where the summation is restricted to those pairs of states l, n for which $|E_l-E_n|\sim g\beta H_0$. M_1 is the magnetic-moment operator of the spin system in the direction of the oscillating field and C is a constant.

Now the matrix elements will be nonvanishing only for $|E_l-E_n|$ near the Zeeman energy and perhaps for satellite, partially forbidden lines. If the line is sufficiently narrow, there is no ambiguity about which pairs of states must be included in the summation, even if the values of the matrix elements are determined (from the measurement of χ'') by varying the magnetic field rather than the frequency. Then, if the moment matrix elements are independent of H_0, the summation may be expressed as an integral over H instead of one over frequency. Hence, for a narrow resonance, and if the moment matrix elements are independent of H_0, the introduction of suitable constants gives Eq. (3) of Sec. II. Now, the interactions already discussed, which relax the selection rule $\Delta m = \pm 1$, will also result in a field dependence of the value of the moment matrix elements. The correction to Eq. (3), however, is only of the order of the fourth power of the line width to the resonant field and may be neglected if the effect of the relaxation of the selection rule is itself unimportant.

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Fast-Neutron Damaging in Nuclear Reactors: Its Kinetics and the Carbon Atom Displacement Rate*†

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It is shown that the radiation damage produced in graphite at near room temperature is labile. A theory describing this lability is developed. Then using this theory and an identification and determination of the portion of the neutron flux spectrum responsible for the damage as obtained in another paper, the displacement rates for the condition that no annealing had intervened are calculated from the number of displacements which had been determined in graphite samples which had been irradiated near room temperature. From several different methods there is obtained, within a factor of 2, the following result: 10^{-21} displacements atom per damaging neutron/cm^2 for the number of displacements which remain after a scattering event involving a fast neutron near the beginning of the irradiation under conditions in which thermal annealing is not occurring.

I. INTRODUCTION

AFTER the discovery of large property changes in graphite subjected to fast-neutron bombardment,[1-3] attempts to determine the relationship between the neutron flux and the rate of displacement of carbon atoms (assumed to be the initiating cause of the property changes) were made by both theoretical calculations and experimental determinations. Among the former were the unpublished estimates of a rudimentary nature made by Wigner and others[4] and of a more detailed character made by Seitz and James. The theoretical problems are difficult because it is necessary to calculate the amount of energy dissipated in one of a number of possible ways in an energy range in which the dissipation is not amenable to exact theoretical calculation. Thus even the recent estimates by Seitz[5] and Snyder and Neufeld[6] differ by orders of magnitude, and the recent estimate by Harrison and Seitz[7] alter Seitz's estimate by a factor of 3. It is therefore desirable to establish an experimental value. Two such attempts (unpublished) were made in the early work, one by I. Estermann from stored energy data, and one by W. H. Zachariasen. Aside from the difficulties of relating the property changes which are observed to the number of displacements, these attempts to estimate the displacement rate suffered from lack of knowledge of the flux of neutrons which traversed the samples and from lack of knowledge of the fraction of originally displaced atoms no longer present in the samples. A similar criticism can be directed against more recent determinations by G. R. Hennig and J. D. McClelland (unpublished) and by Antal, Weiss, and Dienes.[8] In addition it may be mentioned that there has been a variability in property changes which were observed under various

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.
† This paper together with several others (references 35, 9, 10, and 20) form a set on the subject of fast-neutron damaging in nuclear reactors.
[1] M. Burton, J. Phys. & Colloid Chem. **51**, 618 (1947).
[2] M. Burton and T. J. Neubert, J. Appl. Phys. **27**, 557 (1956).
[3] T. J. Neubert *et al.*, Argonne National Laboratory Report, ANL-5472, 1956 (available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.).
[4] F. Seitz, Physics Today **5**, No. 6, 6 (1952).
[5] F. Seitz, Discussions Faraday Soc. **5**, 271 (1949).
[6] W. S. Snyder and J. Neufeld, Phys. Rev. **97**, 1636 (1955).
[7] W. A. Harrison and F. Seitz, Phys. Rev. **98**, 1530(A) (1955).
[8] Antal, Weiss, and Dienes, Phys. Rev. **99**, 1081 (1955).

conditions of irradiation. While these constitute an uncertainty of a smaller magnitude than the above difficulties, its resolution would yield a greater confidence in the results. The establishment of the experimental displacement rate thus involves several steps: (a) the identification and measurement of the portion of the neutron flux spectrum which is the agent responsible for the damage, (b) the establishment of the quantity of property change (from the various ones that have been observed) which is to be associated with the neutron flux, (c) the establishment of the fraction of the originally displaced atoms still present in the sample, and (d) the establishment of the property changes to be associated with a displacement. The solution to the problem (a) is taken from two papers by Primak.[9,10] The problems (b) and (c) prove to have the same solution and constitute a class of problems which have been indiscriminately termed "annealing" in the literature of the subject[11] and are here discussed as the kinetics of radiation damaging. They are treated here in terms of a thermal classification of the radiation damage by means of an activation-energy spectrum, a method which was first employed by Neubert.[3] A complete treatment of the problem (d) involves a treatment of the particular properties in terms of the structure of the solid and is beyond the scope of this paper. Instead the results will be presented in terms of a self-consistent set of irradiation data extrapolated to the condition that no annealing had occurred, and the reliability of the estimates will be evaluated.

II. DAMAGING FLUX

The radiation-damage effects were studied by Primak[9,10] under such a variety of conditions that it became possible to compare the damage with that produced in a calibrated neutron flux. It was shown that the fast-neutron radiation damage produced in a nuclear reactor was to be related to the uppermost two decades of energy below the energy at which the pile neutron spectrum began to fall greatly from a k/E distribution (k is a constant and E is the neutron energy). The neutron flux which, distributed over two decades of energy as k/E, produces an amount of radiation damage equivalent to that which is observed was defined as the damaging flux; and it approximates the actual flux responsible for the damage. Since it has been common to quote the integrated slow-neutron flux associated with an irradiation or the energy expended by fission associated with an irradiation and to refer to them as the exposure, another term is used in referring to the integrated damaging flux: the dosage. The results quoted in this paper are expressed in terms of the dosage so defined.

III. ANNEALING EFFECTS: KINETICS OF RADIATION DAMAGING

A. Simple Isothermal Damaging

Post-irradiation studies of the annealing of irradiated graphite were started shortly after the radiation damage was discovered. Annealing of the damage produced by irradiation at cool-test-hole temperatures[12] (CT) could be found even at room temperatures. However, since pronounced annealing was not observed until 100 to 200°C, and since the damage increased in a fairly regular manner on irradiation, the implications of this observation appear to have been overlooked.[13] Nearly a decade later, the writer examined damage rates and annealing data reported for samples irradiated at different temperatures in the CT range and concluded that a pronounced annealing effect was evident (unpublished). Shortly thereafter, a facility for low-temperature irradiations[14] became available, and it was found that the damage in graphite irradiated there was greater and annealed over a range of temperatures contiguous with and below as well as in the one co-extensive with that for CT irradiated graphite.[15,16] These observations do not themselves establish the existence of an annealing effect in CT irradiations because it is conceivable[17] that the damage produced at low temperatures is different from that found in CT irradiations.

When the irradiated graphite samples were raised to successively higher temperatures, Neubert and his coworkers found that at each temperature the annealing rates became high and then fell to values so low as to be beyond the limit of observation, and concluded that a distribution of activation energies would be needed to describe the results of these experiments. Using Vand's method[18] (which assumes first-order kinetics), Neubert analyzed the kinetic data assuming a frequency factor 10^{13} sec^{-1}. Recently it was shown by the author that work by Ballinger[19] indicates a low order of reaction

[9] W. Primak, Nuclear Sci. Engr. (to be published).
[10] W. Primak, Nuclear Sci. Engr. (to be published).
[11] For example, an examination of the papers in the *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy* (United Nations, New York, 1956), Vol. 7, shows that the term annealing is applied to alterations in radiation-induced property changes, sometimes without regard to the direction of change, and even sometimes when the alterations were caused by further irradiation.

[12] These test holes in nuclear reactors are usually at temperatures above room temperature and well below 100°C. Unless otherwise stated, the nominal range of CT will be considered to be 35 to 60°C.
[13] See, however, G. H. Kinchin, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy* (United Nations, New York, 1956), Vol. 7, Paper 442.
[14] The Brookhaven National Laboratory low-temperature irradiation facility is cooled with liquid nitrogen. According to the late J. Fleeman (private communication), excursions above liquid nitrogen temperature are certainly less than 40°C in routine operation.
[15] D. Keating, Phys. Rev. **98**, 1859 (1955).
[16] G. R. Hennig and J. E. Hove, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy* (United Nations, New York, 1956), Vol. 7, Paper 751.
[17] It will be seen that this effect is not important here but does occur at higher temperatures.
[18] V. Vand, Proc. Phys. Soc. (London) **55**, 222 (1943).
[19] J. C. Ballinger (unpublished); R. E. Nightingale, presented at the American Chemical Society Meeting, September, 1955

(near unity) and a frequency factor between 10^{10} and 10^{14}. Work by Nightingale[19] provides some confirmation of this. It will be convenient here, for purposes of mathematical simplicity, to treat the case of first-order kinetics. From the work by Primak[20] it may be inferred that this will show the major features of the annealing effects and that deviations from first-order kinetics can only be found by detailed kinetic experiments of a kind which have not been reported as yet.

It seems reasonable to assume that at the beginning of the irradiation the damage consists of independent (noninteracting) accumulating events. The case in which these events result in the formation of processes which are subject to isothermal annealing is defined as simple-isothermal damaging. The isothermal annealing is assumed to proceed by the equations derived by Vand.[18] The nomenclature which is used here is that used by Primak.[20] His Eq. (4a) is

$$p=p_0\exp(-Ate^{-\epsilon/\tau}), \tag{1}$$

where p refers to any property and p_0 is the original population of processes. The function $\Theta(\epsilon)\equiv\exp(-Ate^{-\epsilon/\tau})$ is termed the *characteristic-isothermal-annealing function*. For a broad distribution of processes in activation energy ϵ, the annealing behavior is dominated by the exponential dependence in Θ whose properties are therefore reviewed here. The function Θ is sigmoid-shaped as shown in Fig. 1 and varies from $\exp(-At)$ to one. It possesses a point of inflection at an activation energy

$$\epsilon_0=\tau\ln(At), \tag{2}$$

which is termed the *characteristic-activation energy*. Thus ϵ_0 is displaced along the activation-energy axis as the annealing proceeds, the more rapidly the higher the temperature of isothermal annealing. The value of Θ at which the point of inflection occurs is invariant, $\Theta(\epsilon_0)=1/e\cong0.368$; and the slope is $\Theta'(\epsilon_0)=1/\tau e$. Since

$$\Theta(\epsilon)=\exp[-Ate^{-\epsilon_0/\tau}e^{-(\epsilon-\epsilon_0)/\tau}]=\exp[-e^{-(\epsilon-\epsilon_0)/\tau}], \tag{3}$$

it is seen that the shape of Θ is also invariant during isothermal annealing; the whole curve is displaced, as described above for its point of inflection, without changing its shape.

If a sample is being subjected to simple-isothermal damaging at a rate which produces an original population of property changes p_0 per second (this original population of property changes is termed the *nascent-activation-energy spectrum*) which can anneal isothermally, the property change which is observed at the end of an irradiation of time duration t_0 is

$$p(\epsilon,t_0)=\int_0^{t_0}p_0(\epsilon)\Theta(\epsilon,t)dt, \tag{4}$$

i.e.,

$$p(\epsilon,t_0)=p_0t_0\left[\frac{1-\exp(-At_0e^{-\epsilon/\tau})}{At_0e^{-\epsilon/\tau}}\right]\equiv p_0t_0\Psi, \tag{5}$$

where $\Psi(\epsilon,t_0)$ is termed the *characteristic-isothermal-damaging function*. It dominates the kinetics of the damaging when the nascent-activation-energy spectrum is broad and undergoing thermal annealing in the same way that Θ dominates the post-irradiation annealing. The properties of Ψ are investigated here. It is sigmoid-shaped, and it varies from about $(At_0)^{-1}$ to 1. It is a function of

$$\begin{aligned}z&\equiv At_0e^{-\epsilon/\tau}\\&=At_0e^{-\epsilon_0/\tau}e^{-(\epsilon-\epsilon_0)/\tau}\\&=e^{-(\epsilon-\epsilon_0)/\tau}\end{aligned}$$

and may be written

$$\Psi=(1-e^{-z})/z.$$

Thus the shape of Ψ is invariant in time. Further, Ψ moves along the activation-energy axis in an invariant relation to Θ. The relationship is shown in Fig. 1, where Θ and Ψ for $\tau=0.02857$ (about 58°C) are carefully plotted about ϵ_0. Some of the properties of Ψ are the following: at the characteristic-activation energy it has the value $\Psi(\epsilon_0)=1-e^{-1}\cong0.632$, and at this point its slope is $\Psi'(\epsilon_0)=\tau^{-1}(1-2e^{-1})\cong0.264/\tau$; its point of inflection (when plotted as a function of ϵ) occurs at $\exp(z_1)=1+z_1+z_1^2$ or at $z_1\cong1.793$ and hence

$$\epsilon_1\cong\epsilon_0-0.584\tau, \tag{6}$$

where the value of the function is $\Psi(\epsilon_1)\cong0.465$, and the slope is $\Psi'(\epsilon_1)=\tau^{-1}z_1\exp(-z_1)\cong0.298/\tau$.

There are many observations of the curious behavior of the radiation damage that can be explained by applying Eqs. (1) and (5) or step function approximations to them of the sort employed by Vand. Many of the observations are unpublished as yet, at least in detail, and the absence of a specific reference is to be so understood.

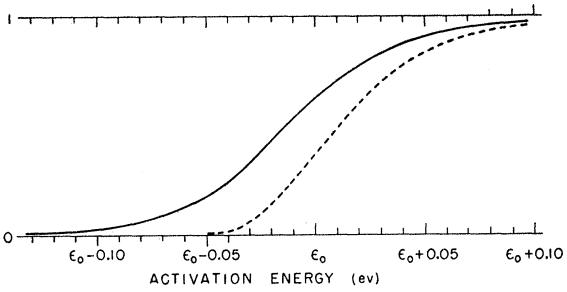

FIG. 1. The isothermal-annealing function (dotted) and the isothermal-damaging function (solid).

(unpublished). The work by Ballinger involved the tempering of a previously isothermally-annealed sample; the conclusion follows from the analysis given by Primak,[20] paragraph 3.1. Nightingale gives results for the isothermal annealing of a previously isothermally-annealed sample, and the results can be analyzed in a similar manner.

[20] W. Primak, Phys. Rev. **100**, 1677 (1955).

1. *Extent of the activation-energy spectrum.*—The usual irradiation times for experiments in which the early stages of the damage have been investigated have covered periods from hours to months. Hence t_0 was in the range 10^4 to 10^7 seconds. The effects will be given here for $\ln A = 30$ (i.e., $A \cong 10^{13}$ sec^{-1}); the results can easily be modified for other values of the frequency factor. Then the range of interest of At_0 is 10^{17} to 10^{20}. Thus for CT irradiations ($\tau \cong 1/35$ ev), it is seen from Eq. (2) that the characteristic-activation energy is 1.1 to 1.3 ev. This would be the region of the lowest activation energies at which the activation-energy spectrum which is observed after irradiation rises prominently. This prominent rise in the activation-energy spectrum will be referred to frequently and will be designated SR. It is clearly shown in the results obtained by Neubert *et al.*[2]

The extension of the activation-energy spectrum beyond SR is largely determined by the nature of the nascent-activation-energy spectrum. When the temperature of irradiation is such that there is a sharp decline (this will be designated SD) in the nascent-activation-energy spectrum shortly beyond SR (less than 0.5 ev), differences in the irradiation conditions or storage conditions will produce a spectacular variability in the total property changes. Since this has been the case for some properties of graphite and diamond in CT irradiations and for other substances at other temperatures, it will be treated in some detail. If the SD is far removed from the SR, equally great (though not proportionately equal) changes will be produced by altering irradiation and storage conditions, but they will not be noticed as readily in the total property changes; they will be easily observed, however, when the activation-energy spectra are determined.

2. *Variability of the radiation damage.*—Since the activation-energy spectrum which is present at the end of the irradiation depends on t_0, the nature of the damage depends on the rate of irradiation: i.e., the damaging flux. Thus the damage produced by a given integrated flux is not the same as that produced by a flux $\frac{1}{10}$ as great for a 10-fold greater length of time. In the latter case, the total damage will be less; and in a tempering experiment, annealing will be displaced to a higher temperature; i.e., SR is displaced to greater activation energies. Further, the damage is sensitive to the temperature of irradiation. It is to be noted that in simple-isothermal damaging, the shape of the activation-energy spectrum (for a given nascent-activation-energy spectrum) is not dependent on the amount of damage, but on the time (t_0) and the temperature of irradiation. In the sense that this fact has not been considered, there are no truly quantitative radiation damage studies that have been performed in nuclear reactors; they must all be classed as semiquantitative.

3. *Lability of the radiation damage.*—The radiation damage once produced is subject to isothermal annealing at the temperature at which it is stored. Thus, much of the long tail extending to low-activation energies which is associated with the low-activation-energy tail of the isothermal-damaging function (see Fig. 1) is rapidly annealed at any reasonable storage temperature by the advance of Θ in activation energy. Major annealing may be followed for the present purposes by considering the relative position of the characteristic-activation energy ϵ_0.

As a first illustration, consider a 10-day room temperature irradiation of a sample for which a damaged property possesses SD at 1.6 ev. After the irradiation $\ln At_0 = 43.5$; and since $\tau = 0.0257$, ϵ_0 is 1.1 ev. After 200 days storage at room temperature, $\ln(At) = 46.8$; hence ϵ_0 is about 1.2 ev. Thus, 20% of the damage has annealed in 200 days as was found by Neubert *et al.*[3] from whose paper these data were taken.

The second illustration is imaginary: the same sample irradiated at about 58°C ($\tau = 0.0286$ ev) for several days (about 10^5 sec); then $\epsilon_0 = 1.18$ ev. After storage for a year at room temperature ($\tau = 0.0257$ ev), $\epsilon_0 = 1.21$ ev; major annealing has occurred even though the storage temperature has been much lower than the irradiation temperature. The effects increase when the irradiation time is shorter compared to the storage time.

4. *Saturation of a second kind.*—Simple saturation of property change occurs when the irradiation is extended until undamaged material is exhausted. However, if there is an SD, then presumably irradiations can be conducted at such a temperature that the SR is sufficiently close to the SD to produce another saturation effect. As an illustration, consider a constant-nascent-activation-energy spectrum for which SD is at an activation energy $\tau \ln(A\alpha)$. Then the damage is

$$P = \int_0^{\tau \ln(A\alpha)} p_0 t_0 \Psi(\epsilon, \tau) d\epsilon.$$

The variable of integration is changed to z and the new limit At_0 is taken as infinite for all practical purposes; then

$$P = p_0 \tau \alpha [1 - E_2(t_0/\alpha)],$$

where E_2 is one of the exponential integrals defined by Placzek,[21]

$$E_m(x) = x^{m-1} \int_x^\infty \omega^{-m} e^{-\omega} d\omega.$$

This result is a monotonically saturating curve. When t_0 becomes very large, $E_2(t_0/\alpha)$ becomes very small; hence saturation ensues at

$$P(t = \infty) = p_0 \tau \alpha.$$

It is the fact that the isothermal-damaging function reclines with increasing temperature that results in the

[21] G. Placzek, National Research Council of Canada Report MT-1 (NRC-1547). Available from the National Research Council of Canada.

effect found here: that the saturation values of the damage is greater at higher temperatures. It is seen below (paragraph 5) that observation of this effect is difficult unless the measurements are performed during the irradiation.

Measurements of the electrical conductivity of graphite during irradiation at various temperatures were made by Neubert and co-workers (unpublished), and their results can be at least partly accounted for by the methods of this paragraph.

5. *Sharpening of the activation-energy spectrum.*—When the SR is close to the SD, there is the appearance of a peak in the activation-energy spectrum. This apparent peak grows sharper at first as the irradiation proceeds. The maximum sharpening occurs when the point of inflection of Ψ (designated ϵ_1) reaches the point of sharp decline ϵ_2. From Eq. (6) this occurs at

$$t=\exp[(\epsilon_2/\tau)+0.584-\ln A].$$

As an example consider a SD at 1.4 ev. Maximum sharpening would require ~3000 years at 25°C, ~10 years at 58°C, ~$2\frac{1}{2}$ weeks at 100°C, and ~2 minutes at 200°C. After this the sharpness would decline somewhat, and eventually the form approached on the low-activation-energy side would be

$$p(0<\epsilon<\epsilon_2,\ t=\infty)=p_0\epsilon^{\epsilon/\tau}/A.$$

Since Θ is more erect than Ψ, even greater sharpening occurs on storage; and its nature is easily perceived.

Sharpening of this kind is readily apparent in the stored-energy data obtained by Lees and Neubert.[22] Extreme sharpening seems to have been observed by R. W. Attree, L. G. Cook, and R. L. Cushing.

6. *A kind of irradiation annealing.*—Phenomena involving a decrease in property change with continued irradiation have been termed irradiation annealing or radiation annealing. The latter term should be limited to a back-reaction caused by the radiation involved. The present phenomenon is entirely an effect of thermal annealing. The mechanism postulated in paragraph (4) leads to saturation only in the case of constant-continuous-isothermal irradiation. If Ψ is replaced with a step-function rising at the characteristic-activation energy, the following result is obtained:

$$P=p_0t_0\tau\ln(\alpha/t_0),$$

which possesses a maximum at $P=0.367p_0\alpha\tau$ and $t_0=\alpha/e$. The saturation which was found in paragraph (4) arose from the support of the low-activation-energy tail of the activation-energy spectrum by the continuing irradiation. Since much of this tail is rapidly annealed by isothermal annealing during most conditions of storage, the saturation formulated in the preceding paragraph will not take place. Instead, the property changes which are observed may reach a somewhat lower maximum or even decline, and this will depend on the irradiation program, the discharge schedule, and the schedule of making measurements.

7. *Spurious irradiation annealing.*—The rate of growth of the activation-energy spectrum at a particular activation energy from Eq. (5) is

$$\partial p(\epsilon,t_0)/\partial t_0=p_0\exp(-At_0\epsilon^{-\epsilon/\tau}).$$

Thus the portion of the nascent-activation-energy spectrum which is undergoing annealing is very sensitive to the temperature of irradiation. A very prominent alteration in the storage of energy in graphite undergoing irradiation was observed by Lees and Neubert.[22] It was associated with a rise in the test hole temperature and can be explained in this manner.

Since irradiation annealing is crucial in the subsequent discussion, it is noted that if good thermal contact between the sample and the point at which temperature is determined is not maintained during irradiation, then as a result of the local temperature rise caused by the absorption of radiation and by nuclear transformations,[23] the observed damage rate will be associated with an incorrect temperature and may wrongly be interpreted as irradiation annealing.

In addition to the quantitative observations given above, there are several qualitative observations that are readily explained on the basis of simple-isothermal damaging. These are the lesser sensitivity of some properties to differences in irradiation temperature and result from a large portion of the integral of the activation-energy spectrum lying beyond the sharp rise. Examples are: the irradiation-induced dilatation of silicon carbide is less sensitive to the temperature of irradiation than the corresponding property in diamond; the irradiation-induced changes in the elastic modulus of graphite are less sensitive to the temperature of irradiation than the irradiation-induced change in the electrical conductivity of graphite.

The many observations which can be explained by the theory of simple-isothermal damaging is some of the most convincing evidence that the damage is to be considered as distributed in activation energy and is conclusive proof that a pronounced annealing of graphite occurs during its irradiation in CT facilities. If the annealing during irradiation could be completely described by simple-isothermal damaging, then what remained of the damage after the simultaneous irradiation and annealing would be completely indicative of what had formed originally. However, in their stored-energy experiments Lees and Neubert[22] found that the rate of growth on irradiation of graphite of the stored-energy activation-energy spectrum in the neighborhood of 2.5 ev was less by about a factor of 2 when the temperature (nominal) of irradiation was 135 degrees C than when it was 65 degrees C. Since thermal annealing for the periods of time of these irradiations would only have affected the activation-energy spectrum in the

[22] R. B. Lees and T. J. Neubert (to be published).

[23] W. Primak, J. Appl. Phys. **27**, 54 (1956).

neighborhood of 1.1 to 1.3 ev, it must be concluded that on irradiation at least in this range of temperature and at least after considerable irradiation, portions of the activation-energy spectrum at activation energies too great to be affected by thermal annealing are dependent on the temperature of irradiation. It is thus evident that at least at these irradiation dosages and temperatures, the damage in this part of the activation-energy spectrum is not simply accumulating. Formally this case could be placed into the framework of the theory of isothermal damaging as developed here by considering the nascent-activation-energy spectrum to be dependent on the irradiation conditions (e.g., dosage, temperature). While this might be useful in developing a phenomenological description of the irradiation, it would not further the present purpose, that of accounting for the displaced carbon atoms. In order to do this and in order to explain the serious deviation from simple-isothermal damaging noted here, it is necessary to examine some of the physical details of the disordering.

B. Localization of the Damage

For the present considerations the neutron flux distribution may be taken to be

$$\phi = k/E_n \quad (10^2 < E_n < 10^6), \tag{7}$$

where ϕ is the neutron flux as a function of energy E_n and k is a constant. The actual distributions found in most reactor facilities which are used for radiation damage studies and which are not in immediate proximity to fuel do not differ by a factor of 2 from Eq. (7), although the upper end of the range may vary somewhat. These deviations are of little importance for the present purposes. In immediate proximity to fuel there is a large contribution of damage from unmoderated neutrons, but in this case the conclusions which are reached here apply in even greater force.

For the present purposes it will be sufficient to consider that the total number of displacements produced by an energetic atom of energy E_a increases linearly from some low energy, taken here as 25 ev, to an energy E_T (order of magnitude 10^4 ev) and is then fairly constant at a value N_0 (order of magnitude 10^2). If isotropic scattering in the center-of-mass system is assumed for the neutron-atom collisions, there is implied a uniform distribution of atoms of energies over the range 0 to αE_n (where α is the maximum fraction of its energy which a neutron can transmit to an atom in such a collision) for every scattering event. The number of carbon atom recoils per cm^3 sec having a given energy

$$E_a = \alpha E_n$$

is then

$$N_1 = \int_{\alpha E_n}^{10^6} [\sigma N_a k/(\alpha E_n^2)] dE_n,$$

where σ is the scattering cross section and N_a is the number of atoms per cm^3. Hence

$$N_1 = \sigma N_a k (E_a^{-1} - 10^{-6})/\alpha$$

and the number of displacements produced per cm^3 sec by recoils of energy less than E_T is therefore

$$N_d(E_a < E_T) = \int_{25}^{E_T} \sigma N_a \frac{kN_0(E_a - 25)}{\alpha E_a (E_T - 25)} dE_a,$$

which is nearly

$$N_d(E_a < E_T) = N_0 k \sigma N_a/\alpha.$$

The number of displacements produced per cm^3 sec by recoils whose energy is greater than E_T is

$$N_d(E_a > E_T) = \int_{E_T}^{10^6\alpha} N_a(k/\alpha) N_0 (E_a^{-1} - 10^{-6}) dE_a,$$

which is nearly

$$N_d(E_a > E_T) = (N_0 k \sigma N_a/\alpha) \ln(10^6\alpha/E_T). \tag{8}$$

Since $10^6\alpha/E_T$ is of the order of magnitude 10^1, the number of displacements produced by atoms of energy greater than E_T is several times greater than the number of displacements produced by atoms of energy less than E_T.

The damage which occurs to the physical properties seems to depend on the number of displacements, and hence it is evident that the damage which is found in reactor-irradiated substances is produced predominantly by recoils which produce a large number of displacements. In this way it differs from the damage which is produced by accelerated protons, deuterons, etc., which produce damage due to low-energy recoils. This has been pointed out by Seitz and Koehler[24] among others. Carter[25] has mentioned specific differences in the ratio of the damage to several of the properties of (a) graphite irradiated by cyclotron-accelerated deuterons to (b) graphite irradiated in nuclear reactors. These differences may possibly be due to this effect, for as will be seen, there results a grossly different subsequent sequence of effects.

It has been estimated by James[26] from the formulas given by Seitz[5] that by the time a primary knock-on in graphite has been slowed to 7×10^3 ev, it is displacing an atom at the rate of one for a distance of an interatomic spacing. A direct determination of the stopping power or the range at these energies is beyond present experimental techniques, and the calculations are approximations which are extended beyond the range of their validity. Recently, proceeding by several other lines of reasoning, Seitz and Koehler[24] concluded that

[24] F. Seitz and J. S. Koehler in *Advances in Research and Applications, Solid State Physics*, F. Seitz and D. Turnbull, editors, (Academic Press, Inc., New York, 1956), Vol. 2, p. 307.
[25] R. L. Carter (private communications).
[26] H. M. James (unpublished document).

the cross section for displacing atoms does not increase quite as rapidly along the range as given by extrapolating the formulas valid at higher energies. As well as can be estimated at present, the energy loss by the primary knock-ons losing energy below E_T seems to be $\sim 10^{10}$ ev/cm. The secondaries which are produced are predominantly of energies 10^2 to 10^3 ev. Accordingly, it must be concluded that the damage in graphite irradiated in a reactor is initially predominantly concentrated in small cylindrical regions $\sim 10^2$ atomic spacings in length and ~ 10 atomic spacings in diameter. Such details as whether the volume is somewhat pear-shaped, as considered by Kinchin,[13] is beyond present knowledge and is not very important in the present case. From considerations given elsewhere,[10] this volume contains $\sim 10^2$ displaced atoms. It is thus continuously damaged although, as will be seen below, not completely disordered. It will be termed a severely-damaged region. The interstitial atom content of the severely-damaged region is several percent; and the average spacing is several atomic spacings, probably representing the stability radius for individual interstitial atoms. The volume of a severely-damaged region is $\sim 10^{-19}$ cm^3.

The formation of the severely-damaged region is a transitory phenomenon. Hennig and Smaller[27] have given evidence from paramagnetic resonance measurements that at least some of the high concentration of damage in the severely-damaged regions is dispersed through the crystal at relatively low temperatures (-100°C) in the early stages of irradiation (at least up to an integrated damaging flux 2×10^{18} neutrons/cm^2). The fraction of the damage which is thus mobile is not yet established.[28] At longer irradiations the mobility seems to be lost.[28] This mobility does not seem to be present in diamond, for under similar conditions the width of the paramagnetic resonance does not alter.[29]

C. Ordinary Saturation and Over Saturation

Evidence of a saturation of property change should be observed when the severely-damaged regions encompass the whole solid. For a cm^3 of solid in which regions r are disordered in stages, the amount of disorder present after the nth stage is

$$y_{n+1}=(r+y_n)(1-y_n)+y_n^2,$$

which gives the differential equation

$$dy/dx=r(1-y_n),$$

where x is the number of stages (i.e., proportional to the flux) and the solution is

$$y=1-e^{-rx}.$$

The saturation period $y=1-e^{-1}$ occurs at $x=1/r$. From N_d/N_0 as obtained from Eq. (8) it was calculated to occur at several times 10^{19} n/cm^2. This occurs at several hundred Mwd/aT (megawatt days per adjacent ton) in a Hanford cooled test hole. It may be noted that at about this point in the irradiation: (a) changes in the nature of the damage or damage rates of the various properties of graphite appear, particularly those changes which anneal at higher temperatures; (b) the greatly increased dilatation rate in quartz appears; and (c) the saturation of density increase occurs in vitreous silica.

In graphite and quartz the saturation period does not mark the approach to a steady state; instead some of the properties show an accelerated rate of change. This continued alteration in properties after several saturation periods is named the *over-saturation phenomenon*.

It is self-evident that after the severely-damaged regions have overlapped appreciably, the incremental changes represented by simple-isothermal damaging can no longer describe the events. It is necessary now that new damaging effects arise. This conclusion also follows from the view that in the severely-damaged regions the interstitial atom content is spaced as closely as stability permits. Then the continuation of damaging beyond several saturation periods would seem to require that the physical conditions within the severely-damaged regions be different than they were when a severely-damaged region had previously been formed in that portion of the material. The effect in graphite and quartz is attributed mainly to the great decrease in thermal conductivity and to a much lesser extent to dynamic annealing (see later).

D. Thermal Spikes

The time required for the energetic carbon atom of energy $\sim 10^4$ ev losing energy at the rate $\sim 10^{10}$ ev/cm to lose most of its energy is easily calculated and found to be between 10^{-15} and 10^{-14} sec, less than the atomic-vibration period. Thus the severely-damaged region in graphite can be considered to be instantaneously heated to a temperature which (from its volume 10^{-19} cm^3, energy 10^4 ev) is seen to be several thousand degrees. The subsequent fall in temperature is then characteristic of the thermal properties of the surrounding graphite. Because of its small diameter, and because it will soon be seen that only its early life is of interest, this thermal spike can be considered to behave like Lord Kelvin's instantaneous line source,[30]

$$\Delta T\cong[3\times 10^{-21}q/cx^2t]\exp(-r^2/4x^2t)$$

(where the symbols are those used by Primak[31]), and may be well characterized by its radius at the points of

[27] G. R. Hennig and B. Smaller (unpublished); some of the results are summarized by Hennig and Hove.[16]
[28] G. R. Hennig (private communication).
[29] W. Primak and B. Smaller (unpublished).
[30] H. S. Carslaw, *Mathematical Theory of the Conduction of Heat in Solids* (Dover Publications, New York, 1945), p. 152.
[31] W. Primak, Phys. Rev. **98**, 1854 (1955).

inflection of ΔT, $r_1=2xt^{\frac{1}{2}}$ and by its temperature at the same point, $\Delta T_1=3\times10^{-21}q/cx^2t$ which is approximately $\frac{2}{3}$ of ΔT at the center. The thermal effects might cause changes in the physical properties and the annealing of changes in the physical properties.

Annealing according to the laws which apply under ordinary conditions may be treated by considering the maximum advance of the characteristic-activation energy $\epsilon_0=\tau\ln(At)$ given by equating its first temporal derivative to zero. The temperature may be considered to vary approximately inversely with time. Thus the maximum advance of ϵ_0 is at about $\ln(At)=1$ which occurs at several times greater than $t=1/A$. The frequency factors for annealing seem to be about an order of magnitude smaller than the atomic-frequency factor (cause or effect?), and hence the temperature of the thermal spike would now be somewhat lower than calculated for the severely-damaged region at formation. However, even if it were not lower, the maximum advance of ϵ_0 would be but several tenths ev (corresponding to ordinary annealing at about 100°K), and the slope of the characteristic-annealing function would be about 3 (corresponding to ordinary annealing over a region about $\frac{1}{3}$ the temperature of ordinary annealing, i.e., about 30°C in the present case). The results of irradiations of graphite at liquid nitrogen temperature are difficult to interpret from the present view because of complications in the nascent-activation-energy spectra in this annealing region. However the broad annealing region for the stored energy is suggestive of the kind of effect described here. It is obvious that annealing in thermal spikes by the kinetics which apply under ordinary conditions does not affect the damage found in graphite irradiated in CT facilities and therefore cannot be invoked to explain the deviations from simple-isothermal damaging noted previously. Indeed it would hardly be expected that such a small difference in ambient temperature as going from 65 degrees C to 135 degrees C would affect the very severe conditions within the thermal spikes. It should be noted that the advances of the characteristic-activation energy are not cumulative except where thermal spikes overlap, a very infrequent occurrence.

At the beginning of over saturation in graphite, the thermal conductivity has decreased some 50-fold to 100-fold. High temperatures in thermal spikes now persist for times an order of magnitude greater than the period of atomic vibrations (though hardly greater than the inverse frequency factor for ordinary annealing), and hence may be responsible for some of the disordering which is produced. A similar effect has been suggested for quartz,[31,32] but here it is not found until the thermal conductivity has fallen to values perhaps several tenths that of graphite at this stage of damage, perhaps related partly to a longer atomic vibration period in quartz.

[32] W. Primak and H. Szymanski, Phys. Rev. **101**, 1268 (1956).

E. Dynamic Annealing

The energy required to permanently displace an atom in the lattice is usually taken to be about 25 ev. However, the energy which must be supplied to displaced atoms to cause them to anneal is much less and is given by the activation-energy spectrum. If the growth of the activation-energy spectrum $p(\epsilon)$ is taken to be proportional to the displacement rate, then

$$p(\epsilon)=U(\epsilon)\,d\epsilon\,R(E)\times0.561E/E_d,$$

where $R(E)$ is the rate of formation of primary knockons of energy E, $U(\epsilon)$ is a distribution function‡ for the resultant damage over activation energy ϵ, E_d is 25 ev, $0.561E/E_d$ is the secondary-atom function given by Seitz and Koehler,[33] and E is taken as 10^4 for all values above 10^4. The dynamic-annealing rate $\nu(\epsilon)$ is

$$\nu(\epsilon)=q(\epsilon)\zeta(\epsilon)d\epsilon R(E)\times0.561E/\epsilon,$$

where $\zeta(\epsilon)$ is the fraction of the body which can be annealed at the activation energy ϵ, and $q(\epsilon)$ is the reciprocal number of times activation statistically occurs before annealing can take place. The result of the events postulated here is a neutron-irradiation-induced back-reaction counter to radiation damaging. It leads to a steady state when the damage is

$$\zeta(\epsilon)=[U(\epsilon)/q(\epsilon)][\epsilon/E_d],$$

which coincides approximately to the case of graphite with the values of the quantities: $U(\epsilon)\sim10^{-1}$ per ev, $q(\epsilon)\sim10^{-1}$ (i.e., the frequency factor for annealing is about 10^{-1} times the atomic frequency factor), and a final disordered state with the whole body distributed in increasing extent over activation energies up to about 7 ev, the heat of sublimation.

A phenomenon is referred to by Woods, Bupp, and Fletcher[34] which they term *nuclear annealing*. The phenomenon is the following: an irradiation is performed until considerable damage is produced. The irradiated sample is then irradiated at a higher temperature, and it is found that annealing has progressed to a greater extent than can be accounted for by thermal annealing for the period of time of irradiation at the higher temperature despite the fact that according to the theory of simple-isothermal damaging it should have been somewhat less. It has already been shown that the effect cannot be explained by thermal spikes as suggested by Woods, Bupp, and Fletcher. Indeed this is obvious without detailed consideration, for the

‡ *Note added in proof.*—Some difficulties arise in a precise description of this function because the subsequent discussion indicates the function is different for different irradiation conditions, and it alters as the irradiation progresses. However the arguments given here require only a precision of several fold, and to this precision the function is quite satisfactory.

[33] F. Seitz and J. S. Koehler, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy* (United Nations, New York, 1956), Vol. 7, Paper 749.

[34] Woods, Bupp, and Fletcher, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy* (United Nations, New York, 1956), Vol. 7, Paper 746.

small alteration in the irradiation temperature they refer to could hardly affect the extreme conditions in a thermal spike appreciably. Therefore, proceeding along another direction, from the above equations, if $\zeta(\epsilon)$ had some appreciable value at the end of the lower temperature of irradiation: then at the higher temperature, for an activation energy

$$\epsilon=\zeta(\epsilon)q(\epsilon)E_d/U(\epsilon), \tag{9}$$

the population will be in a steady state; while for activation energies below this, it will fall; and for activation energies above this, it will rise. Effects of the kind described here have been observed in irradiations above room temperature time $\zeta(\epsilon)$ is 2×10^{-2} per ev. They cannot be explained by Eq. (9) if the functions are independent of temperature, for then ϵ is only about 0.4 ev. However, $U(\epsilon)$ is in fact quite sensitive to temperature in certain ranges of temperature, decreasing greatly as the temperature is increased (see Woods, Bupp, and Fletcher,[34] Fig. 31 and the previously noted findings of Lees and Neubert), and this accounts for the marked annealing effects which are observed.

The sensitivity to temperature of $U(\epsilon)$ for graphite is accounted for in the following way. Much of the damage which anneals at low-activation energies has been attributed to processes involving single interstitial carbon atoms, and the damage which anneals at higher activation energies has been attributed to processes involving carbon atoms which are partially bound to each other as interstitial clusters. It is reasonable to suppose that the rate of clustering is suppressed when the single interstitial carbon atoms are annealing rapidly or when their concentration is low.

In January, 1954, the writer in collaboration with the late Jerome Fleeman irradiated graphite dosage rods in the low-temperature facility in the graphite reactor at the Brookhaven National Laboratory and found an *initial change* of 85% for an irradiation for which the following data were quoted: thermal *nvt*, 7.85×10^{17} neutrons/cm^2; fission energy expended in the whole reactor, 1550 Mw-hr; nominal temperature 40°C.[35] These results have been stated in terms of the damaging flux.[10]

The writer does not possess any data on graphite which is suitable for comparing the low-temperature damage rate with the ambient-temperature damage rate given above. However, Keating[15] has published data which may be used for this purpose. He found that when graphite was irradiated at low temperature, the increase in c spacing was about 0.06 A for an irradiation quoted at 2×10^{19} neutrons/cm^2. (It is shown below that the increase in c spacing rather than the percent increase is the more significant.) This corresponds to about 0.60×10^{-20} angstrom per damaging neutron/cm^2 according to the dosage determination given above. When the samples were warmed to a little above room temperature, Keating states that 41% of the damage annealed. The remaining damage (see below) was what would have been expected had the irradiation been conducted at a little above room temperature. This is in accord with Keating's observation that the low-temperature damage rate he observed was about twice as great as had been observed previously in other locations of the Brookhaven reactor (but for which the damaging flux is not known).

It is thus evident that there is no marked dynamic annealing effect in passing from irradiations at liquid nitrogen temperatures (LT) to CT irradiations; i.e., the function $U(\epsilon)$ cannot be greatly different for LT than for CT, contrary to what is found at somewhat higher temperatures. The accuracy of this result depends on the accuracy of the dosage determination above. It is quite possible, because of the heating effects resulting from the absorption of radiation,[23] that the dosage rods were irradiated at a somewhat higher temperature than the temperature at which they were calibrated. The writer has irradiated vitreous silica at liquid nitrogen temperature in the Brookhaven LT facility and found that the density change after warming to room temperature was such as would have required a 20% greater dosage in CT than the one calculated from the dosage determination given above. The effect of temperature on the damage rate of vitreous silica is not determined, but from the probable explanation of the effect,[31] it is expected to be small. Hence the result for vitreous silica may be taken to confirm the result obtained with the dosage rods to within the precision required here.

Accordingly, the radiation damage which is found in CT irradiations is indicative of the radiation damage which would have been obtained had no annealing occurred. From the number of displacements which was determined for CT irradiations, the number which would have resulted had no annealing occurred can be obtained by multiplying the former number by the inverse ratio of the damage under the respective conditions. Thus the experimental displacement rate can be obtained from the determinations which were made before low-temperature facilities were available. Since the range of values for these determinations is of the magnitude of the values, the factor which is used to convert the CT results to those which would have been obtained in the absence of annealing is sufficiently well known so that it does not introduce any appreciable uncertainty.

IV. DISPLACEMENT RATE

A. Energy Content

The phenomenon.—In CT irradiations, the energy content[36] increases initially at about 0.56×10^{-18} cal/g

[35] The use of the graphite dosage rod and the electrical conductivity to give the dosage in *initial change* units is described by W. Primak and L. H. Fuchs, Nuclear Sci. Engr. (to be published).

[36] Original work by F. D. Rossini and E. J. Prosen (National Bureau of Standards) in collaboration with T. J. Neubert (Metallurgical Laboratory, University of Chicago) (unpublished).

per damaging neutron. This increase in energy content is easily annealed, the stored-energy-activation-energy spectrum[37] showing an abrupt decline at 1.4 ev. The rate of increase in energy content declines markedly from the beginning. It is also quite sensitive to the temperature of irradiation as would be expected, since the width of the prominent part of the stored-energy-activation-energy spectrum present after CT irradiations is only about half an electron volt in width. During LT irradiation the increase of energy content is 2 to 3 times as great as in CT irradiations,[16] annealing of the additional energy content increase occurring at activation energies below and contiguous to those found in CT irradiations.

Interpretation.—The increase in energy content is of the order of magnitude of the heat of sublimation of the estimated number of displaced atoms. This is too great to be associated with a lattice strain. It is therefore associated with the breaking of carbon-carbon bonds in graphite. Since the rate of increase of the energy content declines markedly from the beginning while the changes in the x-ray diffraction patterns continue unabated for much longer periods of irradiation, Austin and Harrison's[38] association of a major part of the increase in energy content with the strain energy is probably unjustified and their comparisons are misleading.

Displacement rate.—The heat of sublimation of a carbon atom of graphite is about 7 ev/atom. Thus an unbound interstitial carbon atom has associated with it 7 ev; and at the time of formation, 7 ev are associated with the vacancy which is generated simultaneously. Estermann[39] attempted to estimate the relaxation about the vacancy from the first experimental annealing data for the energy content, but subsequent experimental work showed that the assumptions which were made were incorrect. The reasoning used here proceeds by the argument given by Hennig and Hove.[16] It is supposed that vacancies do not diffuse until about 1500°C; and hence the relaxation about the vacancy must be at least 6 ev, leaving a 1 ev contribution to the energy content. At least some of the interstitial carbon atoms seem to be ionized and these would then contribute about an ev to the energy content. If C_2 groups are formed interstitially, their binding energy is about 7 ev per C_2 molecule or 3.5 ev per C atom[40,41]; and the increase in energy content is in this case about 4.5 ev per displaced carbon atom. Thus if the initial rates of energy storage noted in CT irradiations correspond to the formation of uncombined or loosely trapped interstitial carbon atoms, the displacement rate is about 3.8×10^{-22} displacements per atom per damaging neutron/cm^2. If some aggregation has already occurred, the displacement rate is greater yet. In LT irradiations the displacement rate would seem to be more than twice as great as in CT irradiations.

Comments.—The displacement rate as determined from the increase in energy content is in doubt from lack of knowledge of the state of the displacements, the contribution of lattice strain, the electrostatic contribution, and the effect of the altered Fermi level.§

B. X-Ray Diffraction Effects

The phenomenon.—In CT irradiations the *c*-spacing increases linearly with dosage to large dosages ($>10^{20}$ damaging neutrons/cm^2) and seems to be insensitive to the kind of graphite.[42] The rate depends on the temperature of irradiation, but for CT a representative value seems to be 0.34×10^{-20} angstrom per damaging neutron/cm^2 and for LT irradiations[15] about twice as great as this. There also occur a much smaller decrease in *a* spacing and intensity changes. Several samples which had been irradiated for a dosage about 6×15^{19} damaging neutrons/cm^2, apparently in the upper range of temperatures represented by CT so that the rate of damage had been somewhat less than indicated above, were investigated in detail by Zachariasen.[43] He found that as well as could be determined, the changes in *c* spacing, *a* spacing, and intensities changed simultaneously as the damage was annealed.

Interpretation.—Zachariasen[43] interpreted the intensity changes to indicate a random distortion in the graphite plane. Assuming the distortion to be the result of interstitial blisters which distorted the planes but did not alter the in-plane C—C bond distances appreciably, he estimated the ratio of blisters to carbon atoms. In another attempt he assumed that the crystal volume pre-empted by a displaced carbon atom would average that of carbon in the most poorly organized carbon blacks, about 10 A^3, and that the vacancy would pre-empt the crystal volume of a carbon atom in normal graphite, 8.7 A^3.

Displacement rate.—If one may extend Zachariasen's[43] finding that the increase in *c* spacing, the decrease in *a* spacing, and the root-mean-square deviation from planeness anneal simultaneously and speculate that they form simultaneously, then the rate of blister formation in typical CT irradiations can be obtained by multiplying his results by the ratio of the *c*-spacing

[37] Original work by R. J. Maurer and R. C. Ruder,[3] B. Leaf and A. A. Novick (Metallurgical Laboratory, University of Chicago) (unpublished), and J. A. Wheeler and J. J. O'Connor (Hanford Engineering Works) (unpublished).

[38] A. E. Austin and R. J. Harrison, Phys. Rev. **100**, 1225 (1955).

[39] I. Estermann (unpublished report, May, 1945).

[40] A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (John Wiley and Sons, Inc., New York, 1947), p. 190.

[41] F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

§ *Note added in proof.*—If the imperfections studied by M. A. Kanter and G. R. Hennig [Bull. Am. Phys. Soc. Ser. 2, **1**, 119 (1956)] are the vacancies considered here, the relaxation energy is at least 2 ev less than given here, and the displacement rate as estimated here must be reduced about 20%.

[42] J. R. Townsend (private communication).

[43] W. H. Zachariasen (unpublished report, May, 1945); W. H. Zachariasen and H. A. Plettinger (unpublished report, January, 1950).

rate of increase for typical CT irradiations compared to the rate of increase for his samples. This gives the result 1.5×10^{-22} to 3×10^{-22} blisters per atom per damaging neutron/cm^2 for CT irradiations. The number of carbon atoms per blister is uncertain but would seem to be several on the average. From the dilatation, the displacement rate is easily calculated to be 4.5×10^{-22} displacements per atom-damaging neutron/cm^2 for CT and would be about twice as great for LT.

Comments.—Zachariasen did not give the details of his calculation of the number of blisters, but he noted that his estimate might be incorrect by an appreciable factor. It should be noted too, that the samples which were examined had been irradiated for about the saturation period. In view of the extensive annealing which, it has been shown, the samples must have undergone and in view of the complexity of the events attendant upon the slowing down of the knock-ons, the correspondence of lattice spacing and intensity changes should be studied experimentally at different dosages. The estimate from the volume expansion is based on *ad hoc* assumptions which are certainly incorrect quantitatively. However, the result it yields is probably as accurate as any of the estimates given here.

C. Electron Traps

The phenomenon.—The Hall effect in graphite is negative. On irradiation it becomes increasingly positive, reaches a maximum at a positive value, about 5.5×10^{-19} damaging neutrons/cm^2, and then declines slowly.

Interpretation.—The change in the Hall effect is due to the change in the Fermi level near the edge of a Brillouin zone. It is assumed that electron traps are formed and as a consequence the Fermi level in the conductor is lowered. Evidence is adduced by Hennig and Hove[16] to indicate that at least part of the traps are associated with interstitial displaced atoms.

Trapping rate.—Hennig and McClelland introduced electron traps into graphite chemically[44] and compared the change in Hall effect with that produced by CT irradiations.[45] It was estimated that the rate of introduction of traps into graphite in CT irradiations was such as would correspond to 5×10^{-22} traps per atom per damaging neutron/cm^2. If on the average one displaced carbon atom is to be associated with each electron trap, the displacement rate is 5×10^{-22} displacements per atom-damaging neutron/cm^2 in CT irradiations.

Comments.—The nature of the electron trapping in reactor-irradiated graphite is uncertain. The traps do not seem to be identical; e.g., only some of them seem to be paramagnetic.[16] The extreme disorder which is produced must also alter the zone structure of the solid. The extent to which a change in zone structure is involved in shifting the Fermi level with respect to the zone edge is unknown, but is probably small, at least in the early stages of irradiation.

D. Other Determinations

Antal, Weiss, and Dienes[8] determined the effect of irradiation on the long-wavelength neutron scattering cross section of graphite. From the localized manner of production of the damage, it is evident that their assumption of dispersed vacancies and interstitial atoms is quite unjustified. This assumption probably affects their results more than it does the other results presented here. More serious, however, is the fact that the dosage of their samples is not given. Their *fast flux* is not defined; and since no other properties of their irradiated sample are given, it is not possible to estimate the dosage by a comparison with property changes in irradiation locations which have been calibrated. They take their results to indicate a displacement rate 1.5×10^{-22} displacements per atom per *fast* neutron/cm^2. It is seen that this result is too low for their *fast flux* to be identified with the damaging flux. Further, the large property change noted and the small amount of it annealing at 250°C suggest that the sample had been irradiated for several saturation periods, and this may account in part for their low value. It may be noted in passing that the annealing of their effect (attributed in part to vacancies) below 900°C, when other investigators[16] have assumed that vacancies are not mobile below about 1500°C, is worthy of further consideration. The result by Antal, Weiss, and Dienes will be disregarded in this summary.

The increase in the energy content (cal/g) of diamond[46] in CT irradiations is about that found for graphite and would lead to about the same displacement rate on the assumptions given above. The effect of the irradiation temperature is unknown.

The dilatation of diamond on irradiation has been treated by Zachariasen[43] in the manner he employed for graphite. Using this method with the data given elsewhere,[10] the result is 3.3×10^{-22} to 4.1×10^{-22} displacements per atom per damaging neutron/cm^2 in CT irradiations.

V. DISCUSSION

The effects which result from the events initiated by the passage of an energetic neutron through a solid are not well understood and are yet in part the subject of unconfirmed speculation. The effects depend on the structure of the solid, and a classification which illustrates the general effects of the passage of energetic atomic particles through solids is given by Seitz and Koehler.[33] The effects which were discussed here were those which involved the displacement of atoms in solids which are usually thought of as not undergoing

[44] G. R. Hennig and J. D. McClelland, J. Chem. Phys. **23**, 1431 (1955).

[45] G. R. Hennig and J. D. McClelland (unpublished).

[46] Primak, Fuchs, and Day, Phys. Rev. **103**, 1184 (1956).

chemical decomposition. Even in this limited group, the effects are quite varied. The effects depend greatly on the physical properties of the solid (or alternatively, the composition and structure) for these determine the energy loss per unit distance, the number of displacements per unit distance, the temperature rise (and associated phenomena) along the path, and the ultimate fate of displaced atoms. The region of energy loss which is of interest is that in which the energy loss by ionization has become small. Details of energy loss in this region are uncertain because it is difficult to perform experiments of stopping power and because the straggling range is a considerable portion of this region. When the research upon which the present paper is based was started, it was hoped that in several solids which do not recrystallize readily and in which the crystal structure is based on localized bonds which are not readily re-formed, the sequence of effects would be preserved. It was seen that this has not been realized and that the radiation damage is labile at ordinary temperatures even in what seems to be one of the most stable substances in this sense: graphite. Although not enough is yet known about diamond and silicon carbide, it is likely that this will be true of them too, but possibly a little less so. However, enough of the sequence of original effects seem to remain in these solids that a reconstruction seems to have been achieved. Parts of this reconstruction are quite general and presumably would be equally valid for other substances, e.g., the theory of isothermal damaging presumably is equally valid for copper and aluminum at low temperatures. Other portions of this reconstruction, like the localization of the damage discussed here, is probably peculiar to only a few substances involving elements in the lower part of the periodic table like quartz, diamond, silicon carbide, and graphite.

The extreme interest in graphite arises from the relative stability of the damage produced in it and from the large amount of data available for this damage. It thus possesses a unique significance in the study of radiation damage entirely apart from its historical contribution and practical value. Hence it is important to establish a reliable value for the displacement rate as a guide in developing the subject. No unequivocal method has yet been proposed for this and they are all based on *ad hoc* assumptions. It is therefore comforting that the methods which have been used all seem to give the same value within a factor of two: 10^{-21} displacement per atom-damaging neutron/cm^2 for the number of displacements which remain after a scattering event involving a fast neutron near the beginning of the irradiation under conditions in which thermal annealing of the damage has not occurred. However, it must be cautioned that in none of the estimates has the complexity of the damage been considered. The extreme concentration in which much of the damage caused by fast neutrons scattered in graphite and diamond is originally produced may seriously affect the estimates and the number of displacements produced as well. It would therefore seem that the value established here is to be considered a lower limit for the number which is sought: one to be compared with the theoretically deduced displacement rate.

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