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Radiation Effects on Materials

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INTERSTITIAL COMPOUNDS OF IRRADIATED GRAPHITE

by

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ABSTRACT

As the result of an attempt to prepare unordered compounds of graphite containing more than 1.5×10^{-3} acceptor per carbon atom by the introduction of both chemical acceptors and radiation damage centers, evidence has been found for mutual destruction of chemical acceptors and damage centers. An analysis of the kinetic behavior of the mutual destruction indicates that the extent of destruction is independent of the order in which the radiation damaging and chemical treatments are carried out.

From some auxiliary experiments made necessary by the discovery of the above interaction it is concluded that the graphite bisulfate residue compounds are stable at room temperature, and that the bisulfate ion is not appreciably decomposed by the gamma flux in the reactor during short irradiations.

The dependence of some electrical properties of graphite on the concentrations of both chemical acceptors and radiation damage centers has been analyzed on the basis of the two-band theory of a semi-conductor above its degeneracy temperature. It is concluded that, whereas the Hall effect may be reasonably well understood, the behaviors of the electrical resistance and magnetoresistance cannot be understood in terms of this theory, so that the introduction of additional hypotheses appears necessary.

INTRODUCTION

It has been shown^(1,2) that the electron population of the conduction bands in graphite can be altered by chemical or physical treatments. Radiation damage by fast particles, such as neutrons, introduces electron traps which deplete the bands. It has proved to be possible to simulate some aspects of radiation damage by introducing certain chemical impurities, such as halogens or bisulfate ions, into graphite. Since bisulfate ions could be introduced electrolytically, the concentration of traps was known quite precisely; thus, it was possible to study the changes in electrical properties

produced by known changes in the electron population. It also was possible to determine that the rate at which traps were produced during neutron irradiation was about 9×10^{-5} acceptor per carbon atom produced per Mwd of bombardment.⁽¹⁾

These studies were severely limited by the fact that only about 1.5×10^{-3} acceptor per carbon atom could be successfully introduced chemically into artificial graphite. Higher concentrations, as high as 0.042, had indeed been measured, but these high concentrations were obtained only in the so-called lamellar compounds, in which the formation of a superlattice probably distorts the original band structure of the graphite. Randomly distributed impurities, as in the so-called residue compounds, at concentrations in excess of 1.5×10^{-3} caused noticeable distortion of the graphite with attendant erratic properties.

The present paper describes attempts to introduce known acceptor concentrations greater than 1.5×10^{-3} . If it were certain that the rate of acceptor production during pile bombardment would remain constant at 9×10^{-5} , such samples could be prepared simply by increasing the bombardment. In order to test the constancy of trap production a different method was attempted; this consisted of introducing less than 1.5×10^{-3} trap by bombardment, then introducing further traps by quantitative chemical procedures. It will be shown that this method failed because the electrolytic introduction of traps caused the destruction of some of the traps produced by bombardment. To study this interaction in more detail, a few samples containing chemical impurities were bombarded in the reactor. A few attempts were made to exceed the acceptor concentration of 1.5×10^{-3} by introducing bromine rather than bisulfate ion prior to the irradiation. It was hoped that bromine might prove more stable than bisulfate under bombardment in a reactor, but these experiments led to the same results as those employing bisulfate residue compounds.

EXPERIMENTAL

Materials

All measurements were made on samples cut from KCF pile-grade graphite. These samples were cut so that the current direction coincided with the direction of extrusion. The pertinent information about the sample is given in Fig. 6 of reference 2.

The sulfuric acid used was Baker and Adamson Reagent Grade concentrated sulfuric acid.

Preparation of Samples

The lamellar and residue graphite bisulfate compounds were prepared by electrolytic oxidation and subsequent reduction of the graphite samples in concentrated sulfuric acid by the method employed in earlier studies,⁽²⁾ excepting that the auxiliary platinum electrode surrounded the sample more completely, thus permitting more uniform oxidation and reduction of the graphite samples. The current leads were tantalum blocks clamped to wolfram rods. It was found desirable to line the tantalum clamps with platinum foil to obtain uniform current flow between tantalum and graphite. The oxidation state of the residue compounds was determined by measuring the relative resistance of the compounds and utilizing the fact, previously demonstrated,⁽²⁾ that residue and lamellar compounds of the same oxidation state have the same relative resistance.

A few samples of graphite bromide compounds were prepared by immersing the graphite in a solution of bromine in carbon tetrachloride for a period of a few hours. These compounds, when placed in an air stream overnight, were converted to the corresponding residue compounds.

Neutron bombardments were performed in the Argonne Reactor CP-3', vertical thimbles #1 and #4 (converter). The flux equivalence, in customary units of Mwd,⁽¹⁾ was established by monitoring the electrical properties.

Measurement of the Electrical Properties

Electrical properties of the sample were determined by passing a current of approximately one ampere, regulated to about one per mil, through the sample. The magnetic field of 12.75 kilogauss was also regulated to one per mil. All potentials were measured to a precision of about one per mil.

The magnetoresistance of graphite at room temperature varies with magnetic field according to the relation:

$$\frac{\Delta R}{R_0} = CH^n \quad , \quad (1)$$

where ΔR is the change in resistance due to the magnetic field H , R_0 is the resistance in the absence of a field, C is the magnetoresistive coefficient, and $n = 1.74$ for unirradiated graphite (for $3 < H < 15$ kilogauss). The data are reported in relative units C/C_0 , where C_0 is the coefficient for untreated graphite. Since the precision with which this coefficient could be measured varied with its magnitude, a given value C is precise to C_0/C per mil. Hall coefficient measurements were repeated until a precision of about 0.001 emu was attained.

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The absence of spurious thermoelectric or contact voltages was established by frequent reversal of the current.

RESULTS

The behaviors of the electrical resistance, the magnetoresistance, and the Hall coefficient of graphite subjected to neutron bombardment are well known.⁽³⁾ The results obtained in the present study are very similar to those already published. The behaviors of the electrical resistance and the Hall coefficient of graphite subjected to electrical oxidation are given in reference 2; however, the behavior of the magnetoresistance coefficient has not been previously reported; this is shown in curves R and L in Fig. 1.

It has been demonstrated that the rate of production of traps during bombardment can be determined by superposing the curves showing the behavior of the Hall coefficient during bombardment and oxidation. Since more precise data are now available, these curves have been replotted in Fig. 2. The correspondence obtained, $1 \text{ Mwd/cT} = 10^{-4}$ acceptor per carbon atom, is seen to hold quite well up to 9 Mwd. Using this correspondence it is possible to plot the changes in resistance and magnetoresistance for oxidation and bombardment on a common basis as in Fig. 1 (curve B) and Fig. 3. It is seen that curves B and R differ markedly, because chemically introduced traps scatter electrons rather weakly.⁽⁴⁾

The resistances of lamellar and residue compounds derived from irradiated graphite by electrolytic oxidation and subsequent reduction in concentrated sulfuric acid are shown in Fig. 4. It will be noted that the five curves corresponding to varying periods of irradiation are similar and, furthermore, are similar to that for unirradiated graphite. This similarity is more strikingly shown in Fig. 5, where the ordinate is R/R_B rather than R/R_0 . The solid curve represents the data for unirradiated graphite and the points are the data for the five different samples of irradiated graphite. A similar plot for the magnetoresistive coefficient is given in Fig. 6.

The behaviors of the Hall coefficients of samples of irradiated graphite during oxidation are shown in Fig. 7. On comparing these curves with those for unirradiated graphite (see Fig. 7), it is seen that the lamellar compounds tend to the same Hall coefficient; a similar trend to a higher Hall coefficient for the residue compounds seems evident.

A few samples of bisulfate or bromine residue compounds derived from unirradiated graphite were subjected to neutron bombardment in the reactor. The results obtained in this series of experiments are given in Table I. In order to demonstrate that these results are not due to spontaneous decomposition of residue compounds, two compounds of moderate

TABLE I

Galvanomagnetic Effects in Irradiated Interstitial Compounds of Graphite

Sample	After Oxidation				After Irradiation				Remarks
	Acceptor Conc. ($\times 10^{-4}$)	R/R ₀	C/C ₀	A _c	Nominal Exposure (Mwd)	R/R ₀	C/C ₀	A _c	
43	-	-	-	-	0.6	1.109 $\pm$ 0.001	0.704 $\pm$ 0.003	-0.543 $\pm$ 0.003	Monitor
44	-	-	-	-	1.1	1.217 $\pm$ 0.001	0.540 $\pm$ 0.002	-0.480 $\pm$ 0.001	
45	-	-	-	-	1.4	1.284 $\pm$ 0.001	0.474 $\pm$ 0.001	-0.430 $\pm$ 0.001	
46	2.6	0.888 $\pm$ 0.001	0.975 $\pm$ 0.002	-0.387 $\pm$ 0.002	0.6	0.999 $\pm$ 0.001	0.625 $\pm$ 0.002	-0.301 $\pm$ 0.002	
47	4.0	0.829 $\pm$ 0.002	0.917 $\pm$ 0.001	-0.067 $\pm$ 0.001	0.6	0.907 $\pm$ 0.001	0.563 $\pm$ 0.001	-0.044 $\pm$ 0.002	Bisulfate Residue
48	10.0	0.626 $\pm$ 0.001	0.456 $\pm$ 0.001	+0.427 $\pm$ 0.002	0.6	0.690 $\pm$ 0.001	0.311 $\pm$ 0.001	+0.344 $\pm$ 0.001	
					1.7	0.837 $\pm$ 0.002	0.195 $\pm$ 0.002	+0.322 $\pm$ 0.002	
49	3.4	0.857 $\pm$ 0.001	0.841 $\pm$ 0.002	-0.409 $\pm$ 0.003	1.1	1.031 $\pm$ 0.001	0.463 $\pm$ 0.001	-0.299 $\pm$ 0.001	
50	6.4	0.743 $\pm$ 0.001	0.683 $\pm$ 0.001	+0.213 $\pm$ 0.002	1.1	0.891 $\pm$ 0.001	0.379 $\pm$ 0.001	+0.158 $\pm$ 0.001	
51	4.2	0.817 $\pm$ 0.001	0.809 $\pm$ 0.001	-0.157 $\pm$ 0.001	1.1	1.082 $\pm$ 0.001	0.344 $\pm$ 0.001	-0.061 $\pm$ 0.001	
52	4.1	0.830 $\pm$ 0.001	0.792 $\pm$ 0.001	-0.023 $\pm$ 0.003	1.4	1.076 $\pm$ 0.002	0.338 $\pm$ 0.002	+0.079 $\pm$ 0.001	
53	2.7	0.884 $\pm$ 0.001	0.936 $\pm$ 0.002	-0.375 $\pm$ 0.001	1.4	1.071 $\pm$ 0.003	0.400 $\pm$ 0.004	-0.077 $\pm$ 0.006	
54	7.8	0.695 $\pm$ 0.001	0.606 $\pm$ 0.001	+0.268 $\pm$ 0.001	1.4	1.021 $\pm$ 0.001	0.243 $\pm$ 0.003	+0.188 $\pm$ 0.005	
					2.5	1.292 $\pm$ 0.001	0.238 $\pm$ 0.001	+0.140 $\pm$ 0.001	
55	4.1	0.828 $\pm$ 0.001	0.764 $\pm$ 0.001	+0.021 $\pm$ 0.001	1.1	1.031 $\pm$ 0.001	0.407 $\pm$ 0.002	+0.037 $\pm$ 0.002	Bromine Residue
57	8.5	0.668 $\pm$ 0.001	0.602 $\pm$ 0.001	+0.399 $\pm$ 0.001	1.1	0.838 $\pm$ 0.001	0.308 $\pm$ 0.001	+0.354 $\pm$ 0.005	Bisulfate Residue
58	8.4	0.678 $\pm$ 0.001	0.605 $\pm$ 0.001	+0.238 $\pm$ 0.001	γ -flux	0.699 $\pm$ 0.014	0.670 $\pm$ 0.005	+0.158 $\pm$ 0.003	
59	-	-	-	-	1.1	1.240 $\pm$ 0.001	0.527 $\pm$ 0.001	-0.473 $\pm$ 0.001	Monitor
60	-	-	-	-	γ -flux	1.000 $\pm$ 0.001	0.984 $\pm$ 0.001	-0.624 $\pm$ 0.001	
61	5.8	0.691 $\pm$ 0.001	0.618 $\pm$ 0.002	-0.860 $\pm$ 0.005	2.8	1.495 $\pm$ 0.008	0.206 $\pm$ 0.003	-0.457 $\pm$ 0.002	Ammonia Residue
62	-	-	-	-	2.8	1.561 $\pm$ 0.002	0.284 $\pm$ 0.001	-0.248 $\pm$ 0.001	Monitor
68	-	-	-	-	7.5	2.336 $\pm$ 0.004	0.084 $\pm$ 0.001	+0.330 $\pm$ 0.002	
69	3.6	0.790 $\pm$ 0.001	0.746 $\pm$ 0.001	+0.032 $\pm$ 0.001	7.5	1.832 $\pm$ 0.001	0.065 $\pm$ 0.001	+0.419 $\pm$ 0.001	Bromine Residue
70	3.8	0.794 $\pm$ 0.001	0.733 $\pm$ 0.003	+0.061 $\pm$ 0.002	7.5	1.768 $\pm$ 0.001	0.069 $\pm$ 0.001	+0.377 $\pm$ 0.001	Bisulfate Residue
71	5.4	0.704 $\pm$ 0.001	0.624 $\pm$ 0.001	+0.261 $\pm$ 0.001	7.5	1.575 $\pm$ 0.001	0.059 $\pm$ 0.001	+0.423 $\pm$ 0.001	Bromine Residue

The initial data for all samples are normalized to: R/R₀ = 1.000 $\pm$ 0.001; C/C₀ = 1.000 $\pm$ 0.002; A_c = -0.650 $\pm$ 0.001. All errors listed are equal to or greater than the standard deviations of the measurements, based on at least two runs for resistance and magnetoresistance and on at least six runs for the Hall coefficient.

acceptor concentrations, which had been boiled for one hour in a concentrated solution of sodium hydroxide, were stored and repeatedly measured over a period of more than one year. The results of these measurements are given in Table II.

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TABLE II
Stability of the Bisulfate Residue
Compounds of Graphite

Sample	Resistance	Resist (12,750 Gauss)	Hall Coefficient
		Resist (No Field)	
<u>No. 63</u> $m = 6.5 \times 10^{-4}$ After	0.0078363	1.0768	+0.2637
35 days in water	0.0078081	1.0746	+0.2674
133 days in water	0.0077625	1.0739	+0.2653
382 days in water	0.0077771	1.0721	+0.2639
<u>No. 64</u> $m = 6 \times 10^{-4}$ After	0.0087063	1.0693	+0.2027
35 days in air	0.0086837	1.0678	+0.2028
133 days in air	0.0087113	1.0676	+0.2009
382 days in air	0.0087102	1.0664	+0.2002

DISCUSSION

Kinchin⁽⁵⁾ has shown that some electrical properties of irradiated graphite can be described reasonably well by the equations derived for a two-band conductor above the degeneracy temperature. This description led to the conclusion that the production of electron traps during weak bombardments is not linear with bombardment. It has been pointed out previously⁽⁶⁾ that the chemical compounds of graphite cannot be described in terms of this model. A more complete discussion, given below, will show that the observed behavior of the Hall coefficient of acceptor compounds can be fitted tolerably well by this theory, but that the observed resistance and magnetoresistance of acceptor compounds is in sharp disagreement with this theory.

According to this theory⁽⁷⁾ the Hall coefficient of a semi-conductor containing both positive and negative carriers of electricity in thermal equilibrium is given by

$$A = \frac{3\pi}{8e} \frac{p\mu_p^2 - n\mu_n^2}{(p\mu_p + n\mu_n)^2} = \frac{3\pi}{8e} \frac{p - nb^2}{(p + nb)^2}, \quad (2)$$

where $3\pi/8e$ is the factor resulting from the use of classical statistics, p is the concentration and μ_p the mobility of the positive carrier, n is the concentration and μ_n the mobility of the negative carrier, and b is the ratio of electron to hole mobility. The assumption of thermal equilibrium imposes the condition

$$np = \text{constant} \equiv n_0^2 \quad (3)$$

on the concentrations at any given temperature.

Introduction of the variable $x = p/n_0 = n_0/n$ into equation (2) gives

$$A(\text{emu}) = \frac{8.9 \cdot 10^{-4} x (x^2 - b^2)}{n_0 (x^2 + b)^2}, \quad (4)$$

if the concentrations are expressed in number per carbon atom, since the density of the graphite used in these experiments was 1.65 g/cm^3 . The acceptor concentration, m , is given in terms of the variable x by the relation

$$m = d + \frac{x^2 - 1}{x} n_0, \quad (5)$$

where d is the concentration of donors present in unoxidized graphite.

Figure 2 shows that the Hall coefficient of bombarded graphite and of oxidized graphite can be brought into coincidence up to an acceptor concentration of 9×10^{-4} per atom, but diverge at higher concentrations. It is of interest, then, to attempt to fit the initial portion of the curves, the object being to determine which, if either, of the diverging curves would be traced beyond the concentration of 9×10^{-4} acceptors/atom.

The three unknowns, b , d , n_0 , found by fitting the experimental curve (Fig. 2) at $m = 0$ and $m = 4.5 \times 10^{-4}$ ($A = 0$) and matching the slope at $m = 4.5 \times 10^{-4}$, are

$$\begin{aligned} b &= 1.4 \\ n_0 &= 3.7 \times 10^{-4} \\ d &= 2.0 \times 10^{-4} \end{aligned} \quad (6)$$

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Equation (4) with the above values, is represented in Fig. 2 by the dotted line, which traces the curve for oxidized graphite, though falling somewhat below it for $m > 10^{-3}$. Kinchin's values⁽⁵⁾ of these parameters, based upon the assumption $d = 0$, derived from the experimental values for irradiated graphite are: $b = 1.25$ and $n_0 = 0.6 \times 10^{-4}$. The resistances of residue compounds calculated with the values of equation (6) diverge markedly from the observed values. Furthermore, it is not possible to find any values of these parameters which will give a fit since the two-band theory always yields a somewhat bell-shaped curve of resistance versus acceptor concentration, whereas the observed curve is exponential in character. An attempt to explain these anomalies by postulating inhomogeneities in the oxidized graphite will be published elsewhere.⁽⁶⁾

An attempt was made to explain the observed changes in the magnetoresistive coefficient by the two-band theory. Extension of the considerations used to derive equation (2) show that the change of resistance in a magnetic field, H , is given by

$$\frac{\Delta R}{R_i} = \frac{9\pi^2}{64} \frac{p\mu_p n\mu_n (\mu_p + \mu_n)^2 H^2}{(p\mu_p + n\mu_n)^2 + \mu_p^2 \mu_n^2 (n - p)^2 H^2} \quad (7)$$

It may readily be ascertained that, for the magnetic field used in our experiments, the second term in the denominator is negligible compared with the first. Thus, we may write

$$C = \frac{9\pi^2}{64} p n \mu_p \mu_n \left(\frac{\mu_p + \mu_n}{p\mu_p + n\mu_n} \right)^2 = \frac{9\pi^2}{64} \frac{p n b (1 + b)^2}{(p + n b)^2} \mu_p^2 \quad (8)$$

Introducing condition (3) and the variable x , one obtains

$$C = \frac{9\pi^2}{64} \frac{b(1 + b)^2 x^2}{(x^2 + b)^2} \mu_p^2 \quad (9)$$

Since μ_p cannot be conveniently determined experimentally, an "apparent" mobility,

$$\mu = \frac{p - n b^2}{p + n b} \mu_p = \frac{x^2 - b^2}{x^2 + b} \mu_p \quad (10)$$

is introduced; this "apparent" mobility is analogous to the "mixed" Hall coefficient given by equation (2)-

Substitution of (10) in (9) yields

$$C = \frac{9\pi^2}{64} \frac{b(1 + b)^2 x^2}{(x^2 - b^2)^2} \mu^2 \quad (11)$$

The mobility μ may be determined independently of the magnetoresistance by using the measurements of resistivity, ρ , and Hall coefficients; thus,

$$\mu \equiv \frac{8}{3\pi} \frac{A}{\rho}.$$

We have finally arrived at the following expression:

$$\frac{C}{C_i} = \frac{x^2(A/R)^2}{(x^2 - b^2)^2} \cdot \frac{(x_i^2 - b^2)^2}{x_i^2(A_i/R_i)^2} \quad (12)$$

for the dependence of the magnetoresistive coefficient on acceptor concentration. If the experimental parameters of equation (6) are substituted in (12), there results

$$\frac{C}{C_i} = \frac{3.21 x^2}{(x^2 - 1.96)^2} \frac{(A/A_i)^2}{(R/R_i)^2}, \quad (13)$$

which is to be compared with the experimental results of Fig. 4. The results of this comparison are disappointing; for, despite the fact that experimentally determined factors are introduced in equation (13), the expression gives values not at all in agreement with the data.

Perhaps this poor agreement may in part be attributed to the rapid change of the mobility with bombardment. To show this, we write equation (9) in the form

$$\frac{C}{C_i} = \frac{x^2}{x_i^2} \frac{(x_i^2 + b)^2}{(x^2 + b)^2} \frac{\mu_p^2}{\mu_{pi}^2}, \quad (14)$$

where the subscript i refers to the untreated graphite. The equivalent expression for the relative resistance is easily shown to be

$$\frac{R}{R_i} = \frac{x}{x_i} \frac{x_i^2 + b}{x^2 + b} \frac{\mu_{pi}}{\mu_p}. \quad (15)$$

From these two equations we obtain

$$\frac{\mu_p}{\mu_{pi}} = \frac{(C/C_i)^{1/4}}{(R/R_i)^{1/2}} = \frac{\mu_n}{\mu_{ni}}, \quad (16)$$

since we assume $b = \text{constant}$ for all acceptor concentrations.

Substitution of the observed values of C/C_i and R/R_i into (16) yields the curves given in Fig. 8. It will be noted that the mobilities of the carriers are very slightly affected by oxidation of the graphite, but neutron irradiation significantly reduces the mobilities of the carriers. This observation is in agreement with conclusions drawn earlier.⁽⁴⁾

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It is apparent from the foregoing that the two-band theory does not describe correctly the electrical properties of chemically treated graphite. Therefore, it cannot be used to interpret the properties of graphite which has been irradiated and subsequently treated chemically or oxidized and then irradiated. For this reason a very simple phenomenological treatment will be attempted.

The similarity of the dependence of the resistance of unirradiated and of irradiated graphite (see Fig. 6) is striking. The data may be fit rather accurately by the expression

$$\frac{R}{R_{\text{initial}}} = e^{-465m} \quad , \quad (17)$$

where m is the acceptor concentration; this expression fits the data of oxidized graphite for $0 \leq m \leq 3 \times 10^{-3}$ with a maximum deviation of less than one per cent. This indicates rather strongly that the effects of irradiation and oxidation are independent; that, so far as the change in conductivity is concerned, an irradiated sample of graphite behaves on oxidation just as an unirradiated sample of abnormally high resistance should behave.

Unfortunately, the data on the behavior of the Hall coefficient of irradiated graphite during oxidation indicate, just as strongly, that the effects are not independent, that oxidation actually destroys some of the effects of irradiation. The extent of this destruction can be estimated from the Hall coefficients. Without this destruction, the acceptor concentration should rise linearly with the addition of chemical acceptors as is indicated by the dotted line in Fig. 9. The observed acceptor concentration is given for samples of four different irradiations by the solid lines. The difference between this observed concentration and the expected concentration is a measure of the destruction of acceptors and is plotted in Fig. 10.

These considerations may be put into a more quantitative form by considering a phenomenological representation of the changes in conductivity upon irradiation and oxidation. The resistance of a substance may be taken to be proportional to P , the probability of scattering the current carriers, and inversely proportional to N , the concentration of the carriers; that is

$$R \propto \frac{P}{N} \quad . \quad (18)$$

In the following we will use the index i to represent untreated graphite, o to represent oxidized graphite, b to represent irradiated (bombarded) graphite, and bo to represent irradiated graphite that has been oxidized.

When graphite is oxidized, the scattering probability is very nearly unchanged;⁽⁴⁾ however, the carrier concentration changes to N_0 . Therefore, from equation (16),

$$\frac{R_0}{R_i} = \frac{N_i}{N_0} = e^{-465m} \quad . \quad (19)$$

When graphite is irradiated with neutrons, the scattering probability is changed to $P_i + P_b$, and the carrier concentration to N_b ; hence,

$$\frac{R_b}{R_i} = \frac{P_i + P_b}{P_i} \frac{N_i}{N_b} \quad . \quad (20)$$

It will be noted that the ratio $(P_i + P_b)/P_i$ may be determined by choosing $N_0 = N_b$ and dividing R_b/R_i by R_0/R_i ; that is, the lower curve of Fig. 3 is divided into the upper. When this is done a (nearly) straight line results, which may be represented by the equation,

$$\frac{P_i + P_b}{P_i} = 1 + 3100b \quad , \quad (21)$$

where b is the acceptor concentration introduced by the bombardment.

When irradiated graphite is oxidized, the scattering probability may be changed by the destruction of the acceptors. If oxidation removes a fraction, α' , of the scattering centers, we may write,

$$R_{b_0} = \frac{P_i + P_b - \alpha' P_b}{N_{b_0}} = \frac{P_i}{N_{b_0}} [1 + 3100b(1 - \alpha')] \quad , \quad (22)$$

where N_{b_0} is the resulting carrier concentration. Thus,

$$\frac{R_{b_0}}{R_i} = [1 + 3100b(1 - \alpha')] \frac{N_i}{N_{b_0}} \quad . \quad (23)$$

However, the ratio R_{b_0}/R_b is of more interest. It is given by

$$\frac{R_{b_0}}{R_b} = \left[1 - \frac{\alpha' P_b}{P_i + P_b} \right] \frac{N_b}{N_{b_0}} \quad . \quad (24)$$

According to equation (19), $N_0/N_i = e^{465m}$ and it is plausible to assume that N_{b_0}/N_b will be given by a similar relation with a term to allow for the destruction of acceptors. If a fraction, β' , of the acceptors is removed, we may write

$$\frac{N_{b_0}}{N_b} = e^{465(1 - \beta')m} \quad . \quad (25)$$

Substituting (21) and (25) into (24) yields

$$\frac{R_{b0}}{R_b} = \left[1 - \frac{3100\alpha'}{1 + 3100b} \right] e^{-465m} e^{465\beta'm} \quad (26)$$

The notation is simplified by writing, $\alpha' = \alpha m$, $\beta' = \beta b$. Then the fact that $\frac{R_{b0}}{R_b} = \frac{R_0}{R_i}$, as shown by Fig. 5, leads to an expression of α in terms of β of the form

$$\alpha = \frac{1 + 3100b}{3100bm} [1 - e^{-465b\beta m}] \quad (27)$$

The quantity α may be obtained from equation (27) by substituting values of β , obtained from Fig. 10. In this manner we obtain Table III for α' and β' .

The values of α' in Table III make it possible to plot the destruction of scattering centers as the chemical acceptors are introduced; this is given in Fig. 11, which, it will be noted, is quite similar to Fig. 10.

A possible mechanism of trap destruction by interaction of radiation damage centers and chemical impurities may be represented by the schematic reactions below:

where $\underline{V}$ represents a lattice vacancy, which may be or may not be an electron trap without affecting the argument, and $\underline{C}$ represents a displaced carbon atom, which is known to be an electron trap; $\underline{V}$ and $\underline{C}$ are predominantly formed as entities in a closely associated cluster, as indicated by the parentheses. The first reaction shows the removal of acceptors without a material change in the scattering properties. The second reaction, which may but does not necessarily occur during the conversion of the lamellar compound to the residue compound, represents the removal of scattering centers by recombination. One would intuitively expect that the first of these reactions is more probable and that the Hall coefficient would thus be more sensitive to the interaction than the conductivity.

The rates of interaction of chemical acceptors and bombardment centers, which are the slopes in Fig. 10 and 11, should be consistent with equations (28) and (29). They indicate that the rate of destruction of acceptors should be proportional to the concentration of damage centers. It is probably independent of impurity concentration, because lamellar impurities apparently enter graphite as complete two-dimensional layers.^(2,9) Equation (29) indicates that the rate of removal of scattering centers should be proportional to the product of $[CHSO_4^{\bar{\cdot}}]$ and $[VHSO_4^{\bar{\cdot}}]$; i.e., to the square of the concentration of remanent damage centers.

TABLE III

Interaction Parameters for Interstitial Compounds of Irradiated Graphite

Sample Exposure	Acceptor Conc. ($m \times 10^4$)	Fraction Acceptors Destroyed (β')	Fraction Scattering Centers Destroyed (α')	Sample Exposure	Acceptor Conc. ($m \times 10^4$)	Fraction Acceptors Destroyed (β')	Fraction Scattering Centers Destroyed (α')
10 2.8 Mwd	0	0.50	0	28 6.1 Mwd	0	1.06	0
	0.5	0.50	0.03		0.5	1.00	0.04
	1.0	0.50	0.05		1.0	0.92	0.06
	2.0	0.50	0.10		2.0	0.85	0.12
	3.0	0.50	0.15		3.0	0.81	0.17
	4.0	0.48	0.18		4.0	0.78	0.21
	5.0	0.46	0.22		5.0	0.75	0.25
	6.0	0.44	0.25		6.0	0.72	0.28
	7.0	0.42	0.27		7.0	0.70	0.31
	8.0	0.40	0.30		8.0	0.68	0.34
	9.0	0.38	0.32		9.0	0.66	0.37
	10.0	0.36	0.33		10.0	0.65	0.40
	11.0	0.35	0.35		11.0	0.63	0.43
	12.0	0.33	0.37		12.0	0.62	0.45
17 4.5 Mwd	0	0.83	0	37 12.8 Mwd	0	2.09	0
	0.5	0.79	0.03		0.5	2.01	0.06
	1.0	0.74	0.06		1.0	1.90	0.11
	2.0	0.68	0.11		2.0	1.59	0.17
	3.0	0.65	0.15		3.0	1.44	0.23
	4.0	0.61	0.19		4.0	1.35	0.28
	5.0	0.59	0.22		5.0	1.27	0.32
	6.0	0.56	0.25		6.0	1.21	0.36
	7.0	0.54	0.28		7.0	1.16	0.39
	8.0	0.52	0.31		8.0	1.11	0.43
	9.0	0.51	0.33		9.0	1.08	0.45
	10.0	0.49	0.35		10.0	1.05	0.48
	11.0	0.48	0.37		11.0	1.02	0.51
	12.0	0.46	0.39		12.0	0.99	0.53

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These postulated dependencies are tested in Fig. 12 and 13. It is seen that the data support the proposal as well as is warranted by the numerous approximations involved. The mechanism outlined actually requires that the data lie on one line each in Fig. 12 and 13. The deviation from this behavior may be due to the accumulation of debris between the graphite planes after heavier bombardments.

When it was attempted to extend these considerations to the magnetoresistance it was realized that an analysis could not be based on Fig. 7. The data of Fig. 7 have meaning only if the value of n in equation (1) is not changed by the various treatments accorded the graphite. The meager data available indicate that oxidation of graphite does not appreciably change the exponent. (The value of n was found to be 1.75 for a bisulfate residue compound with $m = 6 \times 10^{-4}$, and 1.73 for a bromide residue compound with $m = 11 \times 10^{-4}$.) On the other hand, neutron irradiation of graphite increases the value of the exponent. (A sample irradiated for 4.5 Mwd gave $n = 1.86$; a sample irradiated 19 Mwd gave $n = 1.92$.) Unfortunately, the magnetoresistance decreases so rapidly on irradiation that these measurements could not be extended to higher irradiations due to the limited magnetic fields available to us, nor could it be determined whether oxidation of irradiated graphite causes the exponent, n , to tend from higher values back towards the value 1.74.

Equations (28) and (29) represent a destruction of acceptors by the invading HSO_4^- during the formation of a lamellar compound, and a possible destruction of scattering centers by recombination during the formation of a residue compound. This mechanism implies that no destruction should occur if the residue compounds were first formed and then irradiated. As a result of this consideration the experiments leading to the results tabulated in Table I were carried out.

The reliability of the results obtained by these experiments is dependent upon two conditions. The bisulfate ions, which could conceivably be decomposed by ionizing radiation, should undergo negligible decomposition during the irradiations employed. In addition, the residue compounds should be thermally stable during at least this period. The first condition was tested by exposing samples of bromide residue compounds, since the bromide ion must be more stable to ionizing radiation than the bisulfate ion. No appreciable differences were found between bromide and bisulfate residue compounds indicating that the bisulfate ion is not substantially affected by the gamma flux. This is in agreement with earlier observations on alkali sulfates.⁽⁸⁾ The second condition was substantiated by the experiments summarized in Table II, which show that the compounds are stable for periods greatly exceeding the longest bombardment used.

Examination of Table I reveals that, contrary to expectations, there appears to be a mutual destruction of traps regardless of the order in which irradiation and chemical treatment of the graphite are carried out.

This is even more evident when the destruction of acceptors and scattering centers is calculated from this data (Table IV). It has already been pointed out that any destruction at all during bombardment is inconsistent with equations (28) and (29). Nevertheless, it will be shown that the extent of destruction of traps by chemical treatment of a bombarded sample is comparable to the destruction resulting from bombardment of a chemically treated sample. To demonstrate this equivalence for a given sample containing x residue acceptors and y damage centers introduced by bombardment, values were estimated (from Fig. 10 and 11) for the extent of destruction in a sample containing x damage centers and y residue chemical acceptors. The agreement between the two sets of data is reasonably good.

TABLE IV

Destruction of Acceptors and Scattering Centers in
Irradiated Residue Compounds of Graphite

Sample Acceptor Conc. ($\times 10^4$)	Irradiation Mwd	Acceptor Conc. ($\times 10^4$) Destroyed		Conc. ($\times 10^4$) Scattering Centers Destroyed	
		This Sample	Equivalent Sample*	This Sample	Equivalent Sample*
47 4.1	0.5	0.4	0.4	0.09	0.1
48 9.3	1.7	3.5	2.1	0.74	1.3
49 1.8	1.0	0.2	0.3	0.04	0.1
50 6.1	1.0	1.4	1.0	0.27	0.4
51 3.5	1.3	0.7	0.8	0.15	0.25
52 4.4	1.5	0.8	1.0	0.17	0.36
54 6.8	1.5	2.1	1.5	0.50	0.6
	2.6	3.3	2.3	1.05	1.0
55 4.7	1.2	1.1	0.9	0.23	0.3
57 8.7	1.2	2.0	1.5	0.40	0.8
69 4.7	7.8	3.6	4.2	1.68	1.4
70 4.9	7.1	3.7	4.0	1.64	1.35
71 6.7	7.1	4.8	5.2	2.08	2.0

*Order of bombardment and chemical treatment interchanged.

A physical interpretation of the destruction is very difficult. Since chemical treatment introduces approximately three ions for every one that remains in the residue compound, it would appear that chemical treatment of an irradiated compound should be approximately three times as effective as bombardment of a residue compound. Quite aside from this, it is difficult to understand how irradiation destroys chemical acceptors since the damage centers and the residue chemical impurities are thought to be relatively immobile, in contrast to the mobility of the lamellar chemical impurities during the formation of the compound.

CONCLUSIONS

The behavior of the electrical properties of graphite upon the introduction of chemical acceptors cannot be described adequately on the basis of the two-band theory. The Hall coefficient data may be reasonably well represented, but the results for the resistance and magnetoresistance are discouraging. It appears that some further assumption, such as a high degeneracy temperature, or even inhomogeneities in graphite, must be introduced.

The attempt to prepare residue-like compounds, i.e., unordered compounds, of graphite containing more than 1.5×10^{-3} acceptor per carbon atom by combined neutron irradiation and chemical treatment failed due to the mutual destruction of the traps. This is most clearly evident from the behavior of the Hall coefficient; the behaviors of the resistance and the magnetoresistance do not seem to require this hypothesis of mutual destruction, but, nevertheless, they are not incompatible with it. The kinetics of the destruction appear to confirm that the mobility of damage centers is increased by a reversible reaction with the chemical impurities. Contrary to expectation, the extent of destruction does not seem to depend on the order in which damage centers and chemical impurities are introduced.

Furthermore, it has also been found that in the reactor the residue chemical compounds of graphite are affected only by particle bombardment and not by the gamma flux.

There appears to be little likelihood that this process for destruction of damage centers can be used for large scale annealing of radiation damage. The effects observed are quite small and the rate of reaction is inhibited by radiation damage so that the more heavily bombarded graphites show relatively little annealing.⁽¹⁰⁾

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FIGURE 1.
THE MAGNETO-RESISTANCES OF GRAPHITE
CONTAINING ACCEPTORS.

FIGURE 2.
THE HALL COEFFICIENTS OF GRAPHITE
CONTAINING ACCEPTORS.

FIGURE 3.
THE ELECTRICAL RESISTANCES OF GRAPHITE
CONTAINING ACCEPTORS.

FIGURE 4.

THE EFFECT OF CHEMICAL TREATMENT ON THE ELECTRICAL RESISTANCE OF IRRADIATED GRAPHITE.

FIGURE 5.

THE EFFECT OF CHEMICAL TREATMENT ON THE RELATIVE ELECTRICAL RESISTANCE OF IRRADIATED GRAPHITE.

FIGURE 6.

THE EFFECT OF CHEMICAL TREATMENT ON THE RELATIVE
MAGNETO-RESISTANCE OF IRRADIATED GRAPHITE.

FIGURE 7.

THE EFFECT OF CHEMICAL TREATMENT ON THE
HALL COEFFICIENT OF IRRADIATED GRAPHITE.

FIGURE 8.
RELATIVE MOBILITIES IN GRAPHITE
CONTAINING ACCEPTORS.

FIGURE 9.

THE EFFECTIVE ACCEPTOR CONCENTRATION
IN GRAPHITE CONTAINING BOTH CHEMICAL
ACCEPTORS AND DAMAGE CENTERS.

FIGURE 10.

THE DESTRUCTION OF ACCEPTORS IN IRRADIATED GRAPHITE DURING INTRODUCTION OF CHEMICAL ACCEPTORS.

FIGURE II.

THE DESTRUCTION OF SCATTERING CENTERS
IN IRRADIATED GRAPHITE DURING
INTRODUCTION OF CHEMICAL ACCEPTORS.

FIGURE 12.

THE DEPENDENCE OF THE DESTRUCTION RATE OF ACCEPTORS ON THE DAMAGE CENTER CONCENTRATION.

FIGURE 13.

THE DEPENDENCE OF THE DESTRUCTION
RATE OF SCATTERING CENTERS ON THE
DAMAGE CENTER CONCENTRATION.