RADIATION DAMAGE EFFECTS ON GRAPHITE*

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The effects of fast neutron irradiation at about room temperatures, on the electronic and thermal properties of graphite are presented. While these effects are of extreme engineering importance, because of the use of graphite as a reactor moderator, they are also of intrinsic scientific interest since the changes due to radiation are strikingly large. It is possible to separate the electronic effects qualitatively, by use of a two-dimensional band structure, into changes in the electron concentration and changes in the number of scattering centers. In this way, the various properties can be inter-correlated in a very satisfactory manner. Further correlations can be made by thermal annealing of the damaged graphite specimens.

I. INTRODUCTION

Graphite is an important component of many types of reactors both as a moderator and as a structural material. Since it is also responsible, to a large extent, for the temperature profile of the reactor, there is a great deal of technological interest in the effects of radiation on such properties as the thermal conductivity, the specific heat and the structural stability. On the other hand, there is much interest, of a more fundamental type, in the radiation effects on the thermal, electrical and magnetic properties. This is partly due to the fact that the changes in most of these properties, caused by energetic particle bombardment, are strikingly large and the recovery of these changes by annealing is often quite sudden.

The structure of graphite is hexagonal with an alternating (ab type) planar stacking. The planes are rather loosely held together by a van der Waal type potential while the in-plane bonding is generally accepted as due to the ($2s$, $2p_x$, $2p_y$) trigonal hybrids. The conduction electron band in this approximation would then be constructed from the p_z functions. The first calculations of the energy contours, by the tight binding method using the p_z functions only, was done by P. R. Wallace.[1] Including only nearest neighbor interactions, and neglecting overlap effects, he found two bands which just touched at twelve points on the Brillouin zone faces and whose energy contours were symmetrical about the edges of the Brillouin zone. This yielded a symmetrical density of states about the band edge energy. These calculations have been extended by C. A. Coulson,[2] Carter and Krumhansl,[3] D. F. Johnston[4] and ourselves,[5] in every case by inclusion of different interactions which were neglected by Wallace. Although there is still much doubt about the quantitative band structure model of graphite, it is probably true that the qualitative behavior of the electronic properties can be understood on the basis of the Wallace

* Based on studies conducted for the Atomic Energy Commission.

[1] P. R. Wallace, Phys. Rev. **71**, 622 (1947).

[2] C. A. Coulson and R. Taylor, Proc. Phys. Soc. A, **65**, 815 (1952).

[3] J. Carter and J. Krumhansl, J. Chem. Phys. **21**, 2238 (1953).

[4] D. F. Johnston, Proc. Roy. Soc. A **227**, 349 (1955).

[5] J. E. Hove, Phys. Rev. **97**, 1717 (1955).

model. Thus because of the large Gaussian curvature of the energy surfaces near the zone corner, which represents the Fermi level as well, such properties as the magnetic susceptibility and the magneto-resistance are very large, but quickly become normal (i.e. small) as the Fermi surface is depressed away from the corner. Since the density of states is quite small near the corners, the trapping of electrons by radiation induced defects can appreciably lower the Fermi surface and it is easy to visualize why irradiation will affect the electronic properties so strongly.

II. ELECTRONIC PROPERTIES

In general, the effect of particle bombardment, if above a certain critical energy, is to displace an atom from its lattice position. This primary displaced atom will usually have sufficient kinetic energy to displace a further number of secondary atoms, some of which can produce tertiaries. In the case of graphite, most of these displaced atoms will be in interstitial positions between planes and, if bombardment is at room temperature, these interstitials will be quite mobile, since their activation energy is probably of the order of one ev. As damage continues, then, the interstitials will tend to trap other interstitials, either by thermal motion or by the residual momentum imparted by the impinging particle or its secondaries. Thus there will be a gradual buildup of interstitial carbon complexes which will be much less mobile than the single displaced atoms. The vacancies are certainly much less mobile than single interstitials and probably remain as single vacancies.

Both interstitials and vacancies will act as electron traps, which as mentioned previously, can have a strong effect on the electronic properties of graphite. One may employ the simple band picture and formal conduction theory to separate the electronic effects into a dependence on the number of conduction electrons and their mean free path, or relaxation time. In most cases a simplified two-dimensional approximation for the band structure has been used, since this permits analytical calculations to be made. The relaxation time has been taken as energy independent, an assumption which should be reasonably good for boundary scattering at least.

The samples of graphite described herein have been exposed at about 30°C to the neutron flux in a reactor. While the neutron energy ranges from thermal to several Mev, the integrated fluxes appearing in the figures are those in the energy range above 0.5 Mev, which probably represent about one-third of the total flux. The first properties to be considered are the Hall coefficient, the magnetic susceptibility and the thermoelectric power. Assuming an energy independent relaxation time, all of these properties depend only on the number of conduction electrons in the graphite and thus serve to test the internal consistency of the calculations.

In Fig. 1, we plot the Hall coefficient (at room temperature) against the neutron

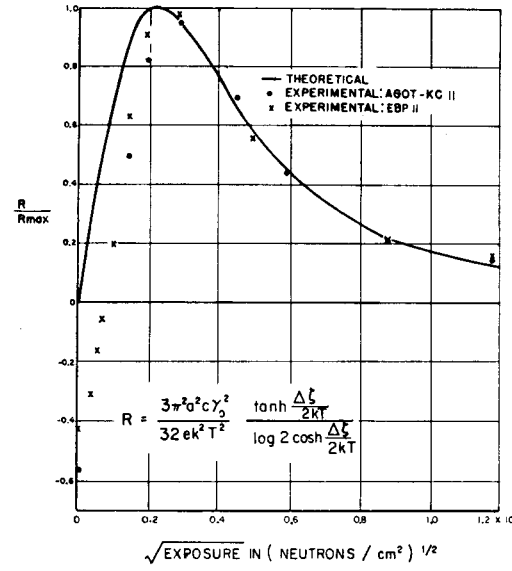


FIG. 1. The Hall coefficient *vs* neutron exposure at room temperature.

exposure for two large crystallite graphites, AGOT-KC and AWG. The curve through the points is that of the theoretical expression given on the figure, which is derived from the two-dimensional band approximation. It may be noted that the data are characteristic of a *p*-type semiconductor, passing through a positive maximum value and decreasing towards a more metallic-type behavior. The values are normalized to the maximum value and therefore the theoretical expression contains only one parameter, $\Delta\zeta$, the lowering of the Fermi level. The relation between $\Delta\zeta$ and the neutron exposure used in determining this fit was

$$|\Delta\zeta| = 1.4 \times 10^{-11}(nvt)^{\frac{1}{2}} \text{ ev}$$

Figure 2 gives the data for the magnetic susceptibility, normalized to the unirradiated value. The theoretical variation, given again by the expression obtained using the two-dimensional approximation, is shown for the above variation of the Fermi level with damage. Thus this theoretical curve is completely forced and it can be seen that, under this circumstance, the agreement is quite satisfactory. Furthermore, the theoretical expression was obtained from the three-dimensional band structure, and then evaluated in the two-dimensional limit by a delta-function approximation about the band edge. This method of approximation can be shown to be valid only for small damage and the correction for higher damage is in such a direction as to compensate for the discrepancy shown in Figure 2. The observed values in this figure have been corrected for the core diamagnetism; the undamaged value is about 22×10^{-6} in cgs units per gram and the core correction, in these same units, is about 1.5×10^{-6}.

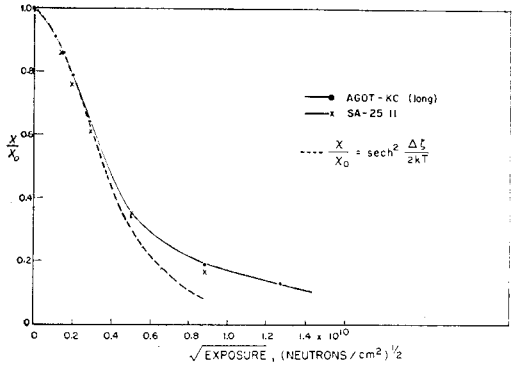


FIG. 2. The magnetic susceptibility *vs* neutron exposure at room temperature.

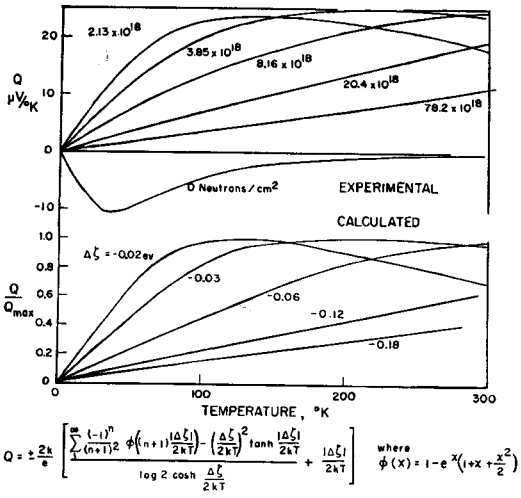


FIG. 3. The thermoelectric power *vs* temperature for differing neutron exposures.

In Figure 3, the thermoelectric power of AGOT-KC graphite is shown as a function of absolute temperature for various irradiations. The lower set of curves is computed by the formula shown, which, again, is derived in the usual way, using the two-dimensional band approximation. For the fit shown, $\Delta\zeta$ was taken to vary somewhat more strongly (about 30 per cent) with damage than was the case for the Hall coefficient. Considering the assumptions used, this is quite immaterial and the agreement shown in Figure 3 can be considered to be highly compatible with the previous measurements. The data and theoretical correlations shown on these three figures are strong evidence that a relaxation time exists and, at least for the large crystallite graphites used, that this relaxation time

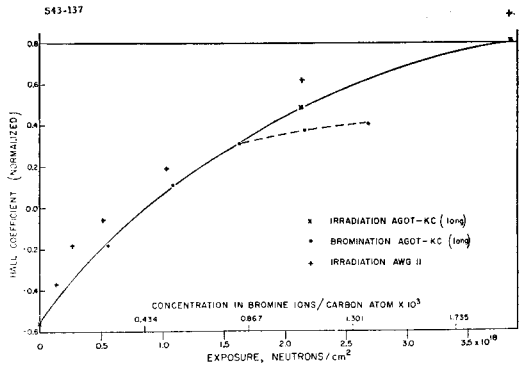


FIG. 4. The Hall coefficient *vs* neutron exposure and bromination.

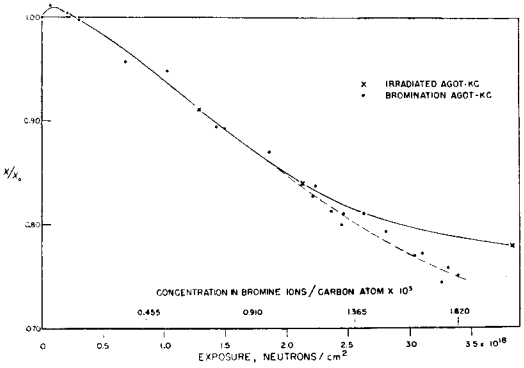


FIG. 5. The magnetic susceptibility *vs* neutron exposure and bromination.

can be considered essentially energy independent.

One may make an interesting comparison between radiation damaged graphite and the so-called residue compounds. These compounds have been extensively studied by Dr. Gerhart Hennig[6] and his co-workers at the Argonne National Laboratories. The effect of forming these compounds is to trap out electrons in a similar manner to that which we have been discussing for radiation damage, except that the degree of ionization, that is, the number of trapped electrons, can be determined accurately by electrolytic means. Figures 4 and 5 show the Hall coefficient and the magnetic susceptibility of residual brom-graphite superimposed on the radiation damage curves. It can be seen that the correlation is good. From this, it appears that the electron trapping rate caused by neutron damage is constant, at least for low damage, and has a value of about

$$5 \times 10^{-22} \text{ electrons per carbon atom per } (nvt).$$

In order to compare this with the value obtained previously, one must find the relation between the change in the Fermi level and the number of trapped electrons. If a two-dimensional band approximation is used to do this, the resulting trapping rate is too small by a factor of about ten. If, however, a three-dimensional energy band calculation is made, the trapping rate so obtained is in excellent agreement with the above value, at least for the small damage values which are given in Figures 4 and 5. As a by-product of this, one may conclude that the rapid decrease in the susceptibility may be attributed almost entirely to the change in the Peierls-type diamagnetism, rather than to the development of, say, paramagnetic damage centers.

The remaining two properties, electrical resistivity and transverse magneto-resistance, depend not only on the number of conduction electrons, but on their scattering probability as well. We may again consider the bromgraphite residue compounds

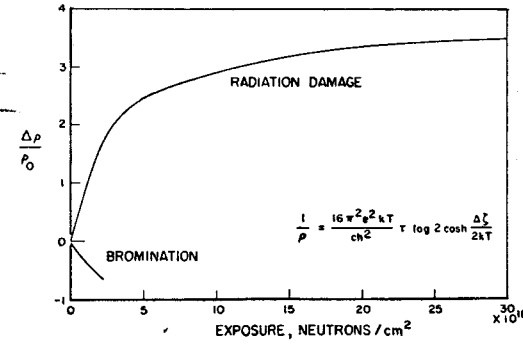


FIG. 6. Electrical resistivity change with neutron exposure and bromination.

[6] G. Hennig, J. Chem. Phys. **20**, 1438, 1443 (1952).

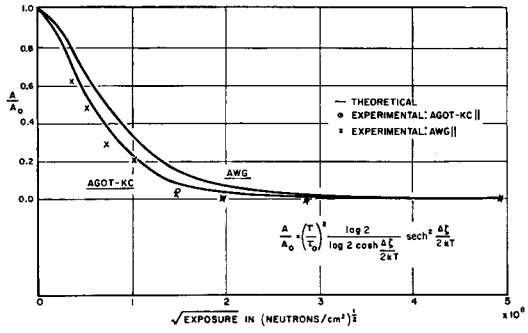


FIG. 7. The magneto-resistivity *vs* neutron damage.

to observe the effect of this dependence of the electrical resistivity on two parameters. Presumably, the bromine complexes residue at crystallite boundaries and hence will have a very small effect on the electronic scattering probability since the boundaries are already good scatterers. Consequently, the bromine compounds should show only the decreased resistivity arising from the increase in effective carriers as the zone is depleted. This is shown in Figure 6. In contradistinction to this, the upper curve of Figure 6 shows the pronounced increase in resistance due to the increased electron scattering off the radiation-induced defects. Using the previously determined variation of the Fermi level, the variation of the scattering probability with damage may now be obtained, using the theoretical expression for the resistivity shown on Figure 6. From these calculations, the theoretical variation of the magneto-resistance is shown on Figure 7 and, even though the agreement is not as good as one might like, it is certainly very satisfactory, considering the great sensitivity of this property on both the scattering probability and the

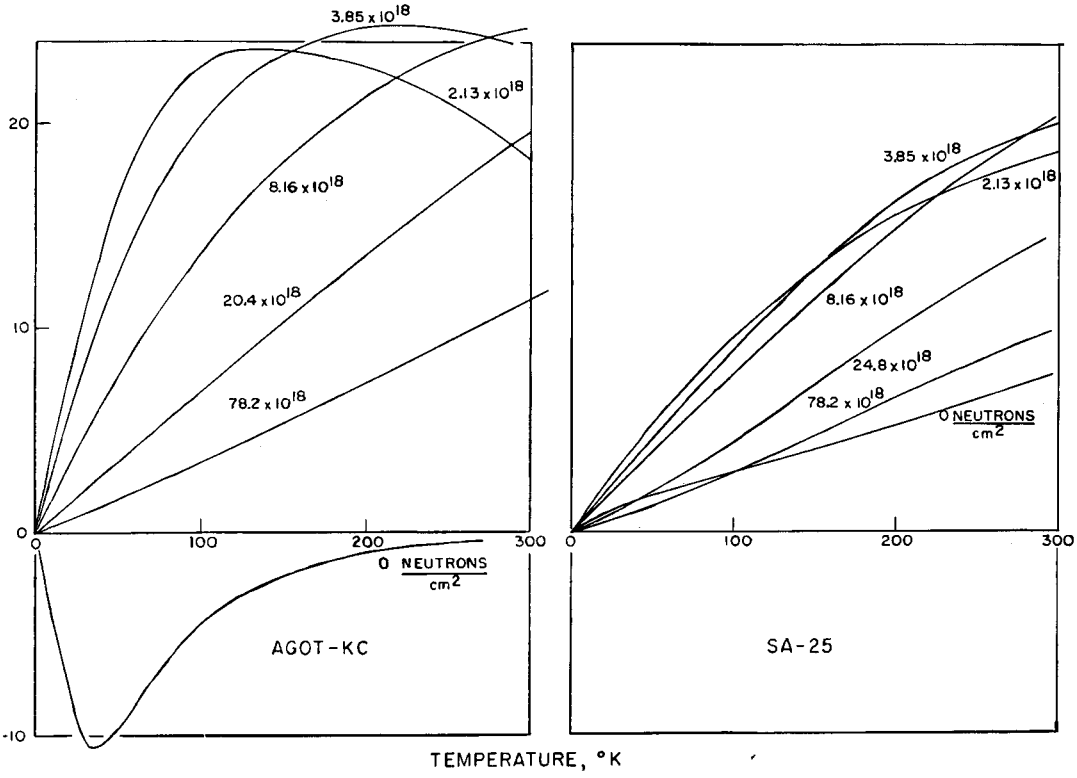


FIG. 8. The thermoelectric power *vs* temperature for two types of graphite with widely different crystallite size. The SA-25 crystallites are 10 times smaller than the AGOT.

number of effective carriers, which would magnify greatly any minor errors. It may be noted that, unlike the electrical resistivity, the magneto-resistance is decreased by both the change in scattering and in the number of carriers. It is this characteristic which makes this property practically vanish at about a hundredth of the neutron exposure for which either the susceptibility or the Hall coefficient become small.

Before considering the behavior of these properties with annealing a few words about the relaxation time should be said. We have assumed that this quantity (which is roughly proportional to the inverse of the scattering probability) does not depend on the energy of the electron being scattered. This is probably valid for scattering from boundaries. For short range spherical scattering centers, it can be shown that the dominant term in the relaxation time should be inversely proportional to the density of states near the energy of the electron. It is improbable that thermal scattering is a major factor in graphite of the type considered here. Because such properties as the Hall coefficient and the thermoelectric power arise from ratios, they are not primarily sensitive to the total number of scatterers, but they will depend on the energy dependence of the relaxation time. In the general case, where damage may be changing the type of scattering center, these properties will be sensitive to the relative density of the various types of centers. This behavior may account for the data shown on Figure 8. Here we have two graphites of much different crystallite size, the AGOT (crystallites of the order of 5000 Å) and the SA-25 (crystallites of the order of 500 Å). We may speculate that in the large crystallite graphite, defect scatter-

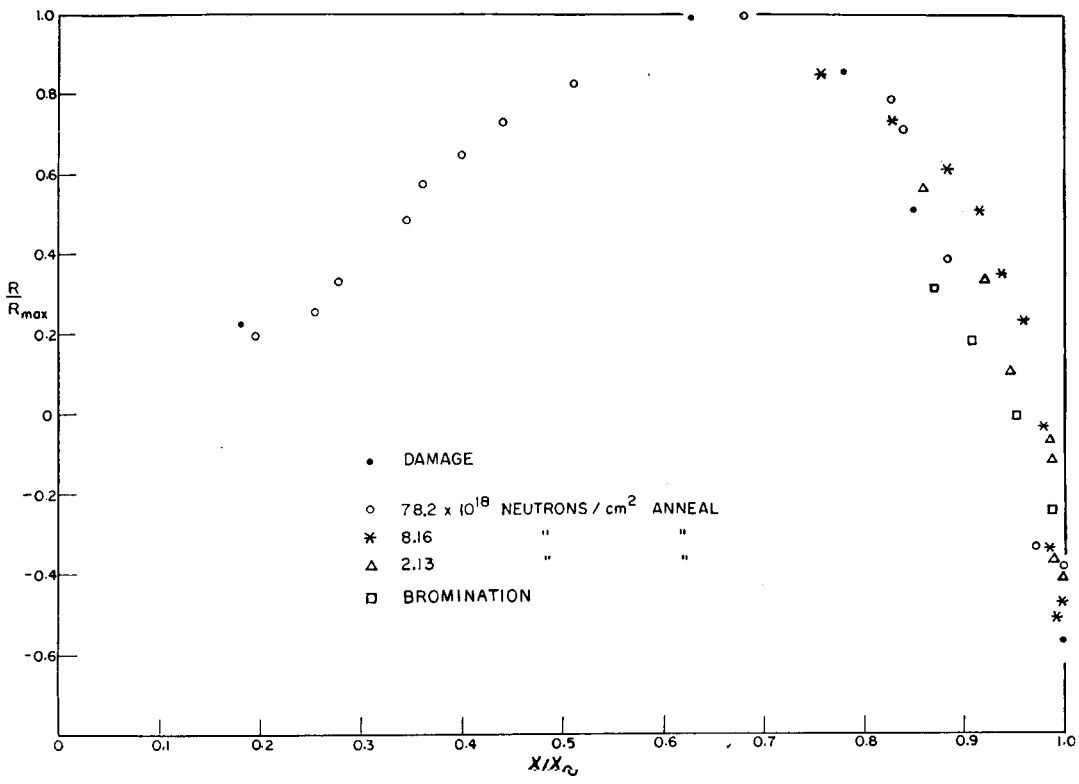


FIG. 9. Correlation of changes of Hall coefficient with susceptibility

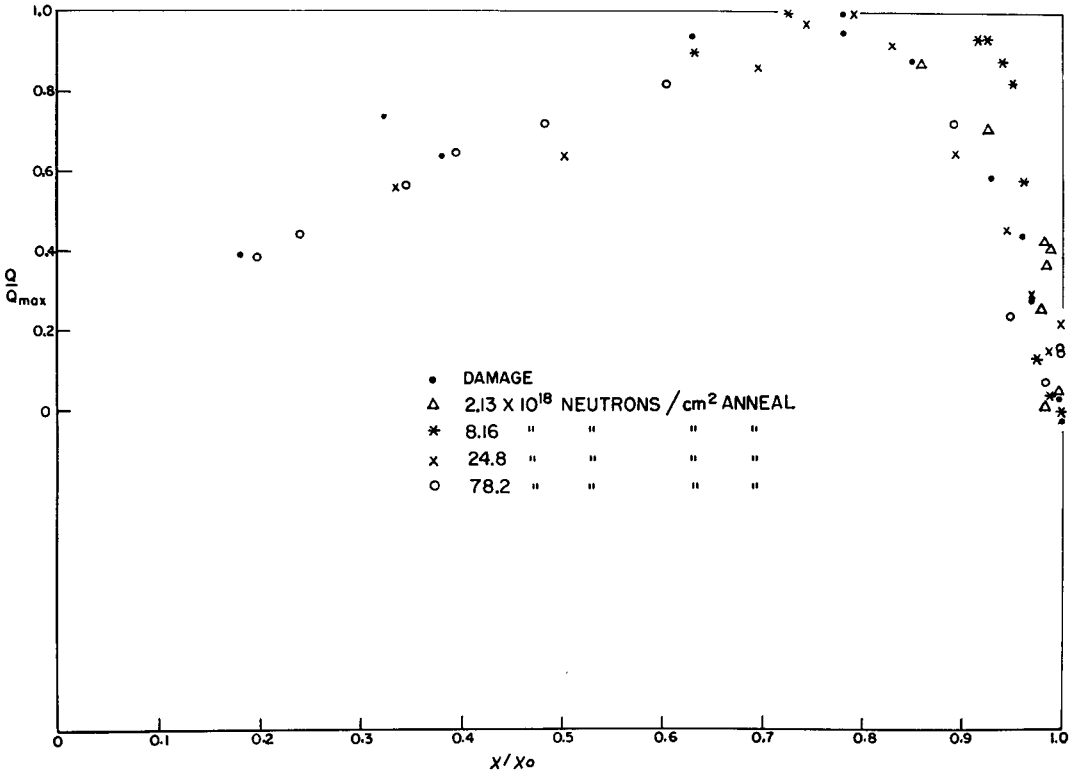


FIG. 10. Correlation of changes of thermoelectric power with susceptibility

ing is already of an appreciable magnitude even in the unirradiated sample. Increasing damage will only increase the number of the same general type of scattering center. In the small crystallite graphite, however, the boundary scattering will remain predominant until fairly high damage. From Figure 8, it may be observed that only after heavy irradiation does the behavior of the two graphite types become identical. The difference in signs of the unirradiated values cannot, of course, be explained in terms of the simple type of scattering which we are discussing. This may be due to surface trapping for the SA-25.

Since the three-dimensional density of states is slowly varying although small, near the zone edge, it is probably true that the relaxation time for small defect scattering is not greatly dependent on energy. This would account for our previous success in neglecting it in the Hall coefficient and thermoelectric power.

The subject of the electron scattering probabilities in graphite is not well understood at present and few detailed calculations have been made. It should be pointed out, however, that the difficulty noted above in the thermoelectric power may be due to an entirely different mechanism, namely the interaction between lattice waves and electrons in a temperature gradient. This has been recently discussed by Frederikse[7] and Herring,[8] and since it depends on the phonon scattering path, it would be quite natural to expect SA-25 to show a much different effect than the AGOT-KC.

It can be demonstrated that, for the large crystallite graphites, the Hall coefficient, the susceptibility and the thermoelectric

[7] H. P. R. Frederikse, Phys. Rev. **92,** 248 (1953).
[8] C. Herring, Phys. Rev. **96,** 1163 (1954).

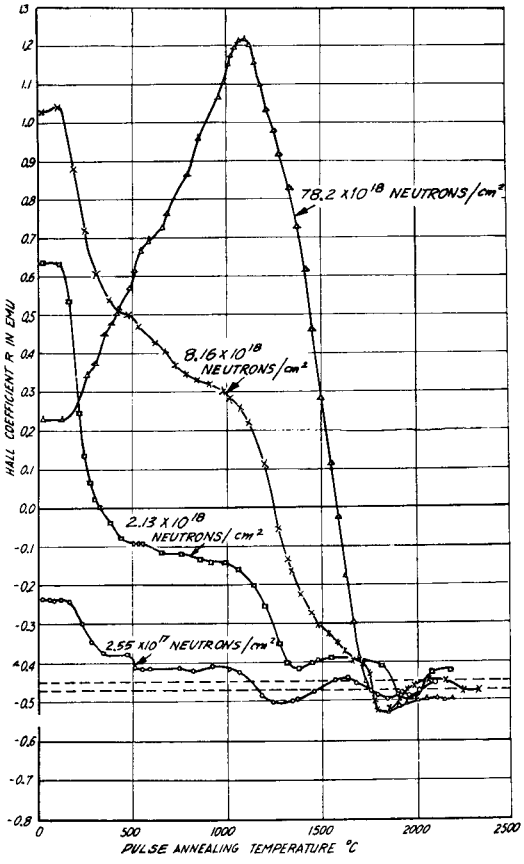


FIG. 11. Pulse-annealing spectrum of the Hall coefficient.

power are one-parameter properties. This is done by cross-plotting them against each other as they are varied by independent mechanisms, such as radiation damage, its thermal annealling, and bromination. Such cross-plots are shown on Figures 9 and 10, and are sufficiently consistent to demonstrate a single parameter dependence.

We shall show only the thermal annealing curves for irradiated graphite which were obtained from the so-called pulse-annealing spectra. These measurements are all made at some base temperature, 25°C in the present case, with the sample raised to an elevated temperature for some precise time (one minute for the present data) between measurements. This is repeated for consistently higher temperatures until annealing is complete. The resulting curve of property against pulse temperature gives a spectrum of the active and inactive annealing regions.

Figures 11, 12 and 13 show pulse-annealing curves for the Hall coefficient, thermoelectric power and magnetic susceptibility.

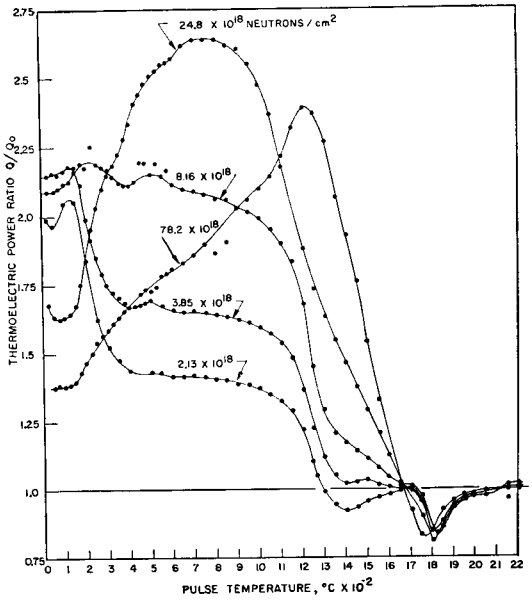


FIG. 12. Pulse-annealing spectrum of the thermoelectric power.

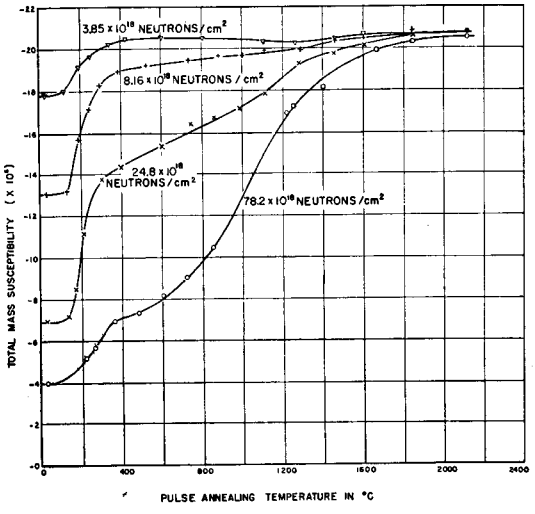


FIG. 13. Pulse-annealing spectrum of the susceptibility.

It is apparent from these curves that the annealing process is neither direct nor possesses simple kinetics. In fact all attempts to analyze these on a basis of first or second order kinetics have been unsuccessful, without employing a spectrum of activation energies. It is evident from these curves that the three properties are changing in a similar manner, however. The degree to which the curves are consistent with the theory presented earlier, can be shown rather well as follows: Figure 14 gives a pulse-annealing spectrum of the electrical resistivity. By using the theoretical expressions, it is possible to find the variation of the relaxation time and the Fermi level and thus to predict how the magneto-resistance will anneal. The results of this calculation are shown on Figure 15. It can be seen that the agreement is most gratifying.

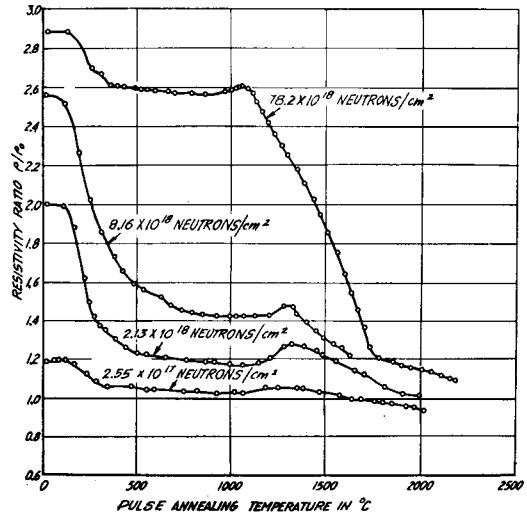


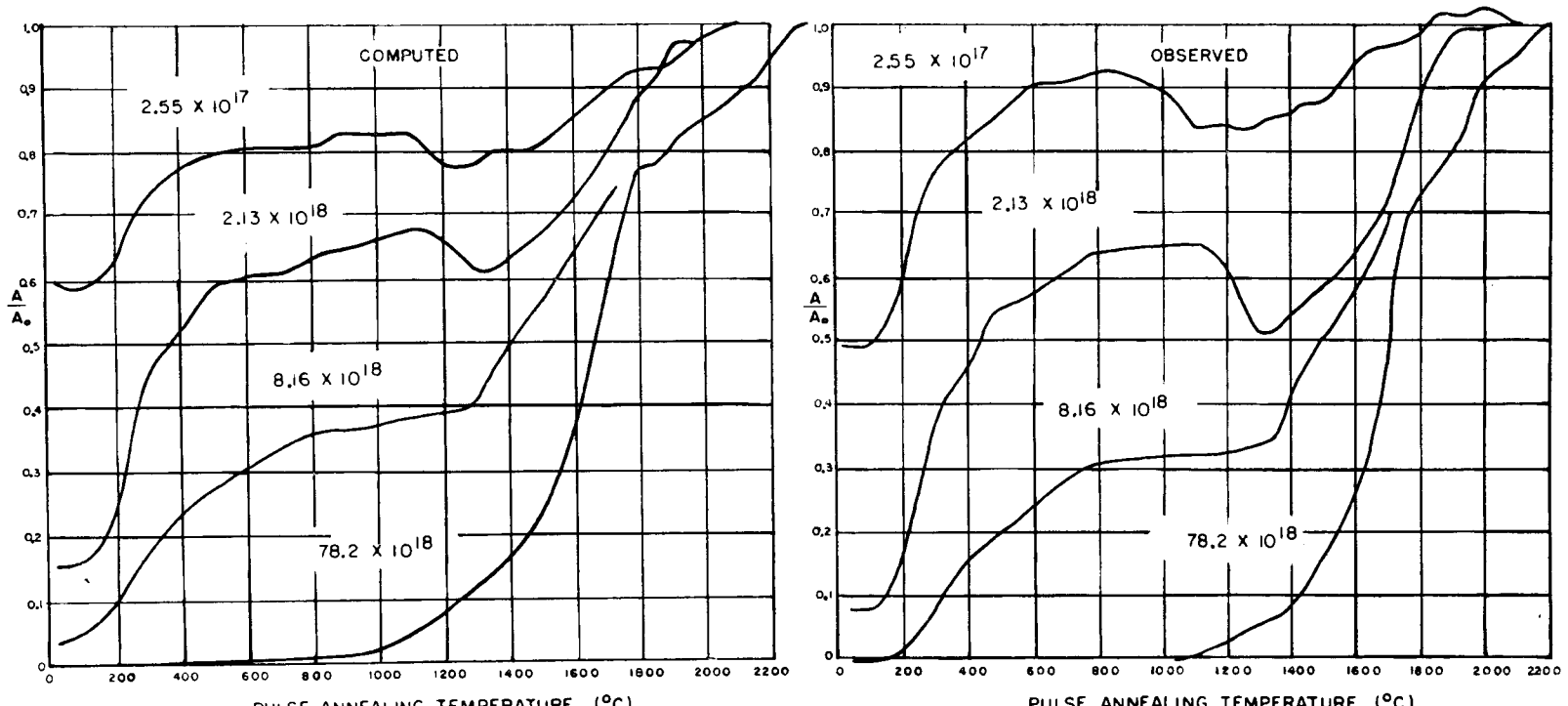
FIG. 14. Pulse-annealing spectrum of the electrical resistivity.

III. THERMAL CONDUCTIVITY

The effect of neutron irradiation on the low temperature (from 10°K to 300°K) thermal conductivity of graphite is twofold. It decreases the magnitude greatly and also decreases the strength of the temperature dependence. Figure 16 shows the temperature variation of AGOT-KC graphite for two neutron exposures together with the unirradiated value. Note that for the higher exposure, which is still quite low compared to most of those which we have been considering previously, the conductivity drops by a factor of about ten. The slope of the unirradiated sample is about 2.7 (this represents the exponent of the temperature since this is a log-log plot) while it drops to about 1.8 for the more heavily irradiated sample. Figure 17 shows a similar behavior for type AWG graphite which has a somewhat smaller crystallite size. If one plots the damaged induced increment only of the thermal resistivity against temperature, one obtains the curves shown on Figure 18. At the lowest temperatures, these curves, for the lowest damage, approach a slope of -2, indicating that the increased thermal resistivity caused by light damage behaves as T^{-2} (where T is the absolute temperature) at low temperatures, becoming less temperature dependent at higher temperatures. For the higher damages, it may be noted that the slope is smaller at the lowest temperatures.

One can qualitatively explain this behavior on the basis of the two-medium theory given previously by A. W. Smith and the writer.[9] Thus, on this model, the total thermal resistance is considered to be formed by that of the graphitic particles (behaving like T^{-2} at the lowest temperatures) and that of the non-graphitic binder (behaving like T^{-3} at low temperatures). For unirradiated graphite, then, the resistance of the non-graphitic region will be the larger at low temperatures, giving a net thermal conductivity varying between T^2 and T^3. Upon damage, however, the resistance of the graphitic material will be proportionately increased over that of the non-graphitic material and the temperature

[9] A. W. Smith, Phys. Rev. **98**, 1563 (1955). J. E. Hove, Phys. Rev. **98**, 1563 (1955).



Magneto-Resistivity Coefficient vs Annealing Temperature.

FIG. 15. Pulse-annealing spectrum of the magneto-resistivity. The computed curve is deduced entirely from the annealing spectra of the electrical resistivity and the susceptibility.

exponent will decrease to the value of two. It may be smaller than two if enough isolated scattering centers are created. This can be understood by considering what happens to the damage defects produced, assuming that these defects are mobile. At first, they will probably migrate to small angle boundaries. Many of these boundaries which would not have had much reflecting power for a lattice wave, now become good scattering boundaries. We may speculate, then, that such readily available sites would soon fill up. The remaining defects would then build up as lattice scattering centers and would soon overshadow the increase in boundary scattering. Scattering from defects of this nature, although increasing the magnitude of the resistance in the graphitic regions, would cause its temperature dependence to become weaker than T^{-2}.

It is not as yet possible to deduce the details of the damage centers from the thermal conductivity changes with irradiation. It has been shown by Krumhansl and Eatherly[10] that the lattice waves effective in thermal conduction are probably polarized in the basal plane and are not the waves which are largely responsible for the low temperature specific heat. This might indicate that vacancies are more effective scatterers than interstitials, although this must depend on the relative regions of lattice strain, since a defect must be of an effective diameter of at least 10 lattice spacings to scatter strongly at these temperatures.

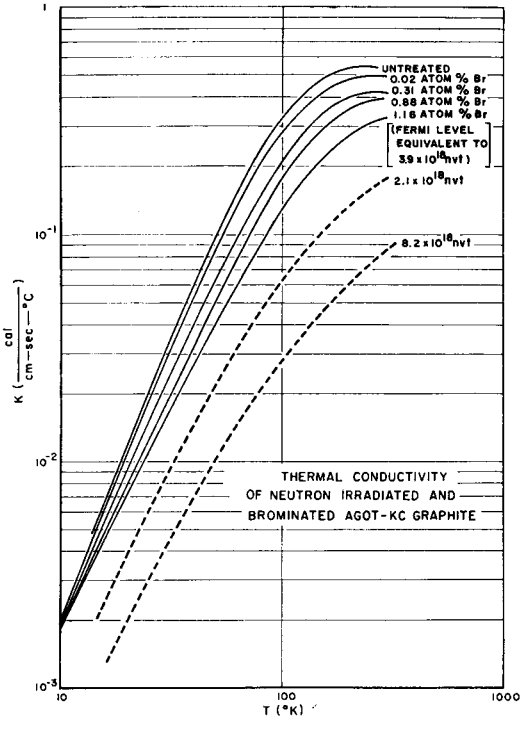


FIG. 16. Thermal conductivity of neutron-irradiated and brominated AGOT-KC graphite.

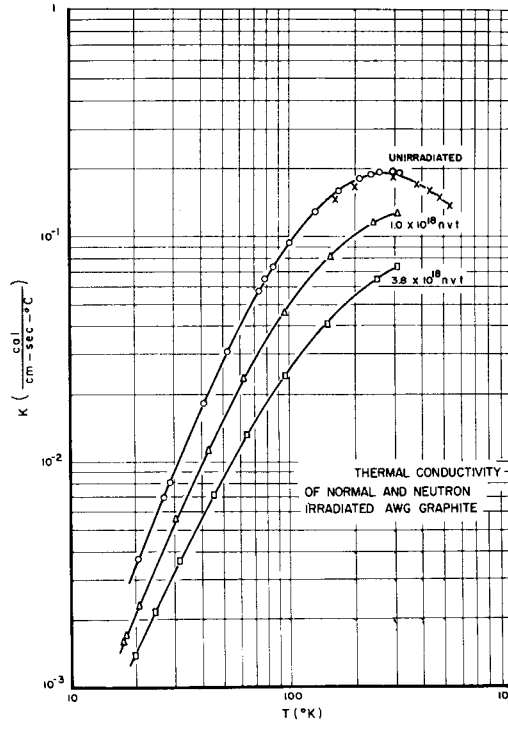


FIG. 17. Thermal conductivity of neutron-irradiated AWG graphite.

IV. CONCLUDING REMARKS

In conclusion, although the damage produced in graphite is probably too complex to permit a detailed description based on

[10] Unpublished work

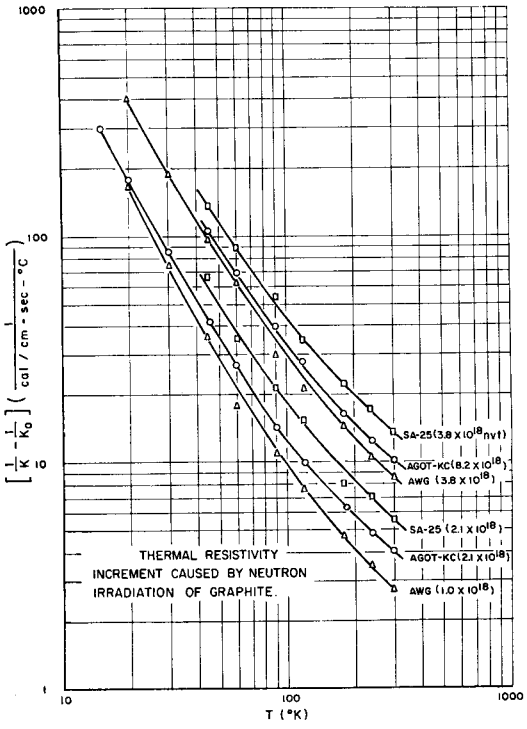


FIG. 18. Thermal resistivity change caused by neutron irradiation.

the present data, it has been found possible to use these radiation damage studies as a tool for the study of the properties of graphite itself. Thus the damage effects of the electronic properties can be separated into a scattering part and an electron trapping part. The self-consistency of many different properties among each other indicates that our general theoretical description of graphite is valid, even though there are discrepancies in some details. Similarly, the damage effects on the thermal conductivity follow the pattern to be expected from the theory, and thus help to confirm the general aspects of the theory, even though many details still remain to be worked out.

The data and interpretations given in this paper represent contributions from a large number of persons in the Radiation Effects Group at North American Aviation. The author would especially like to acknowledge that a large part of the interpretation is due to W. P. Eatherly, who discussed much of this work during a talk at the American Physical Society Meeting held at Baltimore on March 17–19, 1955. In addition, credit is due, for much cooperation and discussion, to staff members of Argonne and Brookhaven National Laboratories and of the National Carbon Research Laboratories. Finally the author would like to express his appreciation to S. Mrozowski for the opportunity to participate in the second Carbon Conference and to the University of Buffalo for its great hospitality during the meetings.