The diffusion coefficients and the activation energy from the present work agree with the values extrapolated from the results on impure crystals.[1,2]

All the available results on self-diffusion in silver are listed on Table II. Most nearly consistent results are apparently obtained by use of both tracer *and* sectioning techniques.

Radiation Damage in Diamond and Silicon Carbide*

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Diamond and silicon carbide were irradiated in nuclear reactors and were found to be damaged in a manner similar to that for graphite. Detailed observations were made of the dilatation and increase in energy content and their annealing. Dilatations as great as about 3.7 percent and increases in energy content as great as about 400 cal/g were observed. The dilatations and the energy content (release of stored energy) seemed to anneal in a parallel manner and could be treated kinetically as a distribution of processes in activation energy. The initial distribution for diamond showed a peak at about 1.6 ev and a plateau extending (at about ¼ the height of the peak at short irradiations and greater proportionately for long irradiations) to activation energies in excess of 3.7 ev. The initial distribution for silicon carbide showed a smaller narrow peak at about 1.6 ev and a very broad larger peak extending from about 2.2 ev to 4.3 ev with a maximum at about 3.4 ev. In many of the samples of irradiated diamond the stored energy exceeded the heat capacity in certain temperature ranges, and catastrophic stored energy release was observed on heating.

INTRODUCTION

AN account of the prediction and discovery of radiation damage in nuclear reactors is given by Burton.[1] Of the substances investigated at first, large changes in physical properties were found only in graphite. (See Neubert et al.[2] for an account of the experimental investigations.) Accordingly it was suggested that the large changes in physical properties found in graphite were associated with its crystal structure. In order to test this, samples of diamond were irradiated. The energy content was the property chosen for investigation because it could be determined in the same manner as for graphite and because it seemed especially significant. A large increase, comparable to the increases observed in graphite, was found. Subsequently the dilatation was investigated and was also found to be large, comparable to that of graphite. Then α-silicon carbide (hexagonal) was irradiated, and it was found to exhibit a similar large dilatation and increase in energy content.

[1] M. Burton, J. Phys. & Colloid Chem. **51**, 618 (1947).
[2] M. Burton and T. J. Neubert, J. Appl. Phys. **27**, 557 (1956); T. J. Neubert et al., Argonne National Laboratory Report ANL–5472 (available from the Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C., 1956).

MATERIALS

Diamond

(a) For heat of combustion measurements, for some of the x-ray lattice constant measurements, and for some density determinations, there was used industrial diamond dust (white bort) 80–100 mesh. It consisted mainly of colorless cleavage fragments with occasional yellow ones and a few dark specks. It was cleaned by heating it with hydrofluoric acid for some hours. It was then washed with distilled water and dried. A sample was examined spectroscopically with the results: detected elements Cu 2, Mg 2, Na 5, Si 50 ppm; detection limits for undetected elements Ag 0.1, Al 5, As 20, B 0.1, Ba 2, Be 0.5, Bi 0.2, Ca 2, Co 2, Cr 1, Fe 1, Hg 5, K 10, Li 1, Mn 0.1, Ni 1, P 50, Pb 0.5, Sb 1, Sn 5, Sr 10, Ti 1, V 1, Zn 20, Zr 1 ppm. Except for a few grains which showed a very weak birefringence, the crystals were isotropic. Samples were heated for half an hour at various temperatures in a stream of purified nitrogen. No change was observed after heating at 300°C, 400°C, 500°C or 600°C. After heating at 700°C the crystals darkened slightly, turning a pale grey, so that they stood out in slightly higher relief against the white background of a porcelain boat.

(b) Colorless octahedra, 1 to 2 mm across (industrial diamond), were used for some density determinations.

(c) White bort, 300–350 mesh, untreated, was used for some of the lattice-constant determinations.

Silicon Carbide

(a) A quantity of commercial black silicon carbide was cleaned by treating it successively with hot hydrofluoric acid for several days and with hydrochloric acid for several days. It was then washed with distilled water and dried.

(b) Light green transparent silicon carbide crystals supplied by the Norton Company (Niagara Falls, Canada) through the courtesy of Dr. Gordon Finlay.

(c) Large crystals of black silicon carbide supplied by the Carborundum Company (Niagara Falls, New York) through the courtesy of Dr. G. M. Butler.

Graphite

(a) A piece of graphite (artificial, Acheson reimpregnated KC[4]) was cut into small pieces $\frac{1}{2}$–1 mm on edge. The granulated graphite was loaded into a graphite capsule, placed into a graphite tube furnace, and heated to a temperature in excess of 3000°C in a stream of helium. The capsule had previously been used to purify some natural graphite crystals which were not completely removed and contaminated the present sample to the extent subsequently determined to be 1.9 weight percent. This sample was used for energy-content determinations (heat of combustion).

IRRADIATIONS

The irradiations were all performed in various nuclear reactors. It is presumed that all of the effects described here (with the partial exception of color changes) were caused by processes initiated by the scattering of energetic neutrons (energies greater than 75 ev). The samples were rather small, and it is presumed that they were uniformly affected ($\pm 10\%$). There is some uncertainty regarding the temperatures of the irradiations because of heating effects in the samples and containers.[3] The matter is discussed further below.

Hanford irradiations were conducted in the cooled test hole facilities described by Woods, Bupp, and Fletcher.[4] The aluminum assemblies in which the samples were placed are termed slugs. Two kinds of slugs were used. Slug I (termed a double casing) was made as follows: The samples were placed into 0.015 in. wall aluminum capsules which were placed in a 27/64-in. by $\frac{1}{16}$-in. wall aluminum tube which was welded shut after replacing the air with helium. This tube was inserted into a closely fitting $\frac{1}{2}$-in. diameter by $\frac{1}{32}$-in. wall aluminum jacket. Two sample capsules were present in each slug: a 1$\frac{1}{2}$-in.-long capsule was filled with granulated graphite, and a 3-in.-long capsule

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

[4] Woods, Bupp, and Fletcher, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955* (United Nations, New York, 1956), Vol. 7, paper 746.

TABLE I. Irradiation data for Hanford irradiated samples.

Irradiation (reference No.)	Exposure (Mwd/aT)	Estimated damaging flux[a] ($10^{18}n/cm^2$)
IW–10	153	26
IW–15	255	43
IW–21	43	7
IW–22	94	16
IW–23	183	31
IW–24	287	49
IW–25	657	111
IW–32	292	50
IW–40	656	112
IW–41	660	112
IW–50	289	49
IW–51	296	50
IW–52	638	108
IW–53	1060	180

[a] W. Primak, Nuclear Sci. Eng. (to be published).

was filled with the sample of interest. Slug II (termed a single casing) was an aluminum tube $\frac{1}{2}$ in. in diameter and 6 in. long with a $\frac{1}{16}$-in. wall; the samples were wrapped in aluminum foil and inserted in this tube, and the ends were swaged shut over about $\frac{3}{8}$ in. of a 1-in.-long solid aluminum plug. The irradiation data for the Hanford irradiated samples are presented in Table I.

One irradiation (IW–90) was performed in the Experimental Breeding Reactor (EBR). The samples were sealed in vitreous silica, cased in stainless steel and exposed in the outer rod circle of the core, position 217, about 3 in. below center for an exposure of 1745 Mw-hr to NaK (the reactor coolant) mostly at about 270°C, the estimated nvt 1.1×10^{21} (within a factor 2), all fast neutrons. From about 0.71 to 0.72 and 0.98 to 0.99 of the total exposure, the temperature was between 70°C and 190°C; and in addition there were 122 startups in the irradiation period which if estimated at $\frac{1}{2}$ hr would give a total of 0.035 of the exposure at low temperature.

Two irradiations were conducted in the Materials Testing Reactor (MTR). The first (IW–95) consisted of samples wrapped in aluminum foil and were placed into an aluminum can containing graphite samples. The can was in position L–45 at center-line for an accumulated thermal flux about $2.5 \times 10^{21}n/cm^2$. The graphite samples in this can were damaged the equivalent of 5000 Mwd/aT (megawatt days per adjacent ton[4]) (extrapolated) in a cooled Hanford test-hole.[5] In the second (IW–106), the samples were packed with alumi-

TABLE II. Additional irradiation data.

Irradiation (reference No.)	Location	Exposure or thermal nvt	Estimated damaging flux (n/cm^2)
IW– 90	EBR–217	1745 Mw-hr to NaK	1.1×10^{21}
IW– 95	MTR–L45	about 2.5×10^{21} thermal nvt	10^{21}
IW–106	MTR–L43	about 2×10^{20} thermal nvt	about 3×10^{20}

[5] A. Whatley (private communication).

TABLE III. Dilatation of diamond and silicon carbide
due to irradiation.

Irradiation (reference No.)	Sample (No.)	Substance[a]	Method[b]	Dilatation[c] 10^{-2}
IW- 10	WP-584	$D(a)$	a	1.0
IW- 10	WP-584	$D(a)$	b	0.99
IW- 21	WP-587	$D(a)$	a	0.415
IW- 22	WP-588	$D(a)$	a	0.794
IW- 23	WP-589	$D(a)$	a	1.268
IW- 24	WP-591	$D(a)$	a	1.696
IW- 25	WP-592	$D(a)$	a	2.608
IW- 25	WP-592	$D(a)$	c	2.71
IW- 40	WP-322	$D(c)$	a	2.85
IW- 41	WP-317	$D(c)$	a	2.88
IW- 50	WP-331	$D(c)$	a	2.05
IW- 51	WP-335	$D(c)$	a	2.02
IW- 52	WP-367	$D(c)$	a	2.75
IW- 53	WP-390	$D(c)$	a	3.49
IW- 90	WP-450	$D(b)$	d	2.55
IW- 95	WP-305	$D(c)$	a	2.79
IW-106	WP-369	$D(b)$	d	3.65
IW- 15	WP-586	$S(a)$	b	0.96
IW- 15	WP-586	$S(a)$	c	1.14
IW- 32	WP-442	$S(b)$	c	1.10
IW- 52	WP-418	$S(b)$	c	2.12
IW- 53	WP-425	$S(b)$	c	2.83
IW- 90	WP-447	$S(b)$	d	2.64
IW- 95	WP-443	$S(c)$	d	2.53
IW-106	WP-387	$S(b)$	c	3.71

[a] Diamond D, silicon carbide S. The lower case letters in parentheses refer to the samples as described in the text.
[b] The letters refer to the methods of determining the dilatation as described in the text.
[c] $\Delta V/V_0 = 3\Delta a/a_0 + 3(\Delta a/a_0)^2$; $\Delta V/V_0 = -(\Delta \rho/\rho_0)[1-(\Delta \rho/\rho_0)]^{-1}$.

num chips in a perforated aluminum can which admitted process water. The can was irradiated in position L-43 (between fuel elements) close to center-line for an estimated accumulated thermal flux of 2×10^{20} n/cm^2.

Data for irradiations other than those performed in Hanford test holes are given in Table II.

PROPERTY CHANGES INDUCED BY IRRADIATION AND THEIR ANNEALING

Dilatation

The dilations were determined by the method which seemed convenient at the time. The following methods were used to obtain the dilatation: (a) precision lattice constant determinations from the back-reflection x-ray powder diffraction photographs, (b) pycnometric density determinations using 1 to 3 grams of coarse powder in a 5-ml pycnometer with water as the fluid, (c) density

TABLE IV. The dilatation of silicon carbide due to irradiation as calculated from the lattice constants.

Irradiation (reference No.)	Sample (No.)	Substance	Percent increase in lattice constant a	Percent increase in lattice constant c	Dilatation[a] (10^{-2})
IW-32	WP-442	$S(b)$	0.41	0.51	1.34
IW-40	WP-321	$S(b)$	0.70	0.71	2.12
IW-41	WP-316	$S(b)$	0.67	0.67	2.02
IW-95	WP-346	$S(c)$	0.73	0.77	2.25
IW-90	WP-447	$S(b)$	0.89	1.09	2.90

$\Delta V/V_0 = 2\Delta a/a_0 + \Delta c/c_0 + (\Delta a/a_0)^2 + 2(\Delta a/a_0)(\Delta c/c_0)$.

determinations of small crystal fragments by the methods of Primak and Day,[6] (d) Ostwald pycnometer determination of the density of a heavy liquid in which the crystal is suspended. Results obtained for the dilatation of diamond and silicon carbide in various irradiations are given in Table III. Additional results for the dilatation of silicon carbide as calculated from the lattice constants are given in Table IV. The lattice spacing corresponding to the maximum of the x-ray diffraction spectrometer tracing of the 002 peak of graphite (a) present in some of the irradiations is given in Table V for comparison.

The x-ray powder diffraction patterns of irradiated diamond and silicon carbide showed no noticeable falling off of coherent intensity in the back-reflection region, an effect which is very pronounced in irradiated graphite, quartz, tridymite, and cristobalite.

Samples of irradiated diamond were sealed in vitreous silica x-ray capillaries and then heated to successively higher temperatures for periods of time. The behavior of the lattice constants is shown in Fig. 1. Similar data obtained by making density determinations on

TABLE V. The lattice spacing corresponding to the maximum of the x-ray diffraction spectrometer tracing of the 002 peak of irradiated graphite.

Irradiation (reference No.)	Sample (No.)	"002 spacing" (A)	Percent increase
Unirradiated	WP-605	6.724	...
IW-21	WP-574	6.744	0.30
IW-22	WP-575	6.783	0.88
IW-23	WP-576	6.804	1.19
IW-24	WP-577	6.858	1.99
IW-25	WP-578	6.997	4.06
IW-15	WP-573	6.888	2.44

grains of irradiated silicon carbide [dilatation method (c)] are shown in Fig. 2. Graphite and silicon carbide were annealed by the methods used to study the annealing of diamond, but the results are not presented in detail. A progressive annealing of the dilatation, similar to that shown by the data presented here, was observed. The annealing of the lattice constants of silicon carbide was smaller than would correspond to the density changes shown in Fig. 2, and this is probably related to the different heating programs employed (see the discussion).

Energy content is defined as the difference in the heats evolved by the irradiated and an unirradiated sample in a reaction in which the end products are in the same state. It is therefore the difference in the enthalpies of the irradiated sample and an unirradiated sample at the temperature at which the calorimetry is performed. The energy contents were determined at the National Bureau of Standards by Prosen, Johnson, Fraser, and Eddy from heat of combusion determinations made as

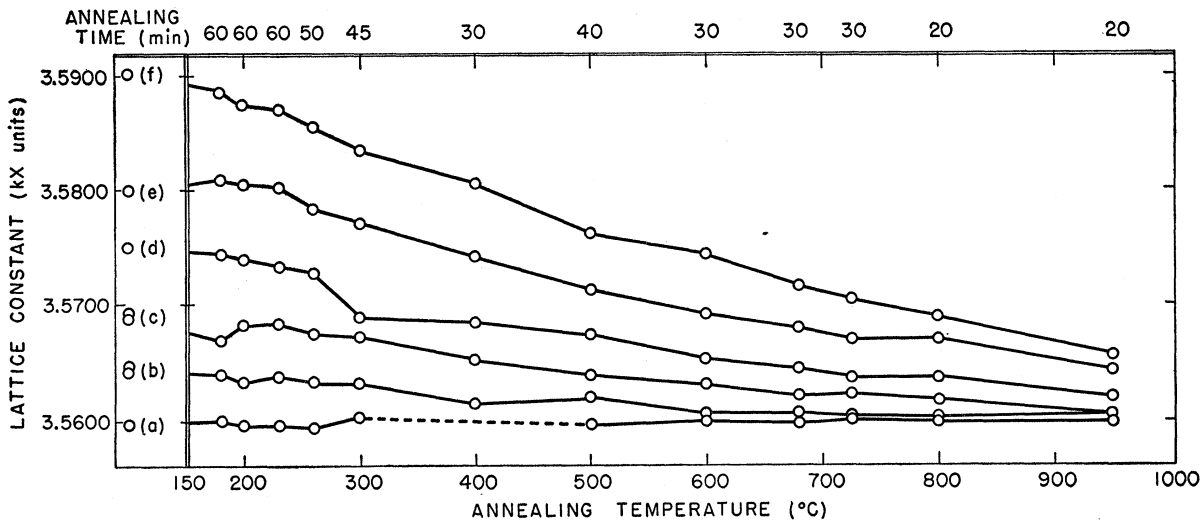[6] W. Primak and P. Day, Anal. Chem. 26, 1515 (1954).

FIG. 1. The lattice constant of diamond samples in a series of successive annealings; (a) unirradiated, (b) WP–587, (c) WP–588, (d) WP–589, (e) WP–591, (f) WP–592.

described by Prosen and Rossini.[7] Results obtained for diamond and graphite irradiated in the same slugs are given in Table VI. The energy content of samples of diamond from one of the irradiations (IW–10) after heating at various temperatures are shown in Fig. 3. A sample of unirradiated diamond (a) was heated to 690°C for half an hour, and its heat of combustion was found to be 7 cal/g less than the heat of combustion of diamond which was not so heated.

Stored energy is defined as the irreversible changes in energy content which are produced by heating an irradiated sample. The rate of stored energy release was determined by differential thermal analysis (DTA). The DTA apparatus used in the present work consisted of 3 small platinum cups (8 mm diam$\times$2 cm high$\times$5 mil wall) mounted on a silica support frame (by 8-mil Nichrome wire stirrups) standing in a silica tube (through which purified nitrogen was conducted) over which was placed a long-tube furnace. In each of two of the cups was placed a charge of about 0.4 g of 40- to 60-mesh corundum, and the sample was placed in the third. A thermocouple was attached to the first cup and a differential thermocouple between the second and third. Thermocouples were made of 2-mil platinum —10% rhodium wires, and the thermal emf's were recorded on automatic potentiometers as the furnace temperature was raised at a rate between 20 and 40 deg/min. The heat flow was analyzed by assuming that Newton's law applied. The heat transfer coefficient was obtained from runs in which the samples consisted of different quantities of diamond which did not release stored energy, assuming published values of the heat capacity. Although the DTA curves were very reproducible, the specific heat obtained with different charges

of diamond did not agree until a term depending on the temperature (an additional fictitious heat capacity) was introduced. This term could have represented thermocouple deviations, errors in heat capacity data, changes in the effective heat transfer coefficient with heat flow, and heat capacities of parts of the apparatus. The value of the fictitious heat capacity was in effect determined experimentally for the condition that the cup temperatures were below ambient temperature. The behavior of the apparatus indicated a negative term of similar magnitude had to be introduced when the sample cup temperatures were above ambient temperature; and since it was inconvenient to determine the value of the fictitious heat capacity under these conditions, it was assumed to have the same value as the positive term. By subtracting the results of a second DTA of the same irradiated sample from a first DTA of it, there is obtained the sum of the stored energy and changes in heat capacity. In the range of temperatures used, the stored energy was so great that
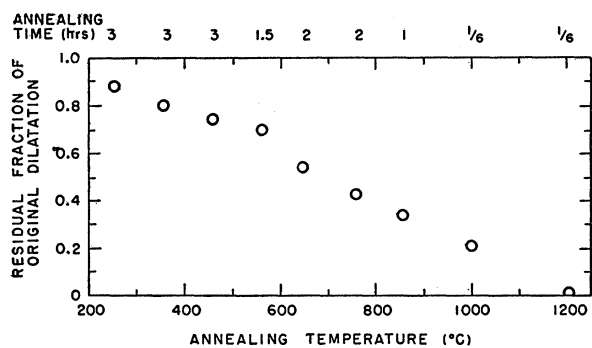

FIG. 2. The fraction of the original dilatation of irradiated silicon carbide sample WP–586 remaining after successive annealings.

[7] E. J. Prosen and F. D. Rossini, J. Research Natl. Bur. Standards **33**, 439 (1944), R.P. 1619.

TABLE VI. Energy content of irradiated diamond and irradiated graphite.

Irradiation (reference No.)	Diamond		Graphite	
	Sample (No.)	Energy content (cal/g)	Sample (No.)	Energy content (cal/g)
IW–10	WP–584	149	...	...
IW–21	WP–587	31	WP–574	17
IW–22	WP–588	90	WP–575	55
IW–23	WP–589	198	WP–576	110
IW–24	WP–591	279	WP–577	138
IW–25	WP–592	370	WP–578	175

the small increases in heat capacity[8] which probably occurred could not have made an appreciable contribution. The rate of stored energy release (dQ/dt $\times dt/dT_1$) is plotted as a function of temperature (T_1) in Fig. 4 for a number of samples (Q is the stored energy, t is time, T_1 is the temperature of the first cup). The integrals of the curves shown in Fig. 4 give the stored energy released over the temperature range. These integrals are compared with the energy content in Table VII.

Irradiations for Small Dosages

Some results obtained in the reactors CP–$3'$ and CP–5 for the dilatation and the stored energy do not agree with the extrapolation of the results given here for larger dosages. It is not yet known whether the disagreement is caused by insufficient precision of the measurements of the samples irradiated for small dosages or whether there is some other cause for the disagreement. Further experiments are in progress.

DISCUSSION

The usual ranges of the deviations obtained in repeated experiments (excluding the occasional larger deviations) are estimated to be: Hanford test-hole exposures 10%, other exposures 20%, damaging flux 20%, diamond lattice constant 0.01%, diamond density 0.05%, silicon carbide lattice constants 0.1%, silicon
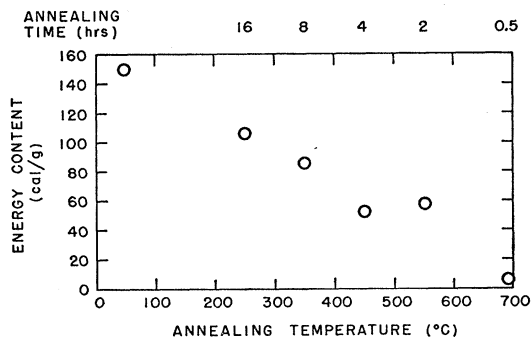
FIG. 3. The energy content of irradiated diamond samples taken from WP–584 after heating them as shown in the graph.

[8] Increases in heat capacity should be easily observable at low temperatures because the heat capacity of unirradiated diamond is so low.

carbide density 0.01%, energy content 2 cal/g, stored energy 25%.

The dilations of the diamond samples irradiated in Hanford test holes are plotted against exposure in Fig. 5. The damage rate in the single casings is noticeably greater than the damage rate in the double casings. This is attributed to a higher temperature of the samples irradiated in the double casings, according to the phenomena discussed by Primak.[8] Evidence for the higher temperature in the double casings is to be found in the
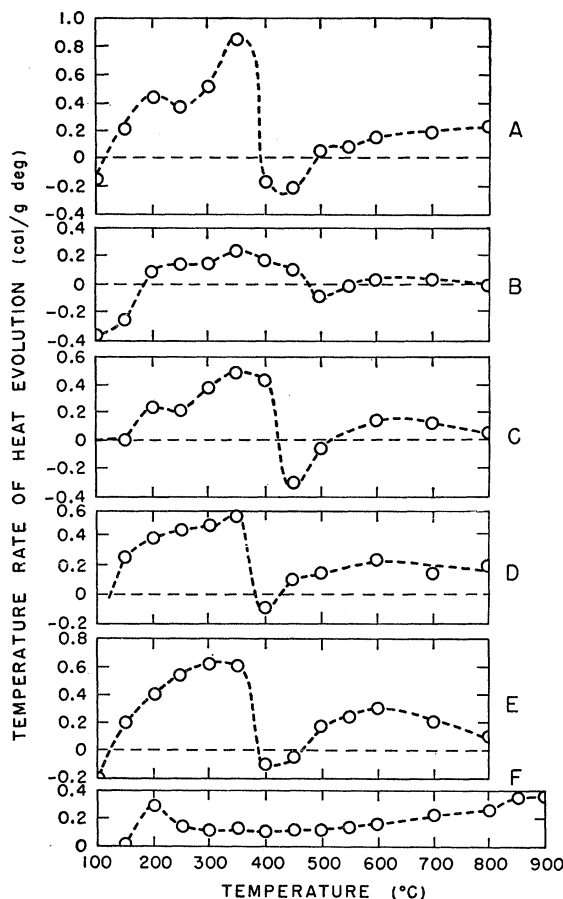
FIG. 4. Stored energy release curves (dQ/dT_1 as a function of T_1) for irradiated diamond: (A) WP–584, (B) WP–587, (C) WP–588, (D) WP–589, (E) WP–591; and irradiated silicon carbide: (F) WP–586.

energy content of the graphite present in these casings. At one time there were test holes at Hanford which operated at higher nominal temperatures than the present 30°C. The energy content of graphite as a function of exposure is well known[9] for these test holes, and the saturation of the energy content of graphite is very dependent on temperature in their range of temperatures. The energy content of the graphite from the double casings saturates in a manner which would

[9] Unpublished data.

correspond to data of the sort obtained in the higher temperature test holes for a test hole between 60°C and 80°C. Additional evidence for the sensitivity of the dilatation of diamond to the temperature of irradiation in this range of temperatures is shown by the two MTR irradiations (IW-95, 106). The damage present in the samples packed with other samples in a dry can (IW-95) is much less than in the samples in the second irradiation which were in contact with process water (IW-106).

The increase in energy content of diamond seems to be more sensitive to the temperature of irradiation than the dilatation. If the data of Table VI are plotted, it is seen that the first two points, both of diamond and of graphite, are lower than the rest while the dilatations found for these samples (Table III) show no such deviation. (The energy content of graphite is also found to be more sensitive to the temperature of irradiation in this range of temperatures than the increases of lattice constant of graphite.) This is attributed to some of the samples having been at a higher temperature during part of their irradiation. The cause of the higher temperature is unknown. Perhaps the first two samples were

TABLE VII. Comparison of the stored energy released up to 800°C with the energy content of irradiated diamond.

Sample	Released stored energy (cal/g)	Energy content (cal/g)
WP-584	160	149
WP-587	45	31
WP-588	100	90
WP-589	170	198
WP-591	190	279

in contact with another sample generating more heat, or perhaps they were cocked in the test hole. Some of the quantitative aspects of annealing during irradiation are treated elsewhere.[10]

It would appear from the data given in Table VI that the rate of increase of energy content in diamond greatly exceeds the rate of increase in graphite; this is fallacious. The initial rate of increase of the energy content of graphite is about 1 cal/g per Mwd/aT exposure in the 30°C Hanford testholes. From the form of the stored energy release curves (also indicated by the data of Table VI), it is inferred that in this temperature range the energy content of diamond is less sensitive to the temperature of irradiation than the energy content of graphite.

The reciprocal percent change in lattice constant of diamond is nearly proportional to the reciprocal exposure.[11] This kind of relation (Novick-Neubert law[12]) is a solution of the differential equation $dy/dx = a^{-1} \times (1-by)^n$ (where x is the dosage, y the damage as

[10] W. Primak, Phys. Rev. (to be published).
[11] W. Primak, Nuclear Sci. Eng. (to be published).
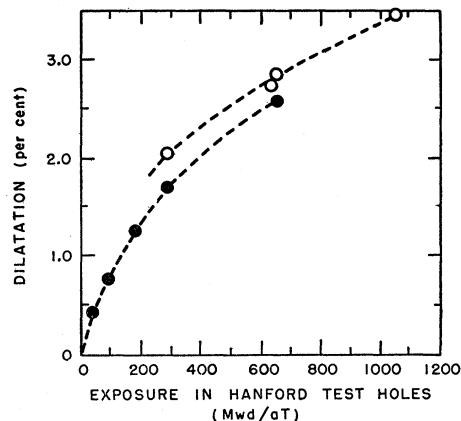[12] W. Primak and L. H. Fuchs, Nuclear Sci. Eng. (to be published).

FIG. 5. The dilatation of diamond samples irradiated in Hanford test holes; open circles, single casings; black circles, double casings.

measured by a suitable property, b is the saturation value, and a is the initial rate of change) for $n = 2$. The data for the dilatation of diamond deviate from this relation by saturating more rapidly at large dosages and act as if n were about 2.3 while the dilatation of silicon carbide saturates less rapidly at large dosages as if n were less than 1. These mathematical relations are useful in comparing data and in utilizing the results for monitoring purposes,[11,12] but can hardly have very much significance in view of the complex processes of annealing which are occurring simultaneously with the damaging.[10]

The irradiation-induced dilatation of silicon carbide is less sensitive to the temperature of irradiation in the range up to 270°C than the irradiation-induced dilatation of diamond as can be seen by comparing the results of the high-temperature irradiation IW-90 with the others.

The stored-energy release curves are the results of a complex kind of tempering experiment. It was shown by Primak[13] that these results could be interpreted as a population of processes distributed in activation energy[14] by introducing a suitable scaling factor. An activation energy near the middle of the range corresponding to various points on the temperature axis is given by

$$y_0 + \ln(y_0 + 2) = \ln(Bc\tau),$$

where $y_0 = \epsilon/\tau$, ϵ is the activation energy (ev), τ is the product of Boltzmann's constant and absolute temperature (ev), c is the inverse heating rate (sec/ev), B is a frequency factor ($\sim 10^{12}$ sec^{-1}). The maximum in the stored energy release curves given here therefore corresponds to about 1.7 ev, a little higher than the corresponding 1.4-ev maximum found for graphite irradiated

[13] W. Primak, Phys. Rev. 100, 1677 (1955).
[14] Such curves for the annealing of radiation damage in graphite were first interpreted in this way by Neubert,[2] using the methods of analysis given by V. Vand, Proc. Phys. Soc. (London) 55, 222 (1943).

under these conditions.[2] Since the spectra for diamond and graphite start at the same value[15] (about 1.1 ev), there is the appearance of a broader peak for diamond than for graphite. The experimental evidence in the case of graphite is that the kinetics is to be explained by a low order of reaction[16] ($\sim$1); and for mathematical convenience in the subsequent discussion, it will be assumed to be unity for diamond, silicon carbide, and graphite since the order of reaction only affects details of the kinetics which will not be dealt with here.[13]

If the rate of temperature rise of the samples had been constant, the stored-energy release curves would have been nearly proportional to the activation-energy spectra for stored energy release. The actual heating rates were increasing as the DTA was started and rose even more steeply because of stored-energy release. Then as the stored-energy release rate declined, the heating rate also declined (even became negative as will be shown below). The heating rate then increased for a while until, as the end of the DTA was approached, it declined again. It is shown elsewhere (reference 13, Sec. 3.2) that for the kind of kinetics involved here, the greater the time rate of change of temperature, the smaller is the temperature rate of stored-energy release and conversely. It is thus seen that the general features of the stored-energy-release-activation-energy spectra corresponding to the stored energy release curves given here are: they start at about 1.1 ev; they show a maximum at about 1.7 ev; and they possess a flat region beyond, whose growth is more pronounced as the irradiation progresses. These features are similar to corresponding activation-energy spectra obtained by others[2,17] for irradiated graphite. The sharp dips and subsidiary peaks indicated by the stored-energy release curves of Fig. 4 are probably spurious (see below).

The activation-energy spectra for silicon carbide are indicated by the one result given in Fig. 4 to be similar to that for diamond, except that the low-activation-energy region is less prominent with respect to the high-activation-energy region. It is clear that there is pronounced energy storage in silicon carbide (not yet demonstrated by energy content determinations), but consideration of its growth will have to await the appearance of additional data.

The stored energy in diamond is of primary significance in annealing studies because of the low specific heat of the substance. Assuming for the moment that the release of stored energy is a function of the temperature only (instantaneous stored-energy release) if the substance should find itself at a temperature T_i at which, for a virtual rise in temperature, the stored energy release per degree exceeds the heat capacity,

[15] This is to be expected since it is related to the temperature of irradiation; see Primak.[10]

[16] Data obtained by J. C. Ballinger and R. E. Nightingale, analyzed by Primak (unpublished).

[17] R. B. Lees and T. J. Neubert (unpublished report, 1949).

then under adiabatic conditions the temperature will instantaneously reach the value T_f determined by

$$\int_{T_i}^{T_f} (dQ/dT)dT = \int_{T_i}^{T_f} CdT,$$

where Q is the stored energy, T is the temperature, and C is the heat capacity. The general phenomenon of such a rise above ambient temperature will be referred to as catastrophic stored-energy release. Under actual conditions, the temperature will not rise instantaneously in this manner for several reasons. One reason is that heat flow occurs. Then (for constant ambient temperature) T_f is determined by

$$\int_{T_i}^{T_f} \left(\frac{dQ}{dT} - \frac{dH}{dT}\right)dT = \int_{T_i}^{T_f} (C'+C)dT,$$

where H is the heat flowing out of the system past the thermal barrier and C' is the heat capacity of substances within the thermal barrier other than the one releasing stored energy. The substances within the thermal barrier will be referred to as the system. In general $(C'+C)$ is an increasing function of temperature, and eventually dQ/dT becomes a decreasing function of temperature, so that the temperature reaches a maximum even if dH/dT is small. However, dH/dT will increase with T. The temperature may then stop rising even though dQ/dT has not begun to decrease relative to $(C'+C)$, because dH/dT has become large. Whatever the cause, as soon as the temperature begins to drop, it does so very rapidly (exponential decay if Newton's law applies) because stored energy release has ceased.

In the case of a DTA the ambient temperature T_0 is rising. Then $(T-T_0)$ is negative at temperatures below that at which catastrophic stored-energy release occurs, and heat flows into the system in accordance with

$$\frac{dQ}{dT} - \frac{dH}{dT} = \frac{dQ}{dT} - \frac{k(T-T_0)}{dT/dt} = C'+C$$

(assuming Newton's law), where t is the time and k is the heat transfer coefficient. It is seen that catastrophic stored-energy release occurs when the temperature of the system reaches the ambient temperature. The temperature of the system now rises until for a virtual rise in T,

$$\delta(dQ/dT) < \delta(dH/dT) + \delta(C'+C).$$

Then simultaneously the temperature begins to fall, and stored energy release ceases. This continues until $T=T_0$ when the temperature of the system once more begins to rise, lagging somewhat behind the rising ambient temperature T_0; and when it reaches the maximum temperature previously achieved in stored energy release, stored energy release resumes in accord-

ance with the preceding considerations. Since dH/dT is the temperature rate of heat flow along the temperature gradient, it remains constant at $-(C'+C)$ during the excursion of the system to lower temperatures. While dQ/dT is a smooth function of T for the conditions assumed here (instantaneous release of stored energy), dQ/dT_0 will show what may be termed false peaks. After these peaks, dQ/dT_0 can become null $(dH/dT_0 = -C'-C)$ but not negative and in general will have some positive value. The preceding considerations are illustrated in Fig. 6. Since dT_1/dt would be nearly the same as dT_0/dt measured at the same time, dQ/dT_1 which is plotted in Fig. 4 should behave like dQ/dT_0.

The sharp drops shown in Fig. 4 at about 400°C look much like the quenching of catastrophic stored-energy release. It was possible to calculate approximate values of the ambient temperature from the experimental data and the computations of k. In one case it was found that the cup temperature had risen 20 to 40°C above ambient and 40 to 80°C above the temperature of the standard sample when quenching occurred. At this point dQ/dT_0 dropped precipitously and did not assume positive values again until the temperature of the standard samples had advanced nearly 100°C. The negative stored-energy release values in this region are attributed to not being able to correct for peculiarities in k under these conditions, to lag and underdamping of the recorder pen, and to other experimental difficulties.

The theory given above predicts a sharp rise in dQ/dT_0 at the point of catastrophic stored-energy release, followed by a sudden drop. The curves, however, indicate a sustained release under catastrophic conditions. This is explained by the fact that dQ/dT_0 is not a function of temperature only, but it also is time-dependent. Then since, as discussed above, the greater the time rate of change of temperature, the smaller is the temperature rate of release of stored energy, and conversely, the kinetics of the processes occurring is a controlling factor rather than a catastrophic one. The small peak at the beginning of the stored energy release
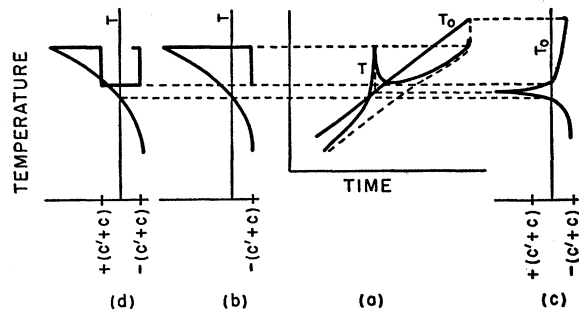

FIG. 6. Heat flow in the 3-cup differential thermal analysis apparatus under conditions of catastrophic stored-energy release for the case of instantaneous stored energy release; (a) behavior of T and T_0 in time, (b) dH/dT as a function of T, (c) dH/dT_0 as a function of T_0, (d) dH/dt times the absolute value of $(dT/dt)^{-1}$ [given to separate the overlapping parts of Fig. 5 (b)].

curves may be due to quenching associated with the changing rates of temperature rise at the beginning of the DTA. The rate of stored-energy release is then maintained at a high level without quenching until past the peak of the activation-energy spectrum where a marked decline in dQ/dT takes place. Since there is no particular amount of stored energy to be associated with a given temperature, dQ/dT has no meaning apart from the heating rates. Even if the data of the DTA could be used to obtain sufficiently precise values of dQ/dT (rather than dQ/dT_0 given here) and dT/dt, they would be very difficult to interpret quantitatively because of the complicated form of dT/dt for the present data.

No evidence of catastrophic stored-energy release was found in the silicon carbide sample in accordance with its much greater specific heat.

A combination of the effects of catastrophic stored-energy release and the effects of the kinetics of processes distributed in activation energy can be found in Fig. 3 which shows the effect of annealing on the energy content of diamond. It would appear from Fig. 3 that the increased energy content of WP–584 due to irradiation is almost completely annealed at 690°C. This is not correct. The decrease in energy content shown by an unirradiated sample heated to this temperature for a like period of time was 7 cal/g and is attributed to graphitization. Part of the decrease in energy content of the irradiated graphite heated at 690°C must also be due to graphitization. The stored-energy release curves would probably be only slightly affected by graphitization because of the rapid heating rates which were used.

The general nature of the activation-energy spectrum for annealing of the dilatations presented in Figs. 1 and 2 can be obtained by using the approximation suggested by Vand.[13,14] It is assumed annealing has occurred for all of the dilatation associated with activation energies below the characteristic-activation energy reached at the end of each step of annealing. The characteristic-activation energy ϵ_0 (ev) at the end of a step of annealing is $\tau \ln(Bt)$, where τ is the product of Boltzmann's constant and temperature (ev), B is a frequency factor, and t is the time. The property change which has occurred in this step of annealing ΔP is approximately the integral of the activation-energy spectrum from ϵ_{01}, the value of ϵ_0 at the end of the previous step of annealing, to ϵ_{02}, the value of ϵ_0 at the end of the present step of annealing. Then $\Delta P/(\epsilon_{02}-\epsilon_{01})$ is the average value of the activation-energy spectrum between ϵ_{01} and ϵ_{02}, and plotting it against ϵ_0 gives an approximate block graph of the activation-energy spectrum.

If this is done for the annealing data for diamond presented in Fig. 1, the general nature of the activation-energy spectra which are revealed for WP–588, 589, 591, 592 (the changes in WP–587 are too small to
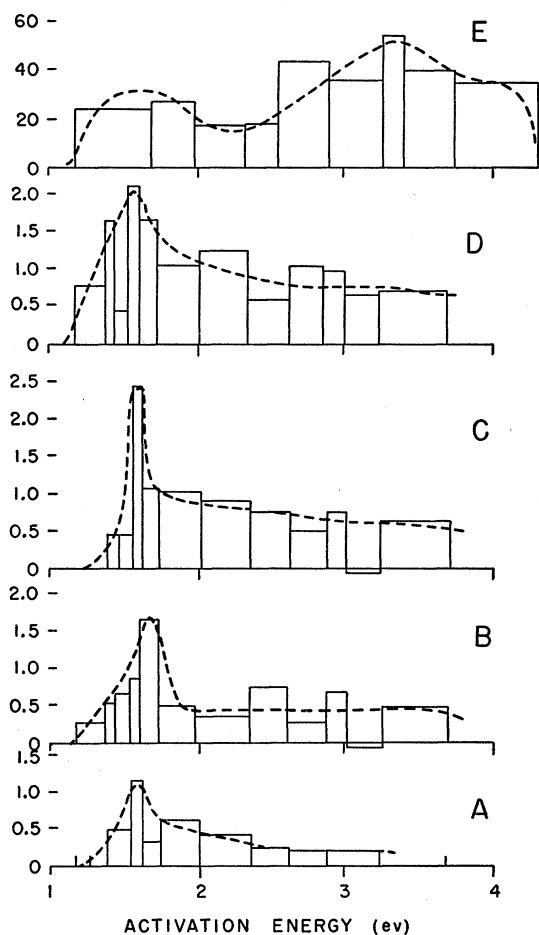
FIG. 7. Approximate activation-energy spectra for the anneal-ing of the dilatation of irradiated diamond and silicon carbide: (A) WP–588, (B) WP–589, (C) WP–591, (D) WP–592, (E) WP–586. For (A), (B), (C), and (D) the ordinate is 100 times the dilatation annealed per ev; for (E) it is the percent of the irradia-tion-induced dilatation annealed per ev.

afford sufficient precision for such an analysis) are similar to the general nature of the activation-energy spectra for stored energy release discussed above and are shown in Fig. 7. The spectra for the annealing of the dilation possess a sharp peak at about 1.6 ev and a plateau about $\frac{1}{4}$ this height which extends to at least 3.7 ev, (the extent to which annealing progressed in the highest temperature of annealing which was under-

taken) up to irradiations involving a damaging flux $\sim 5 \times 10^{19}$ n/cm^2. At longer irradiations, the plateau rises with respect to the peak. This is an example of either the over-saturation phenomenon or the dynamic annealing discussed elsewhere.[10] It is thus seen that diamond on irradiation behaves in a manner similar to graphite and that with equal plausibility the peak in the activation-energy spectrum of irradiated diamond can be associated with the annealing of single carbon atom interstitials and the plateau with the annealing of various carbon atom aggregates.

The activation-energy spectrum indicated by a simi-lar analysis of the data for the annealing of the dilata-tion of silicon carbide given in Fig. 2 is also found to correspond to the stored-energy-release-activation-energy spectrum and is shown in Fig. 7. For the dilata-tion there is a peak below 2.0 ev and a minimum between 2.0 and 2.5 ev. The spectrum then rises in the interval up to about 3.4 ev to a maximum about $1\frac{1}{2}$ times as high as the low-temperature peak The activa-tion-energy spectrum which is revealed by the stored-energy data does not extend further, but the spectrum revealed by the annealing data for the dilatation extends to about 4.3 ev at a level somewhat below the maximum found at about 3.4 ev.

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