9.50 0.955 1600	8.81 0.899 2130			10.12 0.888 1850	8.90 0.893 2025	9.20 0.865 2210	8.97 0.885 2190
E_T (E_T/E_M) T ($^\circ\text{C}$)			9.38 0.939 1725								
E_T (E_T/E_M) T ($^\circ\text{C}$)			8.91 0.892 2180								

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Table VII

High temperature asymptotic annealing data for two samples of
AGOT-W graphite, irradiated ca. 20 L-units

Sample EP-39		Sample EP-40	
Temp. (°C)	r_T	Temp. (°C)	r_T
(As rec'd)	1.189	(As rec'd)	1.196
1100	0.241	1047	0.241
1168	0.258	1199	0.297
1272	0.366	1217	0.338
1316	0.398	1268	0.408
1350	0.384	1300	0.414
1388	0.359	1335	0.404
1402	0.360	1358	0.401
1437	0.337	1408	0.387
1489	0.280	1504	0.308
1597	0.146	1586	0.174
1655	0.096	1668	0.094
1724	0.056	1711	0.039
1783	0.055	1858	0.063

Effect of high temperature annealing on the electrical resistivity of AGOT-W graphite

Sample	WP-206	WP-174	EP-11	EP-12	EP-21	EP-22	EP-23	WP-209	WP-286	WP-126	WP-150
L-units irradiation	none	none	~ 20	~ 20	~ 20	~ 20	~ 20	~ 40	~ 35	~ 30	~ 10
r_x (as rec'd)	0.000	0.000	1.189	---	---	---	---	1.540	1.568	1.516	0.939
r_M (1000°C)	0.000	0.000	0.241	0.241	0.241	0.241	0.241	0.434	0.394	0.337	0.200
$r_{T_{\underline{T}}}$ (°C)	0.005 1400	0.003 1630	0.261 1140	0.303 1480	0.330 1530	0.248 1650	0.013 2180	0.668 1360	0.521 1580	0.024 1850	0.322 1400
$r_{T_{\underline{T}}}$ (°C)	0.009 1600	0.014 2150	0.333 1440	0.167 1600	0.005 2130			0.019 1850	0.005 2025	0.008 2210	0.012 2190
$r_{T_{\underline{T}}}$ (°C)			0.314 1460								
$r_{T_{\underline{T}}}$ (°C)			0.039 1725								
$r_{T_{\underline{T}}}$ (°C)			0.010 2180								

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10. Appendix

Table IX

Irradiation histories of samples used in asymptotic annealing experiments

Sample designation:

- (a) K, C, and W denote AGOT-K, AGOT-C, and AGOT-W, respectively.
 (b) Q, P, and J denote special graphites, fired at 3000°C (quite well graphitized), 2400°C (partly graphitized) and 2100°C (just slightly graphitized).
 (c) The second letter, P or N, indicates the orientation of the specimen axis relative to the axis of extrusion. P = parallel-cut, N = perpendicular-cut.
 (d) PBNG and PBL denote pitch bonded natural graphite, and pitch bonded lampblack, respectively.

Sample	Irrad. L-units	Irrad. Pile Units	Treatment
KP-273 KP-257 KP-219 KP-240 KP-305 KP-185 KP-316 KP-212	0.35 0.47 0.80 1.33 2.00 3.13 3.70 4.33	3.1 Mwd 5.1 Mwd 9.0 Mwd 14.1 Mwd 24.5 Mwd 32.9 Mwd 42.4 Mwd 56.4 Mwd	Irradiated in hole 1867 of the Clinton pile (8 inches from uranium metal); 2 to 4 feet from the center of the pile; sample temperature $32 \pm 5^\circ\text{C}$.
KP-222 KP-263 KP-171	5.30 6.35 7.55	65.9 Mwd 75.4 Mwd 89.4 Mwd	Same as above, except for an unfortunate increase in temperature (to probably $50 - 70^\circ\text{C}$) for the period of irradiation above ~ 60 Mwd.
KP-419 KP-184	8.00 13.7	33.0 Mwd 73.0 Mwd	Irradiated in the uranium metal "doughnuts" in hole No. 1867 of the Clinton pile; sample temperature, $35 \pm 5^\circ\text{C}$.
KP-428 CP-130 WP-150	12 12 12	70.0 Mwd 70.0 Mwd 70.0 Mwd	Irradiated in the uranium metal "doughnuts" in hole No. 1867 of the Clinton pile; pile conditions were such that sample temperatures were $\sim 100^\circ\text{C}$ for the last 25 Mwd.
KP-380 CP-117 WP-133	5.3 5.3 5.3	126.0 Mwd 126.0 Mwd 126.0 Mwd	Irradiated in the central thimble of the CP-3 pile; sample temperature $25 \pm 5^\circ\text{C}$.
KP-300 CP-108 WP-128	5.0 5.0 5.0	100.0 Mwd 100.0 Mwd 100.0 Mwd	Irradiated in experimental hole No. 21 of the Clinton pile; sample temperature $\sim 115^\circ\text{C}$.
KN-459 CN-211 WN-181	3.1 3.1 3.1	76.6 Mwd 76.6 Mwd 76.6 Mwd	Irradiated in the central thimble of the CP-3 pile; sample temperature $25 \pm 5^\circ\text{C}$.
KP-367 KN-166	3.8 3.8	24.2 Mwd 24.2 Mwd	Irradiated in charging channel No. 2064 of the Clinton pile, within 1 ft. of the center of the pile, and adjacent to one uranium metal slug; temperature $\sim 35^\circ\text{C}$.
QP-12 QN-23 PP-12 PN-23 JP-10 JN-23	3.1 3.1 3.1 3.1 3.1 3.1	76.6 Mwd 76.6 Mwd 76.6 Mwd 76.6 Mwd 76.6 Mwd 76.6 Mwd	Irradiated in the central thimble of the CP-3 pile; sample temperature $25 \pm 5^\circ\text{C}$.
PBNG-116	~ 18	108.0 Mwd	Irradiated in the uranium metal "doughnuts" in hole No. 1867 of the Clinton pile; sample temperature, $35 \pm 5^\circ\text{C}$.
PBL-103	~ 25	178.0 Mwd	Same as above, except for an unfortunate increase in the temperature (to probably $90 - 100^\circ\text{C}$) for the last 25 Mwd.

VIII. INCREASE IN INTERNAL ENERGY^{a, b}Robert Maurer^c and Richard Ruder^dABSTRACT

The increase in the internal energy of artificial graphite resulting from fast neutron irradiation at Oak Ridge has been measured. The rate of release of this stored energy during annealing has been studied; it has been shown that a definite correlation exists between the behavior of the stored energy and the neutron-induced increase in the electrical resistivity.

1. Introduction

That the lattice structure of a crystalline solid can be disordered by exposure to fast neutrons was first pointed out by Wigner.⁽¹⁾ Atoms of the solid are ejected from their normal lattice sites by collisions with the neutrons and assume positions within the interstices of the lattice. Teller⁽²⁾ estimated that approximately half of the kinetic energy of a 2-Mev neutron which is slowed down in graphite is lost by elastic collisions with carbon atoms and that the remainder is dissipated harmlessly by electronic excitation and ionization.

Wigner's prediction that the physical properties of graphite would be affected by fast-neutron irradiation was immediately confirmed by the experiments of Burton, Neubert, and their co-workers.⁽³⁾ It has been found that the thermal and electrical conductivities, the elastic modulus, and the breaking strength change as a result of neutron bombardment. X-ray examination by W. H. Zachariasen⁽⁴⁾ of heavily irradiated graphite has revealed an increase in the interplanar spacing and a "blistering" of the layers of carbon atoms. Zachariasen's estimate of the concentration of blisters agrees well with an estimate by Estermann⁽⁵⁾ of the concentration of displaced atoms.

^aBased upon work done in the Radiation Physics Section of the Metallurgical Laboratory, University of Chicago (now Argonne National Laboratory) during the period 1944-1945.

^bThis article was originally intended for publication as paper 3.14 of Vol. 10B, Radiation Chemistry, of the National Nuclear Energy Series (Plutonium Project Record) under the editorship of Milton Burton.

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The effect of fast neutron irradiation upon the properties of graphite may be reversed by annealing the graphite at temperatures under 1000°C. The extent to which the effect of irradiation is removed depends upon the temperature and the duration of the anneal. Presumably, during the anneal the interstitial atoms diffuse back to the vacancies in the lattice or to the surface of the graphite crystal.

The transfer of carbon atoms from their normal lattice sites to interstitial positions by irradiation results in an increase in the internal energy of the graphite. This stored energy is released as heat during annealing of the material. The work reported in this paper represents a test of a useful method for the determination of the stored energy content of irradiated graphite samples and the results obtained from an examination of graphite removed from the moderator structure of the Oak Ridge pile (i.e., the original graphite pile at Oak Ridge Laboratories).

2. Experimental

2.1 Method and Apparatus

Since it was expected that stored energy would be evolved over an extended temperature range on heating of an irradiated graphite specimen, it appeared that the methods which had been developed for the study of thermal effects associated with phase changes of the second kind were suitable.^(6, 7) The relative differential method of Sykes⁽⁶⁾ was chosen. The ratio of the specific heat of an irradiated sample to that of an unirradiated sample was measured as a function of temperature. Over a temperature range in which evolution of stored energy occurs, this ratio is abnormally small. Among the advantages of the method are the simple equipment which is necessary and the high sensitivity obtainable with small samples.

The two samples of the same mass and shape were mounted upon insulating supports in chambers of a massive copper block whose temperature was raised at the constant rate of dT_3/dt . The rate of rise of the temperature of each sample was given by the equation

$$dT/dt = (k/MS) (T_3 - T) \quad , \quad (1)$$

where k is a constant, M is the mass of the sample, and S is its specific heat. The fundamental assumption of Eq. (1) is that the flux of heat into the sample is proportional to the difference in temperature of sample and block. For this assumption to be satisfied temperature variations within the sample and block must be negligible and the specific heat of the insulating material which separates sample and block must be negligible.⁽⁷⁾ Calculation indicated that with the rate of temperature increase used in these experiments the first condition was satisfied and the second was met by use of a gas as the insulating layer.

The arrangement of the two samples in the copper block was symmetrical. Consequently, the value of the constant, k , was the same for each sample, and the ratio of the specific heats was

$$\frac{S_1}{S_2} = \frac{T_3 - T_1}{T_3 - T_2} \left[\frac{dT_2/dt}{dT_1/dt} \right]. \quad (2)$$

The bracketed term of Eq. (2) is close to unity when the rate of release of stored energy is small. This assumption will be shown later to be a good approximation for these experiments.

The temperature differences $(T_3 - T_1)$ and $(T_3 - T_2)$ were measured with differential thermocouples in series with a galvanometer. Because the galvanometer deflection, d , was proportional to the temperature difference, Eq. (2) may be rewritten

$$S_1/S_2 = d_1/d_2. \quad (3)$$

The energy released from unit mass of material between the temperatures T_A and T_B is

$$U_{BA} = - \int_{T_A}^{T_B} (S_1 - S_2) dT, \quad (4)$$

where S_1 is the specific heat of the irradiated sample and S_2 is the specific heat of normal unirradiated graphite.

Figure 1 is a scale section of the copper block and two graphite samples. The block, X , was a cylinder 3-7/8 in. long and of 1.5 in. o.d. The samples F_1 and F_2 were mounted in the cylindrical chambers of the block on fused silica rods, E , which were 1/8 in. in diameter. These chambers were closed by copper plugs K_1 and K_2 .

Fig. VIII. 1. Apparatus. A_1 , A_2 , B_1 , B_2 , C thermocouples. D , cylindrical hole. E , silica rods. F_1 and F_2 , graphite samples. K_1 and K_2 , copper plugs. X , cylindrical copper block.

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The samples were 1 in. long and 0.426 in. in diameter with an axial 1/8-in. diameter hole. Each sample weighed approximately 3 grams. The thermocouple junctions A_1 and B_1 were inserted in holes 3/16 in. diameter and 1-1/8 in. deep. The junction $\underline{C}$, which measured the temperature of the copper block, was in a 3/16-in. diameter hole of 1-13/16 in. depth. A second identical hole $\underline{D}$ was drilled to keep the block symmetrical. The junctions A_2 and B_2 were inserted through 1/8-in. holes in the plugs, K_1 and K_2 , and rested in the 1/8-in. axial holes of the samples.

The pairs of junctions A_1 , A_2 and B_1 , B_2 were connected externally to form a pair of differential thermocouples. Either differential couple could be connected through a Leeds and Northrup thermocouple switch to the galvanometer. The galvanometer sensitivity was chosen so that a temperature difference of 1° C corresponded to a scale deflection of 1 cm. The emf of couple $\underline{C}$ was read on a Rubicon portable potentiometer to ± 0.02 mv.

Iron-constantan wires of 28-gauge insulated with glass fiber were used for the original thermocouples. The junctions were welded in a carbon arc and silver-soldered into copper cylinders which were a snug fit for the thermocouple wells. For temperatures above 300° C, the glass insulation of these wires was unsatisfactory and Chromel-Copel wires insulated with Pyrex or silica quills were used.

The copper block was mounted on ceramic rods in a horizontal tube furnace. The temperature of the oven was manually controlled to give a uniform rate of rise of temperature of the copper block of approximately 2° C per minute. For experiments in which the maximum temperature was 300° C the oven atmosphere was air. For temperatures above 300° C the oven was filled with tank nitrogen or helium.

With air as the oven atmosphere and a rate of rise of block temperature of 2.5° C per min the temperature difference between samples and block was approximately 10° C.

2.2 Materials

Measurements were made upon two types of graphite samples. The first samples, X-3, were cut from a stringer bar of AGOT-W graphite which had been taken from the structure of the Oak Ridge graphite pile after 54 megawatt-days of pile operation (ca 6 L-units) at a temperature under 100° C. The second, 59- ϵ , were cut from a similar stringer bar of AGOT-W graphite removed from the pile after 175 megawatt-days of operation (ca 24 L-units) at a temperature under 130° C.

2.3 Results

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Figure 2 is a sample of data obtained from 59- ϵ graphite. Curve A is the ratio of the specific heat of the irradiated sample to that of the unirradiated sample during the first rise in temperature.

Fig. VIII. 2. The ratio of the specific heats of irradiated and unirradiated 59- ϵ graphite. Curve A, first heating, calculated with equation 3. Curve B, second heating. Dashed curve calculated with equation 2.

Ordinate: S_1/S_2

Abscissa: Temperature, $^{\circ}\text{C}$

Curve B was obtained after cooling the samples and apparatus to room temperature. Since the ratio of the specific heats of the samples was almost constant during the second rise in temperature there was no release of stored energy during the reheating of the irradiated graphite. The ratio of the specific heats was slightly less than unity during the reheating as a result of slight asymmetries in the apparatus. Curve A shows that during the first heating of the samples the release of stored energy began at a temperature slightly over 100°C and had not entirely ceased at 300°C .

Curve A was calculated with the use of the approximate equation 3. The effect of this approximation is shown by the dashed curve of Figure 2 which was calculated with the use of equation 4. The most important difference between the dashed and the solid curves is the result of plotting the dashed curve with the sample temperature instead of the block temperature as abscissa. The dashed and solid curves differ little in form and the difference between stored energies calculated from them is negligible.

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The stored energy released during the heating of the irradiated sample was obtained by graphical integration of the area between the two curves A and B of Figure 2. A tabulation of these energies is given for several samples of X-3 and 59- ϵ graphite in Table I.

TABLE I
Stored Energy of X-3 and 59- ϵ Graphite

Sample	Stored energy released	
	Heated to 300°C (cal/g)	Heated to 500°C (cal/g)
X-3	1.8	2.0*
X-3	1.9	2.1*
X-3	2.0	2.2*
59- ϵ	5.9	6.4*
59- ϵ	6.4	7.0*
59- ϵ		7.2
59- ϵ		9.0
59- ϵ		5.2

* Estimated

Specific heat ratio curves obtained from X-3 graphite were similar to those of Figure 2. The minimum in the ratio curve occurred at the same temperature during the first heating of the samples as in the case of 59- ϵ graphite, and the same structure was shown by the ratio curve between 200°C and 300°C.

Figure 3 shows the results of a typical experiment upon 59- ϵ graphite in which the maximum temperature was above 400°C. These experiments were not as satisfactory as the preceding ones. The higher temperatures produced the shift in the relative position of the curves (clearly obvious at low temperatures) which may be observed in Figure 3. The stored energy calculated from the data of Figure 3 is undoubtedly too large. One experiment was carried to 500°C and there was no detectable release of energy above 400°C. The results of these stored energy determinations upon 59- ϵ graphite are listed in Table I.

Some experiments were performed to determine the effect of annealing at constant temperature upon the stored energy content of the graphite. Two samples of X-3 and two samples of 59- ϵ graphite were held at 225°C for 5 minutes. After this anneal the stored energy content was

Fig. VIII 3. The ratio of the specific heats of irradiated and unirradiated 59- ϵ graphite. Curve A, first heating. Curve B, second heating.

Ordinate: S_1/S_2

Abscissa: Temperature, °C

Fig. VIII 4. The ratio of the specific heats of irradiated and unirradiated 59- ϵ graphite which has been annealed for 5 minutes at 225°C.

Ordinate: S_1/S_2

Abscissa: Temperature, °C

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determined in the usual manner. Figure 4 shows typical results. The data are summarized in Table II. The estimated values for heating to 500°C were obtained by adding 10 percent of the stored energy content of the unannealed graphite to the values obtained in these experiments on heating to 300°C. The final column of Table II, labeled "ratio," gives the ratio of the stored energy remaining after the anneal to the original stored energy content.

TABLE II.

Stored Energy of X-3 and 59-€ Graphite
Annealed Five Minutes at 225°C

Sample	Stored Energy Released		Ratio ^b
	Heated to 300°C (cal/g)	Heated to 500°C (cal/g)	
1 X-3	1.1	1.3 ^a	0.62
2 X-3	1.1	1.3 ^a	0.62
1 59-€	2.3	3.0 ^a	0.44
2 59-€	3.3	4.0 ^a	0.59

^aEstimated

^b"Ratio" is the fraction of stored energy residual after the anneal.

It has been found⁽⁸⁾ that a 5-min anneal at 235°C reduces the neutron-induced increase in electrical resistivity of X-3 graphite to 60 percent of its original value. It appeared, therefore, that there might be some correlation between the behavior of the electrical resistivity and the stored energy.

As a test of this correlation a second annealing experiment was performed. Two samples of X-3 graphite were held at 132° for 9 days. The stored energy remaining after this anneal is listed in Table III. The final column, labeled "ratio," is again the ratio of the stored energy remaining after the anneal to the original stored energy content. There is again a good correlation between the behavior of the stored energy and the electrical resistivity since such an anneal reduces the neutron-induced increase in electrical resistivity of X-3 graphite to 46 percent of its original value.⁽⁹⁾

TABLE III.

Stored Energy of X-3 Graphite Annealed Nine Days at 132°C

Sample	Stored Energy Released		Ratio ^b
	Heated to 300°C (cal/g)	Heated to 500°C (cal/g)	
1	0.92	1.1 ^a	0.52
2	0.95	1.2 ^a	0.57

^aEstimated.^b"Ratio" is the fraction of stored energy residual after anneal.

A final test of the correlation between resistivity and stored energy was made in the following manner. The rate of change with time of the resistance of a sample of X-3 graphite was measured with the sample temperature rising at the rate of 2.5°C per minute. The quantity $1/R (dR/dT)$ was compared with the rate of change of the stored energy with temperature, $1/U (dU/dT)$, which was measured under the same conditions. For the resistance measurements the graphite sample was in the form of a cylinder 2 in. long and 5/32 in. in diameter. This sample was press fitted with graphite rings into which were inserted copper current leads. A thermocouple junction was inserted into a hole in one of the rings. A constant current of 0.2 amp was passed through the sample and the potential drop across a 1-in. length was measured potentiometrically by means of the copper wire electrodes which were twisted about the sample. The unit was inserted into the same oven which had been used for the stored energy determinations. The potential drop across the sample was measured at 1-min intervals with the current reversed on alternate readings to eliminate the effect of thermoelectric emfs.

In Figure 5 the rate of relative decrease with temperature, $1/R (dR/dT)$, of the neutron-induced increase in resistance is plotted as a function of the temperature. This is compared with the rate of relative decrease with temperature, $1/U (dU/dT)$, of the stored energy, which is the negative of the specific heat ratio curve of X-3 graphite on its first heating at a rate of rise of temperature of 2.5°C per min. The dashed curve of Figure 5 has been corrected for the small change with temperature of the specific heat of normal graphite. Each curve in Figure 5 is normalized so that the area under it is unity.

Fig. VIII. 5. A comparison of the relative decrease of neutron-induced increase in resistance with the relative decrease of neutron-induced stored energy.

Ordinate: $10^3 X^{-1} (dX/dT) (\text{deg C})^{-1}$

Abscissa: Temperature, °C

The agreement between the curves of Figure 5 leaves little doubt but that the mechanism which gives the increase in resistivity is closely related to that which results in the increase in internal energy.

It is a curious feature of the behavior of graphite that the neutron-induced increase in resistivity is not well correlated with the corresponding increase in elastic modulus. The increase in elastic modulus shows little change after prolonged annealing at 132°C but can be quickly reversed at higher temperatures under 500°C. The conclusion seems inescapable that the mechanism which produces the change in the modulus involves little increase in the internal energy.

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IX THE HALL EFFECT^{a,b}Robert Maurer^c and Richard Ruder^dABSTRACT

Two irradiated graphites were examined. One had a small negative, the other a small positive Hall constant. The sign and magnitude of the Hall constant apparently depend on the extent of exposure. Annealing for 1 hour at 500°C results in a change of the Hall constant to a large, negative value. Unirradiated graphite possesses an even larger negative Hall constant. The data support the view that a result of neutron irradiation is the production of electron traps which may be interstitial atoms and vacancies; not all these electron traps are removed by the 500°C anneal. A transverse magnetic field greatly increases the resistivity of unirradiated graphite; the result is in conformity with these ideas.

1. Introduction

The electrical conductivity of graphite decreases as the result of fast neutron bombardment. Since the electrical conductivity of a solid is proportional to the product of the concentration, n , of charge carriers and of their mean free path, ℓ , it is not possible to separate the effects of irradiation on these two quantities without the use of further information. The quantity known as the Hall constant⁽¹⁾ is inversely proportional to the concentration of charge carriers for many substances, and even if this simple relation is not valid an observed change in the Hall constant provides good evidence of a change in n . The sign of the Hall constant depends upon the sign of the charge carriers and for electronic conductors

^aBased upon work done in the Radiation Physics Section of the Metallurgical Laboratory, University of Chicago (now Argonne National Laboratory) during the period 1943-1945.

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would be expected to be negative. Many metals, most notably the alkaline earths, possess positive Hall constants. This effect is now known to be due to the periodic field of the lattice ions. Such conductors are referred to as "hole" conductors.

The Hall constant is measured in the following manner. Consider a solid in the form of a rectangular parallelepiped carrying an electric current in a direction perpendicular to one pair of faces. A magnetic field is applied perpendicular to a second pair of faces. A potential difference will appear across the third pair of faces of the solid. This Hall emf, V_H , is given by the equation

$$V_H = RH_i/d \quad , \quad (1)$$

where R is the Hall constant, H is the magnetic field intensity, i is the magnitude of the electric current, and d is the separation of the pair of faces of the parallelepiped which are perpendicular to the magnetic field direction.

When the current is carried by a gas of either free electrons or "holes," simple expressions for R can be given for the two cases of non-degeneracy and complete degeneracy.

$$R = \ell/nec \quad ; \quad \text{degenerate case (2a)}$$

$$R = (3\pi/8)(\ell/nec) \quad . \quad \text{non-degenerate case (2b)}$$

In Eqs. (2) the concentration of carriers is given by n ; e is the electronic charge, and c is the velocity of light. The magnetic field is expressed in emu units and all other quantities in esu units in Eqs. (1) and (2).

The purpose of the measurements described in this paper was the examination of the effect of fast neutron irradiation upon the Hall constant of graphite in order to obtain information as to the effect of such irradiation upon the concentration of charge carriers.

2. Experimental

2.1 Materials

Measurements were made upon three types of graphite and in each case samples cut parallel and perpendicular to the axis of extrusion were examined. The samples were in the form of flat plates of nominal dimensions 1 inch x 1/2 inch x 1/8 inch. Samples labeled longitudinal were cut so that the axis of extrusion was parallel to the long dimension of the plate which was the direction of current flow. Transverse samples had the axis of extrusion perpendicular to the length of the plate and to the direction of current flow.

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The three types of graphite consisted of unirradiated AGOT-K graphite and two AGOT-W graphites which had received different irradiations at the Oak Ridge graphite pile. The AGOT-W graphite labeled X-3 had been exposed during 54 megawatt-days of pile operation (ca 6 L-units) at a temperature under 100°C . The type known as 59- ϵ had been exposed during 175 megawatt-days (ca 24 L-units) at a temperature under 130°C .

2.2 Method and Apparatus

The permanent magnet was of Alnico, fitted with soft pole pieces which were two inches in diameter. The sample holder was a snug fit in the $3/8$ -inch gap. The field strength, as measured with a flip coil and fluxmeter, was 7270 gauss.

A full-size illustration of the sample holder is given in Fig. 1. It was constructed of a $3/8$ -inch Lucite plate, L , which was recessed to receive the graphite sample. The copper electrodes, I_1 and I_2 , allowed a constant current of 2 amp to be passed through the specimen. The brass screw, N , clamped the sample between the current electrodes. The electrodes, H_1 and H_2 , for measurement of the Hall emf were pointed brass screws. The pointed brass screws, P_1 and P_2 , were used for measurement of the resistivity of the samples. With a constant current passing through the sample, the potential difference between H_1 and H_2 was measured with a Leeds and Northrup Type K-2 potentiometer with the sample between the pole pieces of the magnet and after removal of the sample from the magnet field. The difference between these measurements was taken as the Hall emf. The current through the sample was determined by measurement of the potential drop across a standard resistor inserted in series with the sample.

Fig. IX. 1
Sample holder
for Hall Effect
measurement.

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The Hall emfs of the various samples were between 4 and 30 microvolts and were measured to ± 0.5 microvolt. The precision of measurement was, therefore, small.

2.3 Results

The measured values of the Hall constants of unirradiated AGOT-K graphite are tabulated in Table I. With the exception of Sample 1 there was a negligible change in the Hall constant, $\underline{R}$, on annealing. There appeared to be measurable difference in the value of $\underline{R}$ for longitudinal and transverse samples.

TABLE I

Hall Constants of Unirradiated AGOT-K Graphite

Sample	Before Annealing, $R \times 10^{22}$	After Annealing (1 hr at 500°C), $R \times 10^{22}$
1-Longitudinal	-5.3	-7.2
2-Longitudinal	-7.0	-7.1
3-Transverse	-5.5	-5.2
4-Transverse	-5.4	-5.5

Table II lists the measured values of $\underline{R}$ for the X-3 graphite samples. This irradiated graphite had a small negative Hall constant. Heating for 1 hour at 500°C resulted in a Hall constant considerably more negative. It is known that a 1-hour anneal at 500°C reverses almost completely the effects of fast neutron bombardment upon such other physical properties as the thermal and electrical conductivities and the elastic modulus.⁽²⁾

The data for 59- ϵ graphite, both annealed and unannealed, are given in Table III. The 59- ϵ graphite had received a larger dosage than the X-3 and the Hall constant before annealing was positive. A 1-hour anneal at 500°C produced a reversal of the sign of the Hall constant, although it remained less negative than that of the unirradiated AGOT-K graphite. Since the properties of the X-3 and 59- ϵ graphite before irradiation are unknown it is not possible to draw any certain conclusion from this behavior. A plausible interpretation is that the anneal for 1 hour at 500°C did not completely restore the material to its original state.

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TABLE II

Hall Constants of Irradiated X-3 Graphite

Sample	Before Annealing, $R \times 10^{22}$	After Annealing (1 hr at 500°C), $R \times 10^{22}$
1-Longitudinal	-0.96	-3.0
2-Longitudinal	-0.85	-5.1
3-Longitudinal	-0.65	-3.9
4-Transverse	-1.0	-4.6
5-Transverse	-0.44	-4.3

TABLE III

Hall Constant of Irradiated 59-ε Graphite, in Units of
 $10^{20} \text{ sec}^2 (\text{g cm})^{-1/2}$

Sample	Before Annealing	After 7 Days at 132°C	After 1 Hour at 500°C	After 2 Hours at 500°C
	R	R	R	R
1-Longitudinal	+4.3		-1.5	
2-Longitudinal	+4.6		-1.9	
3-Transverse	+4.0		-2.0	
4-Transverse	+3.8		-2.0	
5-Longitudinal	+5.0	+2.1		-1.4
6-Longitudinal	+4.7	+2.0		-1.4
7-Transverse	+4.4	+1.4		-2.0
8-Transverse	+4.5	+1.3		-1.8

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Samples 5 to 8 inclusive were given a 7-day anneal at 132°C. As indicated in column 3 of Table III, the Hall coefficient was decreased in magnitude by this treatment but remained positive.

A 7-day anneal at 132°C decreased the neutron-induced increase in resistivity by approximately one half.⁽³⁾ On the other hand, the neutron-induced increase in elastic modulus is decreased by only a few tenths of a per cent by such an anneal. Since the Hall constant changed substantially during 7 days at 132°C, it appears that the modulus changes are not correlated with the alterations in the Hall constant. Apparently the neutron-induced changes in the structure of the graphite lattice which produce the changes in resistivity are also responsible for the behavior of the Hall constant.

3. Discussion

The very large effect of fast neutron irradiation upon the Hall constant of graphite makes very reasonable the inference that the effect of such irradiation is not confined to a decrease in the mean free path of the charge carriers but also produces a decrease in their concentration.

The large negative value of the Hall constant of unirradiated AGOT-K graphite indicates that the surface of the Fermi distribution of the conduction electrons is near the bottom of an almost empty band of allowed energy levels. The lowest level of this band probably lies below the uppermost level of a lower band of allowed levels. It may be that this lower band is not completely filled with electrons at room temperature and that the current is carried chiefly by electrons and partially by "holes." Under these conditions Eqs. (2) are not valid, since they assume either exclusive electron or "hole" conduction. If we assume the validity of Eqs. (2), the density of conduction electrons in unirradiated AGOT-K graphite is about 10^{20} per cm^3 , which is a very reasonable result.

A possible explanation of the change in sign of the Hall constant upon irradiation is the following:

Ejection of carbon atoms from normal lattice sites by fast neutrons will produce vacancies and interstitial atoms in the graphite lattice. We assume that the interstitial atoms, and perhaps the vacancies, introduce into the electronic energy spectrum discrete levels which lie below the uppermost filled levels. Electrons will be transferred from the surface of the Fermi distribution to these discrete levels because this process lowers the energy of the system. If the lowering of the surface of the Fermi distribution is sufficiently great, the Hall constant will become positive since "hole"

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conduction will outweigh electron conduction. The reversal of sign of the Hall constant upon annealing implies that the interstitial atoms have disappeared by diffusion to the vacancies or to the surface of the crystal.

It will be noted, however, that there remains a small residual effect which is related to the length of exposure after annealing. This residual effect may be understood on the basis of two assumptions: first, that the vacancies introduce discrete energy levels into the spectrum; second, that a significant number of the vacancies remain after the anneal at 500°C. The latter conclusion also was reached on the basis of fact that the increase in resistivity caused by neutron bombardment is not completely removed by such an anneal.⁽⁴⁾

When the surface of the Fermi distribution of an electronic conductor lies close to the boundary of a Brillouin zone it is distorted from a spherical form. This results in a large increase in electrical resistivity upon application of a magnetic field.⁽¹⁾ This behavior is exhibited by graphite, as shown in Table IV.⁽⁵⁾ The second column of Table IV lists the resistances, r_0 , of individual samples of unirradiated AGOT-K graphite in the absence of a magnetic field, and the third column lists the resistances, r_H , of these samples in a transverse magnetic field of 7270 gauss. The fourth column shows the percentage increase in resistance. These percentage increases are several hundred times those shown by the alkaline earth metals under similar conditions.

TABLE IV

Change of Resistance of Unirradiated AGOT-K Graphite
With Magnetic Field

Sample	N_0 Field, $r_0 \times 10^4$ (ohms)	Transverse Field, $r_H \times 10^4$ (ohms)	$r/r_0 \times 100$
1-Longitudinal	2.01	2.08	3.5
2-Longitudinal	2.15	2.23	3.7
3-Transverse	2.63	2.70	2.7
4-Transverse	2.84	2.90	2.1

The results are further evidence that in graphite the surface of the Fermi distribution is close to the upper boundary of a band of allowed energy levels for the electrons.

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X. RATE OF BROMINE ABSORPTION^aA. Novick^b and T. J. Neubert^cABSTRACT

When exposed to bromine vapor, graphite absorbs about 84% of its weight of bromine, giving an atom ratio of one bromine atom to eight carbon atoms. The structure, according to X-ray studies, corresponds to layers of bromine atoms separated by two layers of carbon atoms. Experiments indicate that the initial rate of bromine absorption is sharply decreased by previous exposure of the graphite to fast neutrons. The effect disappears when the graphite samples are heated, and the increase in rate correlates well with the healing of the elastic modulus changes.

1. Introduction

An interesting approach to the determination of the detailed structure of normal, artificial and neutron-bombarded artificial graphites is furnished by application of a method derived from the work of Rüdorff.⁽¹⁾ He exposed samples of various types of graphite to bromine vapor and found that graphite can absorb as much as 84% of its weight of bromine. When the partial pressure of bromine was reduced, bromine came off the graphite rapidly. From this result it was concluded that bromine, unlike fluorine, which reacts vigorously with graphite under certain conditions, dissolves in graphite without compound formation. An X-ray diffraction study of the material gave evidence of a period of 10.4 Å not present in normal graphite. Rüdorff assigned the structure given schematically in Fig. 1 to the brominated graphite. Bromine atoms occur in layers between every second pair of graphite planes. When graphite contains its maximum amount of bromine, 84%, there is one bromine atom per eight carbon atoms. The assigned structure agrees with the density change observed upon bromine uptake.

^aBased upon work done at the Metallurgical Laboratory, University of Chicago (now Argonne National Laboratory) during the period 1943-1945. This article was originally intended for publication as paper 3.19 of Vol. 10B, Radiation Chemistry, of the National Nuclear Energy Series (Plutonium Project Record) under the editorship of Milton Burton.

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Fig. X. 1.
Schematic Structure of
Brominated Graphite

The Wigner effect in graphite involves alteration of crystal structure. Therefore, some changes in behavior toward bromine might be expected in graphite after exposure to fast neutrons. Some simple experiments conducted here indicate a marked effect on the rate at which bromine is absorbed but no systematic difference in the total uptake after long standing in bromine vapor.

2. Experimental

2.1 Technique

Cylindrical artificial graphite samples, 0.4 cm diameter and 3.5 cm length, were used. Specimens in open weighing bottles were placed in a large dessicator containing bromine at room temperature, with no precautions being taken to remove air. After the desired time of exposure (~ 10 min) the weighing bottles were removed, quickly stoppered, and weighed. Samples listed in any one of the following tables were exposed simultaneously to the bromine so that the conditions of absorption would be constant.

2.2 Results

An experiment in which two graphite samples, one irradiated and one unirradiated, were exposed to bromine indicated a marked Wigner effect on the rate of bromine uptake. In this experiment the unexposed sample was Whiting graphite and the irradiated sample was taken from a structural member (a stringer bar) of the air-cooled Clinton pile which had received ~ 5.7 L exposure. Table I presents the results obtained.

TABLE I

Effect of Exposure on Rate of Absorption of Bromine by Graphite

Samples were exposed simultaneously for 10 min at 25°C

Irradiation	Init. wt. (g)	Br abs. (g)
Unexposed	0.6876	0.0344
Exposed, ~ 5.7 L	0.7237	0.0146

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An experiment was made to see whether the change in rate is affected by heating, as is the case with the neutron-induced elastic modulus and electrical resistance increases.^(2, 3) Two samples were taken from a stringer exposed to ~ 4.3 L at Clinton. One was heated to 600°C for thirty minutes, while the second was not heated. The results, recorded in Table II, demonstrate a thermal reversal like that for the other changes associated with the Wigner effect.⁽³⁾

TABLE II

Thermal Reversal of Bromine Effect

Samples were exposed simultaneously for 10 min
at 25°C

Sample	Treatment	Init. wt. (g)	Br ₂ abs. (g)
X-2	Exposed, ~ 4.3 L Heated at 600°C	0.7869	0.0222
X-4	Exposed ~ 4.3 L	0.7084	0.0100

In order to confirm these observations and to determine possible correlation of the phenomenon with the changes in resistivity or in elastic modulus, the following experiment was performed. A number of samples were cut from the bar which had been in the Clinton pile for ~ 5.7 L operation. Groups of these samples were heated at different temperatures for sufficient lengths of time to attain the steady states at the particular temperatures.⁽³⁾ The resulting changes in elastic modulus and electrical resistance at these temperatures were observed. Then, two samples from each group were exposed to bromine vapor for ten minutes. Table III shows that changes in the bromine effect correlate fairly well with changes in elastic modulus but not with changes in electrical resistance.

No systematic differences appeared in the total amount absorbed after samples listed in Table III remained in contact with bromine vapor for long times. Table IV shows the results of this experiment.

3. Discussion

The results given in the preceding section indicate a large decrease in the initial rate of bromine absorption associated with changes wrought in graphite by fast-neutron bombardment. This effect is roughly correlated with increases in elastic modulus. There is, however, no difference in total take-up by graphite which has been in contact with bromine for long times.

TABLE III

Relation Between Effect on Rate of Absorption of Br_2 by Graphite and Healing of Electrical Resistance and Elastic Modulus

Samples were exposed simultaneously for 10 min at 25°C

Healing Temp. ($^\circ\text{C}$)	Initial weight (g)	Wt. Br_2 abs.	$W_M - W_T$	$R_T - R_M$	$E_T - E_M$
		Init. wt.	W_M	R_M	E_M
-	0.6823	0.0040	0.77	0.50	0.52
-	0.6887	0.0057	0.68		
131	0.6816	0.0040	0.77	0.21	0.47
131	0.6960	0.0047	0.73		
240	0.6956	0.0116	0.34	0.08	0.21
240	0.7028	0.0100	0.43		
1000	0.6888	0.0175	0.02	0	0
1000	0.6951	0.0180	-0.02		

Key: The symbol W_T represents the weight of Br_2 absorbed in 10 min at room temperature by a sample heated to the temperature T until attainment of a steady state. (3) The subscript M indicates the corresponding value for a sample heated to 1000° . The values for R (electrical resistance) and E (elastic modulus) data were taken from a similar typical set of samples from the 5.7-L stringer.

An interpretation of these results is that fast neutron bombardment causes tighter binding in the direction normal to the planes of the graphite lattice and thereby increases the activation energy and decreases the rate constant for the bromine diffusion process. Increases in elastic modulus are properly attributable to increases in force constants. The principal significant increase in the latter in the case of graphite must be for interplanar vibrations; the amount of the increase is a non-linear function of the number of displaced atoms. The force constant between planes and the activation energy required to separate planes an adequate distance for intrusion of bromine are both functionally related to the number of atoms between the planes. The mutual relationship between them is much the same as between force constant and dissociation energy for states of a diatomic system.

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TABLE IV

Total Bromine Absorption and Wigner Effect
 Samples were exposed to bromine for 24 hrs at 25°C

Healing temp. (°C)	Wt. Br ₂ abs.
	Initial wt.
-	0.646
-	0.765
131	0.675
131	0.687
240	0.675
240	1.000
1000	0.680
1000	0.765

Alternatively one could postulate some blocking of the entrances to the spaces between planes. This mechanism, however, seems less reasonable since even in normal graphite the crystal edges already must be considerably blocked by the atoms saturating the free valencies at the plane edges. Further addition of blocking atoms should not produce the large effects observed.

In the cases reported here, except for one example, the total amounts of bromine absorption differ from the average by not more than 6%. One interpretation of this result is that the total "lattice destruction" does not exceed a figure close to that quantity. Samples of considerably larger exposure are now available. It is possible that additional experiments of this type may prove useful for the detection of gross lattice destruction in irradiated graphite.

REFERENCES

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