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STORED ENERGY RELEASE IN GRAPHITE IRRADIATED AT LOW TEMPERATURES

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STORED ENERGY RELEASE IN GRAPHITE IRRADIATED AT LOW TEMPERATURES

BY:

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TABLE OF CONTENTS

		Page No.
	Abstract	4
I.	Introduction	5
II.	Description of Experiment	6
III.	Analytical Method	8
IV.	Experimental Details	11
V.	Experimental Results and Discussions	21
	References	37

LIST OF TABLES

I.	Specimen Description	20
II.	Integrated Stored Energy Release	21

LIST OF FIGURES

1.	Loading and Annealing Apparatus	12
2.	Details of Specimen Thermocouple Probe	13
3.	Thermocouple and Recording Circuits	14
4.	Photograph of Apparatus (except recorder)	16
5.	Photograph of the Annealing Block and Loading Pan in Place, in the Styrofoam Block	16
6.	Typical Function of $\frac{mc}{\alpha}$ vs ΔT	19
7.	Spectral Anneal. 1,909 Mwh Irradiation	23
8.	Spectral Anneal. 5,915 Mwh Irradiation	24
9.	Spectral Anneal. 22,293 Mwh Irradiation	25
10.	Isothermal Anneal for AWG Specimens Between 200° K and 213° K	32
11.	Isothermal Anneal for AWG Specimens at 2.6° C	33
12.	Isothermal Anneal for AWG Specimens at 23.0° C and 23.2° C	34
13.	Isothermal Anneal for AWG Specimens Between 57.2° C and 63.4° C	35
14.	Isothermal Annealing Rate as a Function of Stored Energy Released at 200-213° K	36

ABSTRACT

Previous measurements of electrical and thermal resistivities and paramagnetic resonance have shown that graphite, when irradiated at or near liquid nitrogen temperatures, retains considerable damage which anneals out at below room temperatures. This report deals with the release of stored energy associated with this damage. To compute stored energy release, the relative specific heat of an irradiated specimen is compared with that of the specimen after annealing. Various types of artificial and natural graphite were irradiated in the liquid nitrogen facility of the Brookhaven reactor. The stored energy release spectrum during steady temperature rise shows a peak at 215° K for graphite having large crystallities i.e., 3,000 Å length and about 185° K for fine-crystallite graphite i. e., 300 Å length. If it is assumed that the defects diffuse out of the crystallites on heating, the dependence of the annealing behavior on crystallite size can be be accounted for with an activation energy of approximately 0.4 ev. The total stored energy releasable at below 275° K accumulates linearly with neutron exposure at a rate of 1.4 cal/gm per 10^{18} nvt. By estimating the number of responsible defects from neutron scattering data, the stored energy per atomic displacement is found to be in the order of 3 to 6 ev. An apparent increase in specific heat appears at low temperatures and can be qualitatively accounted for on the basis of isolated interstitial atoms behaving as Einstein oscillators.

I. INTRODUCTION

In the course of following a program aimed at discovering the fundamental mechanisms of irradiation damage to graphite and of subsequent removal of this damage by thermal annealing, it has recently been established that fairly sizeable damage effects can be retained at liquid nitrogen temperatures which will anneal out at room temperature. [1, 2] The initial studies at this laboratory were made with graphite samples irradiated at low temperature by high-energy deuterons from the 60 inch cyclotron at the University of California, Berkeley. More recently, facilities became available at Brookhaven National Laboratory for neutron irradiations at or near liquid nitrogen temperatures.

The observed effects for low temperature irradiation indicated that it might be possible to observe more fundamental processes of damage and recovery between liquid nitrogen and room temperatures, than occur above room temperature. This low temperature region, therefore, offers increased possibility of eventual attainment of the intitial goal of understanding the processes of radiation damage and thermal annealing. One property which is of fundamental importance, and which is probably simply related to the nature of damage, is stored energy. This report therefore describes accumulation and thermal release of stored energy in graphite specimens irradiated at or near liquid nitrogen temperatures, and this work extends similar experiments performed earlier at higher temperatures. [3, 4, 6]

During irradiation of the graphite lattice by energetic nuclear particles, the lattice suffers various types of disruptions, with the displaced atoms becoming lodged in metastable positions in the lattice, and the lattice surrounding the vacancy probably becoming somewhat distorted. These lattice distortions have associated with them a certain amount of potential energy which is released and degrades into thermal energy when annealing occurs. The lattice is thereby permitted to resume its normal structure. This associated energy is referred to as stored energy, and the kinetics of accumulation and release of the stored energy may yield some limited insight into the nature of radiation damage and thermal annealing.

In accordance with these considerations, graphite samples were prepared for irradiation in the liquid nitrogen facility of the Brookhaven Reactor. These

irradiations were obtained through the courtesty of the Physics Group at Brookhaven. The main purpose of the experiments described in this report was to obtain a broad perspective of the stored energy annealing behavior between the irradiation temperature and room temperature, and to relate the behavior in a qualitative manner to various proposed models of radiation damage and thermal annealing.

II. DESCRIPTION OF EXPERIMENT

The graphite samples were irradiated in the liquid nitrogen facitity at Brookhaven to three different amounts of irradiation. The intermediate irradiation i.e., 5915 Mwh was accomplished in October 1954, while the short i.e., 1909 Mwh and long i.e., 22,293 Mwh irradiations were accomplished during February and March 1955. These irradiations correspond[15] to approximately 3.4×10^{18} nvt, 1.0×10^{18} nvt, and 1.3×10^{19} nvt, respectively, of neutron flux > 1/2 Mev. The maximum temperature in the facility during irradiation was 123° K, which was the controlling maximum temperature for the automatic replenishment of liquid nitrogen. In addition, one sample was irradiated on the Cyclotron at Berkeley with 1.8 Mev protons to the extent of approximately 48 μ-amp-hrs/cm^2 or 1.08×10^{18} protons/cm^2. The maximum temperature during irradiation was 105° K. Following irradiation, all specimens were kept submerged in liquid nitrogen and were not permitted to warm up before the experiment.

The method used for measuring stored energy release is similar in some respects to that used in a previous experiment.[4] In this and the present experiments the heating characteristics of the sample during stored energy release and of the same sample when fully annealed were compared to obtain a measure of the apparent specific heat change, and hence of the stored energy release in the irradiated sample, as annealing progressed.

The design of the apparatus was simple in keeping with the initial purpose of the experiment. The apparatus consisted of:

1. A pan for mounting the specimen at liquid nitrogen temperature
2. A guide tube
3. A tube for inserting the specimen into the central cavity of
4. A massive annealing block

The temperature of the block was controlled in such a manner as to give the desired temperature program to the specimen. In order to thermally isolate the annealing block, it was located within a large block of plastic Sytrofoam. Thermal contact between the specimen and the block was obtained by gaseous conduction.

Two types of annealing programming were made with this apparatus. One method, termed "spectral" anneal, utilized a steady temperature rise from liquid nitrogen temperatures to approximately room temperature.[5] The amount that the specimen temperature lagged behind that of the block, and the block temperature were observed simultaneously. The second method, termed the "isothermal" anneal, was performed by holding the block temperature stable and rapidly inserting the specimen from the loading pan into the block. During the latter the specimen temperature quickly approached the block temperature, over-shot same by several degrees as energy was released, and finally equilibrium between specimen and block temperatures was approached.

During each of these types of anneal, an irradiated, unannealed specimen was first subjected to the appropriate temperature program, then, disturbing the specimen position as little as possible, it was subjected again to the same thermal treatment. These treatments constituted the annealing run and post-annealing run, respectively. In both types of anneal, the specimen temperature tended to rise faster and remain higher during the annealing run than during the post-annealing run. This, of course, was due to the release of stored energy in the specimen during the former, and the lack of such release in the latter. From this difference the amount of stored energy could be calculated, as described in the next section.

The raw data consisted of thermocouple voltages, one indicative of the temperature of the block, the other indicative of the temperature difference between the block and the specimen. These voltages were amplified, and continuously recorded. The data from the early runs were recorded with two synchronized recording potentiometers, but later a two-pen recording potentiometer was substituted.

III. ANALYTICAL METHOD

During the course of an experiment, an inert specimen finds itself at a temperature lower than that of the block, whether the block temperature continually rises as in the spectral anneal or is initially higher as in the isothermal anneal. The temperature of the sample will then approach that of the block at a rate governed by Newton's law of cooling, which relates heat flow, from the block to the specimen, to the temperature difference between them or:

$$\frac{dE}{dt} = \frac{dH}{dt} = \alpha \Delta T \qquad \ldots (1)$$

and by the thermal mass of the sample,

$$\frac{dE}{dt} = \frac{dH}{dt} = \frac{dH}{dT_s} \cdot \frac{dT_s}{dt} = mC \frac{dT_s}{dt} \qquad \ldots (2)$$

If an irradiated sample is used, so that stored energy is released as the sample rises in temperature, the equivalent equation will be:

The symbols used are:

- H = Heat transferred from block to specimen by gaseous conduction.
- L = Stored energy released in sample and degraded into thermal energy.
- E = $(H + L)$ = total thermal energy appearing in the specimen.
- C = Heat capacity of inert specimen at constant pressure.
- C^* = Apparent heat capacity of sample as it releases stored energy.
- Q = Thermoelectric power of measuring thermocouples.
- T_s = Temperature of specimen.
- T_b = Temperature of block.
- ΔT = Temperature difference $(T_b - T_s)$.
- α = Thermal transfer coefficient.
- m = Mass of specimen.
- t = Time.
- a = Subscript denoting annealing data.
- p = Subscript denoting post-annealing data.

$$\frac{dE}{dt} = \frac{dH}{dt} + \frac{dL}{dt} \qquad \ldots (3)$$

$$= \alpha \Delta T + \frac{dL}{dt}$$

$$= mC \frac{dT_s}{dt}$$

This equation will be treated differently for each of the two types of anneal.

A. STEADILY RISING TEMPERATURE (SPECTRAL ANNEAL)

From equation (3) we may define an "apparent" specific heat (C^*) which is different than the normal specific heat only when there is a stored energy release:

$$\alpha \Delta T = mC \frac{dT_s}{dt} - \frac{dL}{dt}$$

$$\frac{\Delta T}{dT_s/dt} = \frac{m}{\alpha}\left(C - \frac{1}{m}\frac{dL}{dT_s}\right) = \frac{m}{\alpha} C^* \qquad \ldots (4)$$

It will be noted later that it is not necessary to determine the value of $(\frac{m}{\alpha})$.

In the computational procedure, $\frac{m}{\alpha} C^*$ was computed as a function of the specimen temperature from the annealing data, ΔT and dT/dt. The normal specific heat $\frac{m}{\alpha} C$ was computed similarly from the post-annealing run. These two curves were plotted on a common graph of C or C^* vs T_s, which was used in conjunction with the next equation for finding stored energy release. Rewriting equation (4),

$$\frac{1}{m}\frac{dL}{dT_s} = (C - C^*) = C(1 - C^*/C) \qquad \ldots (5)$$

In this equation, the value of C outside the bracket can be given the absolute values obtained by other experimenters and serves in a sense, as the calibrating factor for evaluating the stored energy release. The ratio C^*/C inside the bracket is the experimental value obtained from these computations. Values of $\frac{m}{\alpha} C^*$ and $\frac{m}{\alpha} C$ were obtained from the graph at conveniently spaced temperatures. Since, for a given temperature, $\frac{m}{\alpha}$ is the same for both the anneal and post-anneal runs, it will cancel out as the ratio is determined at each temperature. At each of these temperatures the appropriate value for the specific heat of graphite as given by DeSorbo and Tyler [5] is used to complete the calculations for stored energy release.

B. ISOTHERMAL ANNEAL

In this type of experiment, equations (1), (2), and (3) are used again, but not in the same manner as with the spectral anneal. The main difference lies in evaluating the time-rate of stored energy release at a specific nearly constant temperature, instead of the temperature-rate of release at successively higher temperatures. The temperature of the block remains constant while the specimen temperature approaches equilibrium with the former, according to the amount of stored energy released. Since the heat flow from block to specimen is the same for both anneal and post-anneal runs for a given value of the temperature difference, we can rewrite equations (1), (2), and (3) as:

$$\frac{dH}{dt_a} = \frac{dH}{dt_p} = \alpha \Delta T = mC \frac{dT_s}{dt_p} \qquad \ldots (6)$$

$$\frac{dE}{dt_a} = \frac{dH}{dt_a} + \frac{dL}{dt_a} = \alpha \Delta T + \frac{dL}{dt_a} = mC \frac{dT_s}{dt_a} \qquad \ldots (7)$$

Combining these equations we obtain:

$$\frac{1}{m} \frac{dL}{dt_a} = C \left[\frac{dT_s}{dt_a} - \frac{dT_s}{dt_p} \right] \qquad \ldots (8)$$

It can be seen that when the specimen temperature overshoots the block temperature on an annealing run the algebraic sign of ΔT and consequently of $\frac{dT_s}{dt_p}$ is reversed. This reflects the situation that the specimen is hotter than the block and gives heat back to the block as stored energy is released. As the release rate diminishes, the specimen temperature tends toward equilibrium with the block temperature.

The computational procedure consisted of utilizing the difference in rate of temperature increase during the annealing run and post-annealing run for each of a number of suitably spaced values of ΔT. The values of specific heat given by DeSorbo and Tyler were used for C in equation (8).

IV. EXPERIMENTAL DETAILS

Fig. 1 illustrates the general configuration of the apparatus. The annealing block was a copper cylinder 3 inches x 2 inches in diameter with a centrally located cavity 1 inch x 3/4 inch diameter. Around the block was wound a bifilar heating coil of flattened nichrome wire. The wire was insulated from the block with a thin sheet of mica. The mica and wire were both firmly bonded to the block with "epon"* cement, in order to provide good thermal contact between the wires and the block. The temperature difference between the outside surface of the block and the wall of the cavity was calculated to be 0.06° C or less corresponding to a time lag of approximately one second or less at the most rapid rate of temperature rise used in this experiment. The thermocouple junctions in the block were located adjacent to the end of the cavity, along a diameter of the block, and were in a well at a depth calculated to be at the same temperature as the cavity wall while the block is being heated.

In addition to the copper block there was a "loading pan" in which the specimen could be mounted at liquid nitrogen temperatures. The specimen "insertion guide" was a 1/4 inch diameter thin walled stainless steel tube, which extended from the block, through the pan and approximately one foot beyond the latter. The top side of the tube was notched at a point which was in the center of the pan in order to allow mounting of the specimen. Inside the 1/4 inch diameter insertion guide was a 3/16 inch diameter thin walled stainless steel "insertion tube." On the upper end of the insertion tube there was mounted a glass capillary tube, the tip of which carried a thermocouple junction as shown in Fig. 2. The specimen, which had been drilled previously was mounted by simply impaling same on the thermocouple and insertion tube tip. The specimen was then inserted into the block when desired.

The thermocouples already mentioned were for the purpose of measuring the temperature of the block T_B and the temperature difference between the block and the specimen ΔT. The thermocouple leads were teflon-coated, 0.003 inch in diameter and of chromel and constantan. The circuitry contained an ice reference junction, potentiometers, amplifiers, and a recorder, as indicated in Fig. 3.

* Product of Shell Oil Co.

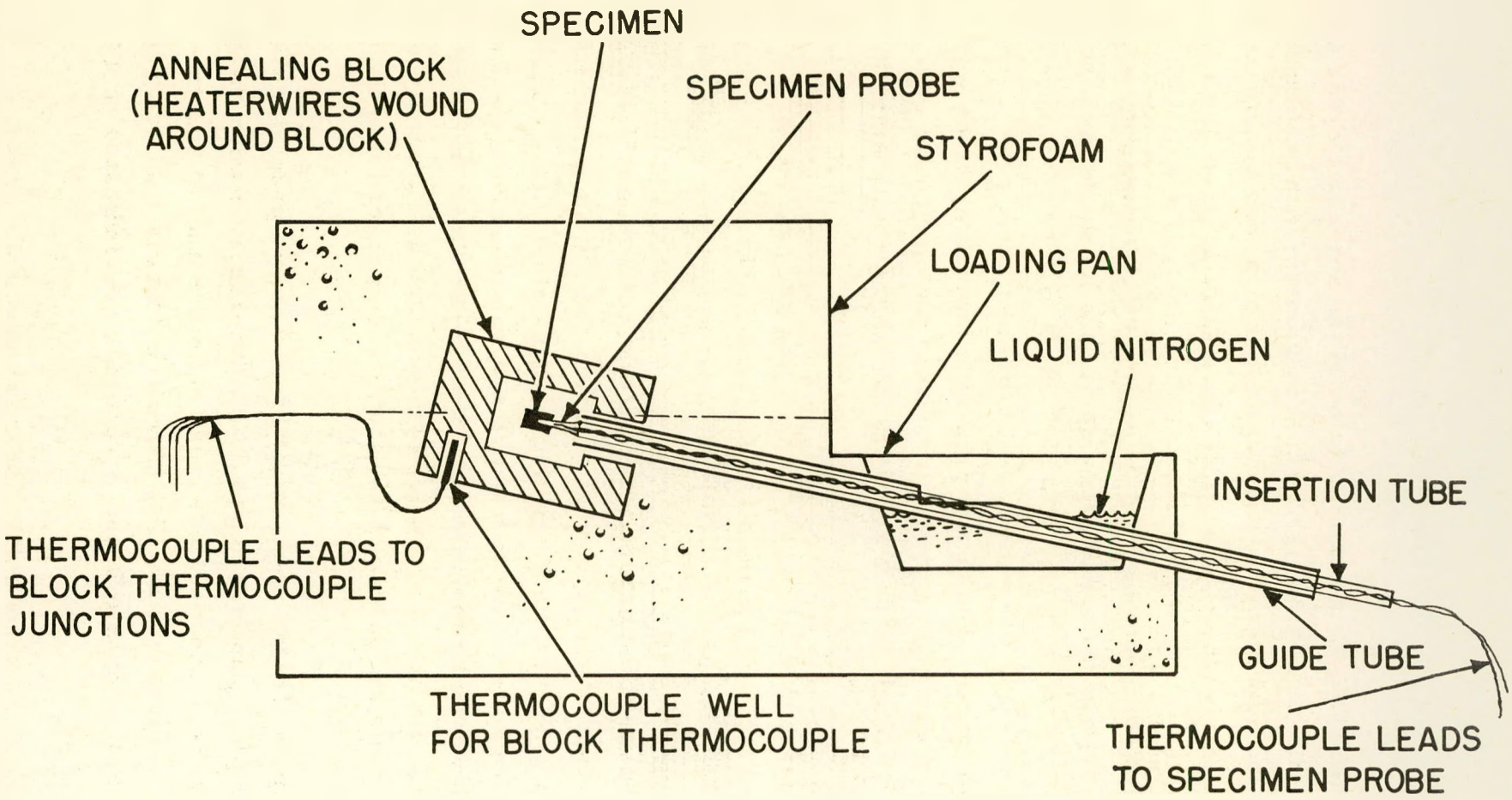

Fig. 1. Loading and Annealing Apparatus 9601-4384

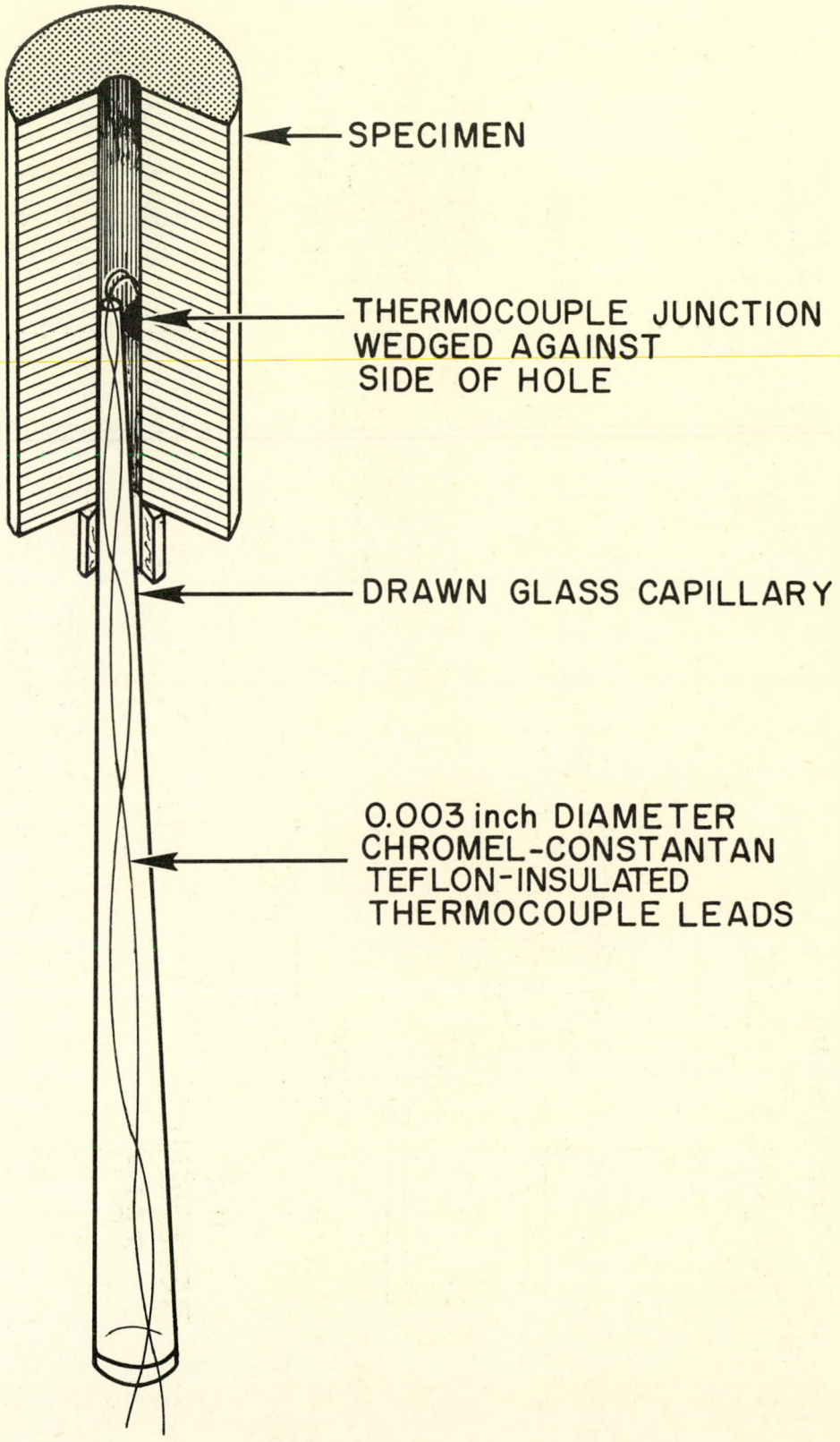

Fig. 2. Details of Specimen Thermocouple Probe

14

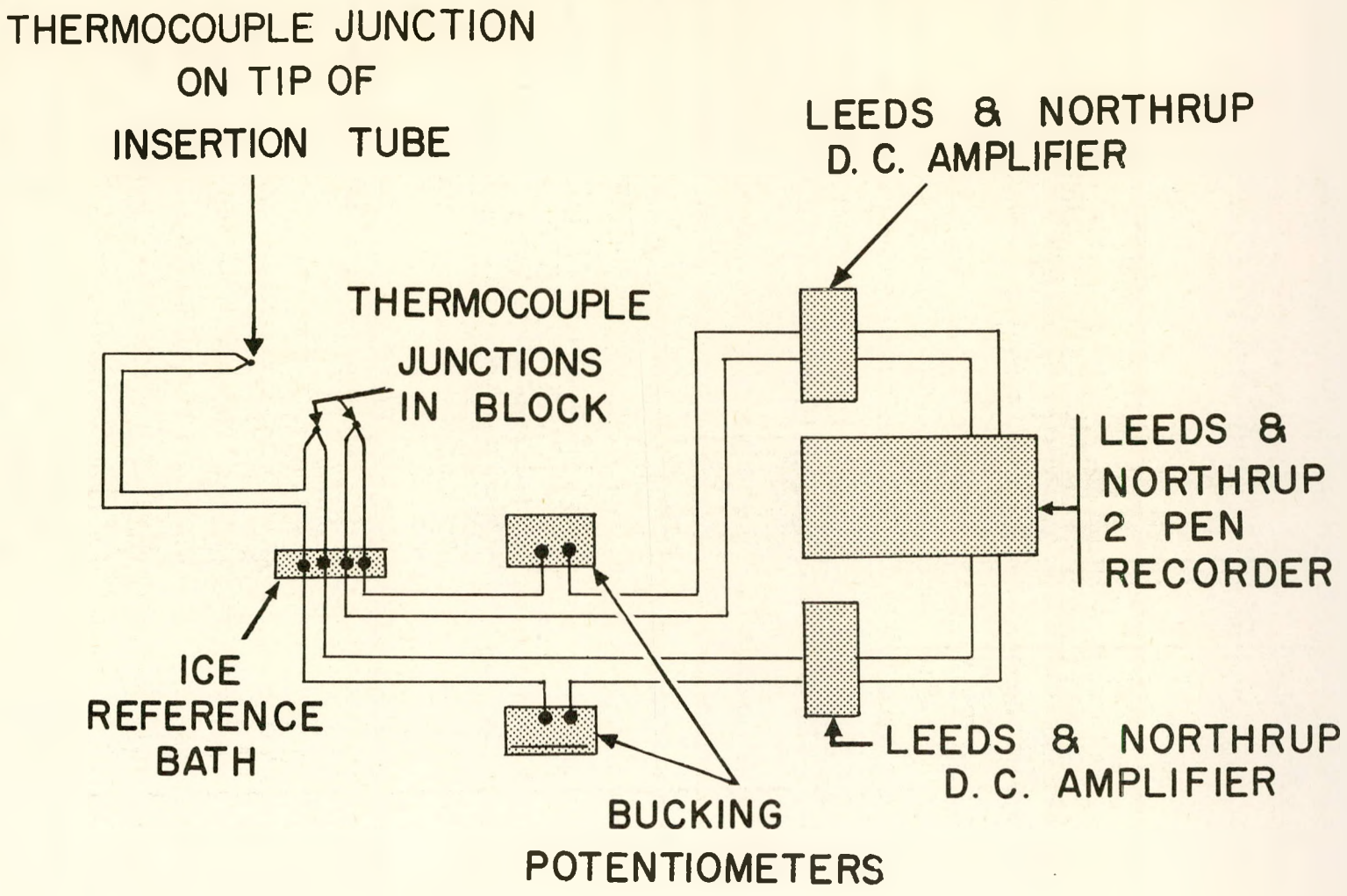

Fig. 3. Thermocouple and Recording Circuits 9601-4372

Figs. 4 and 5 are photographs of the apparatus except for the recorder. The copper tube that appears wound around the block was intended for cooling purposes, but was not needed. Two of the potentiometers shown in Fig. 4 were used in the thermocouple-recording circuitry, while the third was used to monitor the heating current.

Early in the trial experiments it was found that traces of moisture on the specimen or in the block cavity would cause considerable disturbance in the specimen's thermal behavior at 0° C. Consequently in preparing for an experimental run, steps were taken to eliminate moisture. Care was taken to keep the specimen dry, and keep moisture from condensing. The cavity was therefore flushed with dry nitrogen while warm and also while the block was being cooled to the desired temperature. Thus, a dry nitrogen atmosphere was always provided in the cavity, permitting reproducible energy transfer characteristics between the cavity walls and the specimen.

In preparation for the spectral anneal type of experiment, the block was cooled by simply pouring liquid nitrogen onto the copper block through a hole in the top of the styrofoam block. The specimen was then mounted on the tip of the insertion tube as shown in Fig. 2 and pushed part way into the guide tube to permit evaporation of the liquid nitrogen from the specimen. Change of the thermocouple output indicated on the recorder when the nitrogen had boiled off. Before the specimen temperature rose to an undesirable level, the specimen was inserted on into the block. With this final insertion the annealing run was begun.

At the same time that the specimen was inserted into the cavity center, the heating current was started through the heater winding on the block. During the course of the experiment the current was kept constant, resulting in a steady but not quite constant rate of temperature rise, which varied from approximately 4.1 degrees per minute at 110° K to approximately 2.5 degrees per minute at room temperature. The thermal mass of the block was great in relation to the thermal mass of the specimen so that the heating rate of the block was not significantly affected by the stored energy release from the specimen.

When the anneal had been carried to the maximum temperature desired, the system was cooled again to liquid nitrogen temperature and the heating cycle was

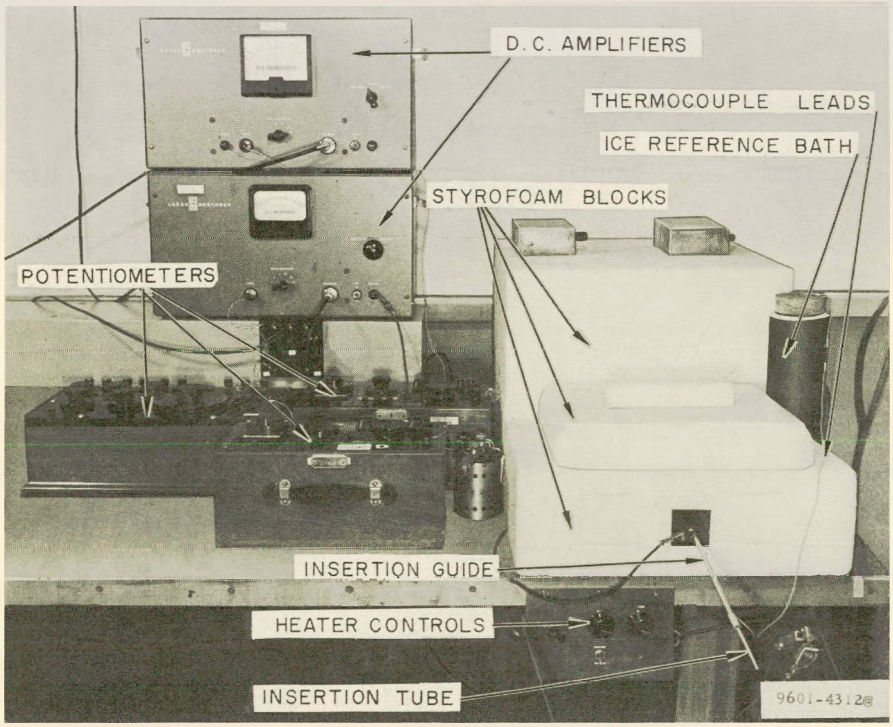

Fig. 4. Photograph of Apparatus (except recorder)

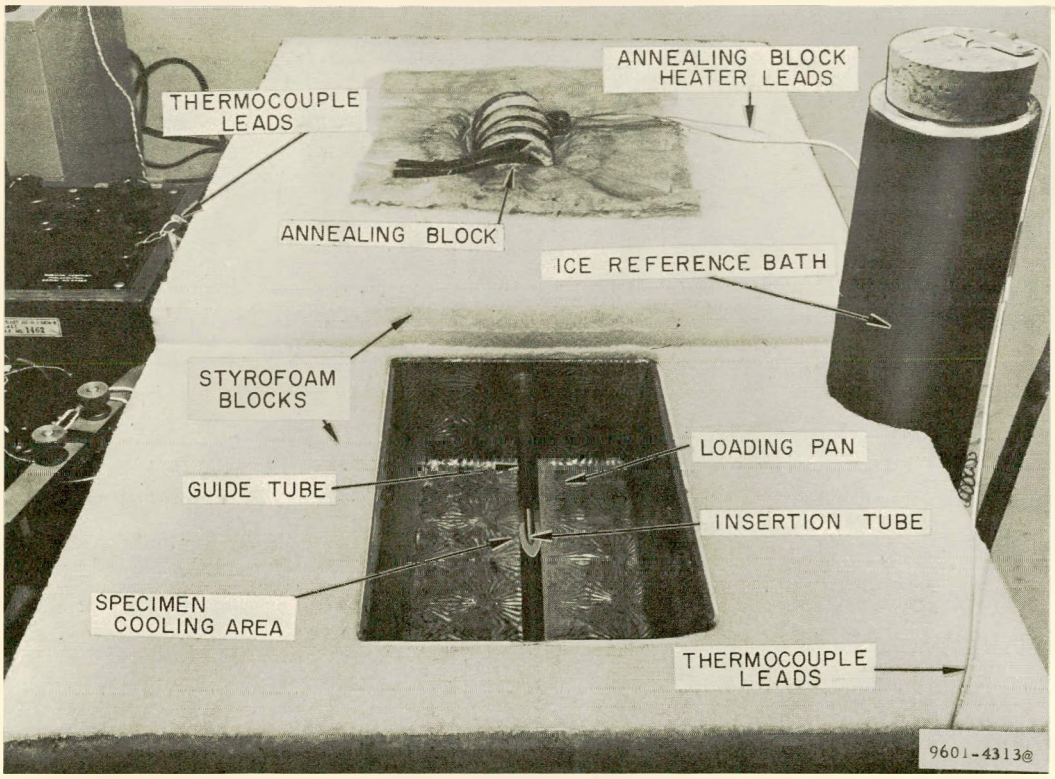

Fig. 5. Photograph of the Annealing Block and Loading Pan in Place, in the Styrofoam Block

repeated for the post-anneal run. This was done without disturbing the specimen so that precisely the same geometrical conditions would exist for both runs.

The method of performing an isothermal anneal was somewhat different. The top piece of the styrofoam block was replaced with one containing a vertical six inch diameter cylindrical hole in the center, which permitted exposure of the top side of the annealing block. To stabilize the block temperature at 200° K this hole was filled with crushed dry ice, and then covered with an insulating cover. For stablilizing at 0° C, a plastic bag filled with ice and water was positioned in the hole. For temperatures above room temperature, a heater, suspended in the water-filled bag, was utilized. At each of the temperatures, the system was maintained for a day or more to allow all parts to come to thermal equilibrium before the experiments were performed.

For the isothermal anneal, as with the spectral anneal, the sample was rapidly inserted and the specimen temperature recorded as the anneal progressed. When the anneal had progressed for a reasonable length of time, the post-anneal run was made. To prepare for the post-anneal run, the specimen was withdrawn into the loading pan, cooled once more to the starting temperature and then re-inserted. In doing so, the specimen was inserted to the same geometrical position as nearly as possible.

On the spectral anneal, we may assume that all of the stored energy has been released during the annealing run, except at temperatures close to the maximum annealing temperature. At the termination of an isothermal anneal, there is still a measurable release which complicates computations for the post-anneal run. It can be shown that the continued stored energy release during the post-anneal run leads to an effective shift from zero of the ΔT value at equilibrium conditions. Since the short time interval needed for a post-anneal run did not permit an appreciable change in the rate of stored energy release, and since the effective zero-shift is readily obvious on the recorder chart, the corrections have been easily incorporated into the isothermal anneal calculations.

Data obtained from the isothermal anneals shows that two assumptions made for the spectral anneals were not strictly valid. It was assumed that the transfer coefficient was a function of only T and not of ΔT. Close examination of data from

post-anneal isothermal runs disclosed that there was a slight dependency between α and ΔT, as shown in Fig. 6. However, since ΔT was usually between 0 and 2.0° K for the spectral anneals, there was no gross error involved in assuming α to be independent of T. The other difficulty was in assuming $\Delta T = 0$ for equilibrium conditions. Actually, $\Delta T = + 0.1°$ K at low temperatures and - 0.05° K at room temperature for equilibrium conditions. The error introduced into the evaluation of α, and therefore of $\frac{dL}{dT}$, from this source was, in the worst case, a maximum of 15 per cent at 100° K, 5 per cent at 140° K, 2 per cent at 180° K, 0 per cent at 220° K, and 3 per cent at 300° K. The justification for the simplifying assumptions lies in the initial intent of the experiment, and in the great amount of work that would otherwise be necessary to completely calibrate the experiments. Notice that these errors effect absolute values only, and not reproducibility between annealing run and post-anneal run. Since both of these discrepancies could be easily measured for the isothermal anneals they were incorporated into the calculations for same.

In all of the computations, it was assumed that the specific heat of the specimens annealed to room temperature was that of normal graphite. The preciseness of this assumption is not known, but it is probably sufficiently good for this experiment, for the following reasons. Irradiations at room temperature introduce relatively small changes in specific heat for the light irradiations reported here[7, 13] and presumably annealing to room temperature will produce approximately the same damage condition as an equivalent room temperature irradiation. It has been reported recently[12] that there is a variation of specific heat between Ceylon natural graphite and Acheson graphite CS grade, wherein the variation reaches a maximum of about 8 per cent at 290° K. While careful consideration of all these points will affect absolute values of stored energy release, the relative variation with temperature is not significantly altered. The values of specific heat published by DeSorbo and Tyler[5] were accepted as typical.

Since the recorder charts reflected the functions of T_B and ΔT *vs* time, the experimental data were measured from the charts as T_b, dT_b/dt, T, and $d\Delta T/dt$. The accuracy of these measurements, hence of $\frac{m}{\alpha} C$ and $\frac{m}{\alpha} C^*$, was within 1 per cent excepting for the extended periods of isothermal annealing. On the spectral

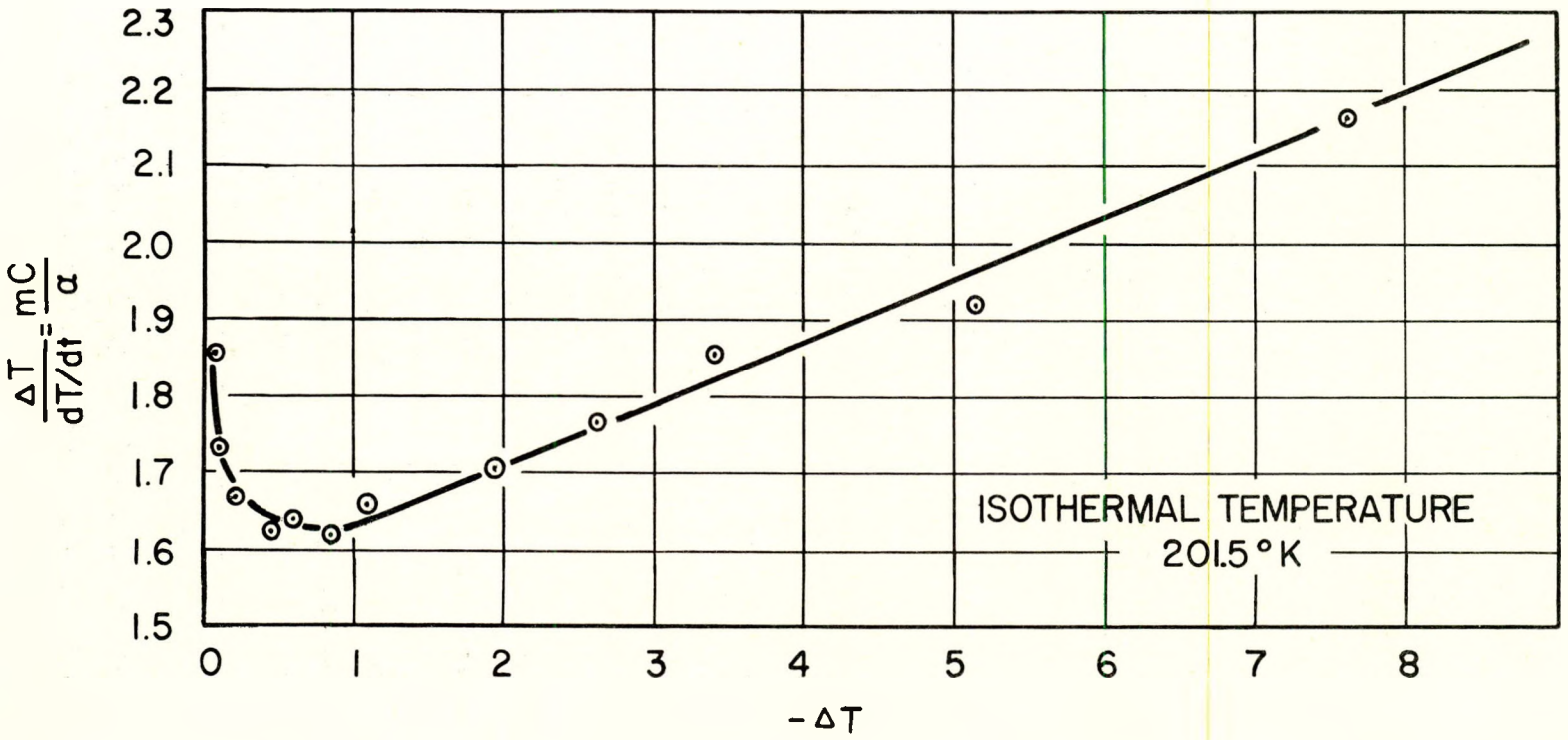

Fig. 6. Typical Function of $\frac{mc}{\alpha}$ vs ΔT °K

9601-43124

TABLE I

SPECIMEN DESCRIPTION

Sample Number	*Size	Graphite Type	Irradiation Period	Hanford Equivalent
B-1	S	AWG	5,915 Mwh	20 Mwd/ct
B-2	S	AWG	5,915 Mwh	20 Mwd/ct
B-3	S	AWG	5,915 Mwh	20 Mwd/ct
B-4	S	AWG	5,915 Mwh	20 Mwd/ct
B-5	S	AWG	5,915 Mwh	20 Mwd/ct
B-6	S	AWG	5,915 Mwh	20 Mwd/ct
B-7	S	AWG	5,915 Mwh	20 Mwd/ct
B-8	S	AWG	5,915 Mwh	20 Mwd/ct
B-9	S	AWG	5,915 Mwh	20 Mwd/ct
B-17	L	PBNG-C	5,915 Mwh	20 Mwd/ct
B-18	L	AWG	5,915 Mwh	20 Mwd/ct
B-19	L	AWG	5,915 Mwh	20 Mwd/ct
B-20	L	SA-25	5,915 Mwh	20 Mwd/ct
B-25	S	AWG	22,293 Mwh	74 Mwd/ct
B-30	L'	AWG	22,293 Mwh	74 Mwd/ct
B-33	S	AWG	1,909 Mwh	6 Mwd/ct
B-35	L'	AWG	1,909 Mwh	6 Mwd/ct
B-36	S	PBNG-G	22,293 Mwh	74 Mwd/ct
B-37	S	PBNG-G	22,293 Mwh	74 Mwd/ct
B-51	S	PBNG-I	22,293 Mwh	74 Mwd/ct
B-62	S	SA-25	22,293 Mwh	74 Mwd/ct
B-74	S	Ceylon Natural	22,293 Mwh	74 Mwd/ct
C-385	†	AWG	1.8 Mev deuterons 48 1/2 ± 2 hr/cm^2	- -

* S = Small Sample 1/8 in. diameter by 3/16 in. long

L = Large Sample 5/32 in. diameter by 1/4 in. long

L' = Large Sample 3/16 in. diameter by 1/4 in. long

† Six disks 1/8 in. diameter by 1/32 thickness, enclosed in a thin-walled graphite capsule for annealing.

anneal this 1 per cent accuracy results in reproducibility of 0.0002 (cal/gm)/° K at 77° K and ± 0.002 (cal/gm)/° K at 300° K.

In view of the care exercised during the experiments, it is believed that the variation in the experimental factors which could influence reproducibility i.e., moisture, gas composition, and geometrical positioning, do not cause errors greater than the data-measuring errors.

V. EXPERIMENTAL RESULTS AND DISCUSSION

Data relative to the graphite specimens which were irradiated at low temperatures and annealed in the two manners described are listed in Table I. The data derived from the annealing experiments are given chiefly in the form of graphs. General qualitative considerations of the data will be made in the following discussion.

TABLE II

INTEGRATED STORED ENERGY RELEASE

Brookhaven Low-Temperature Irradiation	Hanford Equivalent	Peak Height @ 210° K	Energy Release in Range 110° K - 275° K	Total Release ^{14} Above Room Temperature
Mwh	Mwd/ct	cal/gm/°K	cal/gm	cal/gm
1,909 Mwh	6.3	0.0146	1.36	4.3
5,915	20.	0.0478	4.95	13.
22,293	74.	0.170	16.50	45.

A. DAMAGE RATES

Table II denotes measurements of irradiation damage in Peak Height at 210° K and in Total Stored Energy released between 110° and 275° K. The rate of accumulation of energy, releasable between 110° K and 275° K, in the Brookhaven reactor low temperature facility, is approximately linear to at least 22,000 Mwh, and is quantitatively approximately (0.76 calories/gram) 1000 Mwh or (1.4 cal/gm/10^{18} nvt.

From the scattering experiments of Antal, et al,[16] we can estimate the fractional number of atoms displaced from the lattice. If we estimate that one-third of these are responsible for the low-energy annealing, then the above figures on stored energy correspond to approximately 3 to 6 ev per annealing atom. This is about the same as the 4 ev estimated[17] to be required for the energy of vacancy formation in graphite.

The amount of irradiation received in the Brookhaven reactor can be related to equivalent Hanford irradiations by a factor* obtained in this laboratory.[15] Table II lists these equivalent values, and gives the values of total stored energy release for specimens receiving the same amounts of irradiation at room temperature.[14] By comparing data it is seen that the amount of stored energy released below 0° C is approximately one-third that released above 30° C.

Of some interest is the so-called "catastrophic" release of stored energy, that is, a temperature rate of energy release that is greater than the specific heat. From the data presented here, it is seen that a "catastrophic" release at about 200° K does not occur for irradiation less than about 35 Mwd/ct equivalent Hanford irradiation. According to the work done by Lees and Neubert[6] a catastrophic release does not occur at about 200° C for irradiations of less than about 39 Mwd/ct. One can estimate from the data of Lees and Neubert,[6] and by use of visual comparison between dL/dT and C in Fig. 9, that with an irradiation of 100 Mwd/ct at liquid nitrogen temperature, the graphite temperature could rise spontaneously in a more or less adiabatic environment from 150° K to around 300° C. It may be interesting, perhaps from an engineering sense, to consider the rate of temperature rise resulting from "catastrophic" energy rise, when adiabatic conditions are assumed. Such a temperature rise, estimated from the annealing data presented in the next section, would be between the extreme limits of 5 and 19° K/min at 220° K, i.e., near the low-temperature annealing peak, for the 22,293 Mwh irradiation. This rate of temperature rise is too small to be deemed explosive, and compared to rates of temperature excursion in reactor operation, would appear to be of minor consequence even if it should ever be considered as affecting reactor behavior, unless considerably longer, low-temperature irradiations were anticipated.

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* The equivalence factors are: 300 Mwh (Brookhaven) = 1 Mwd/ct (Hanford) = 1.7×10^{17} nvt for energies > 0.5 Mev.

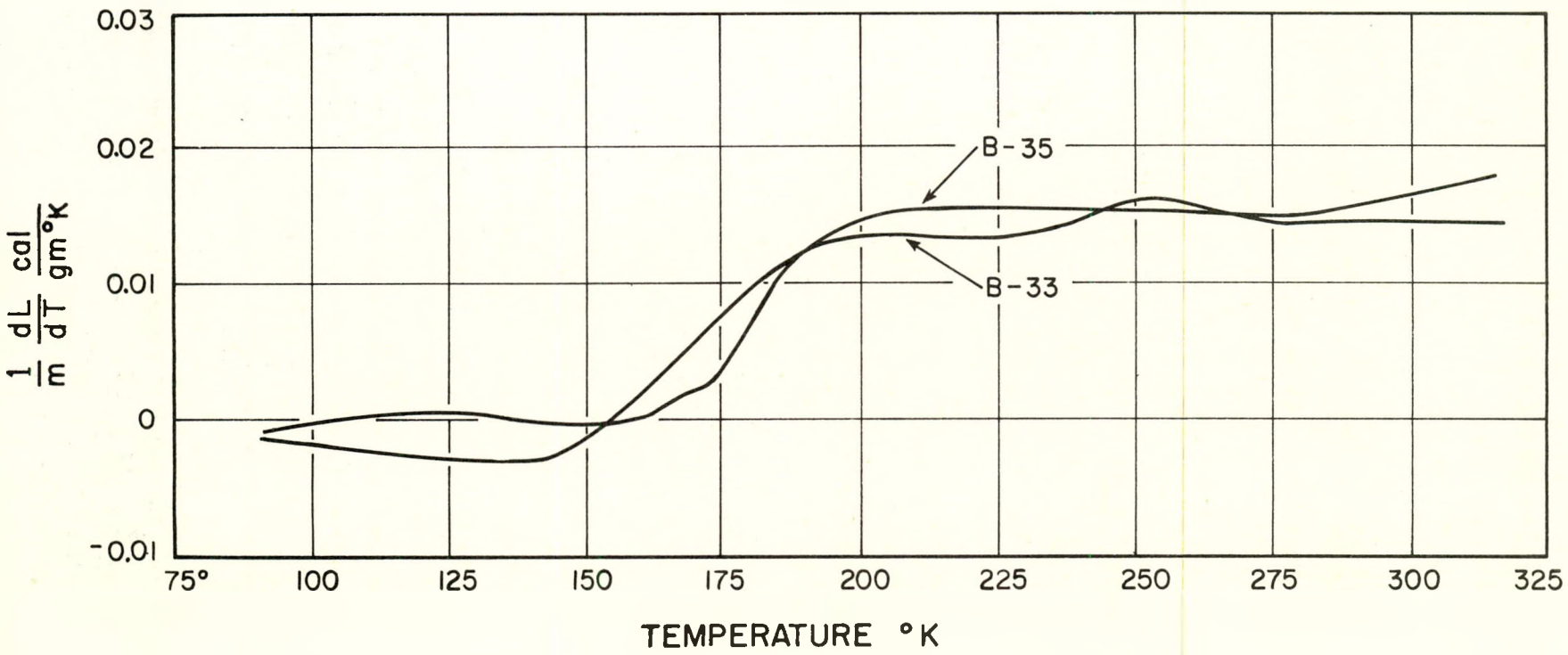

Fig. 7. Spectral Anneal. 1,909 Mwh Irradiation

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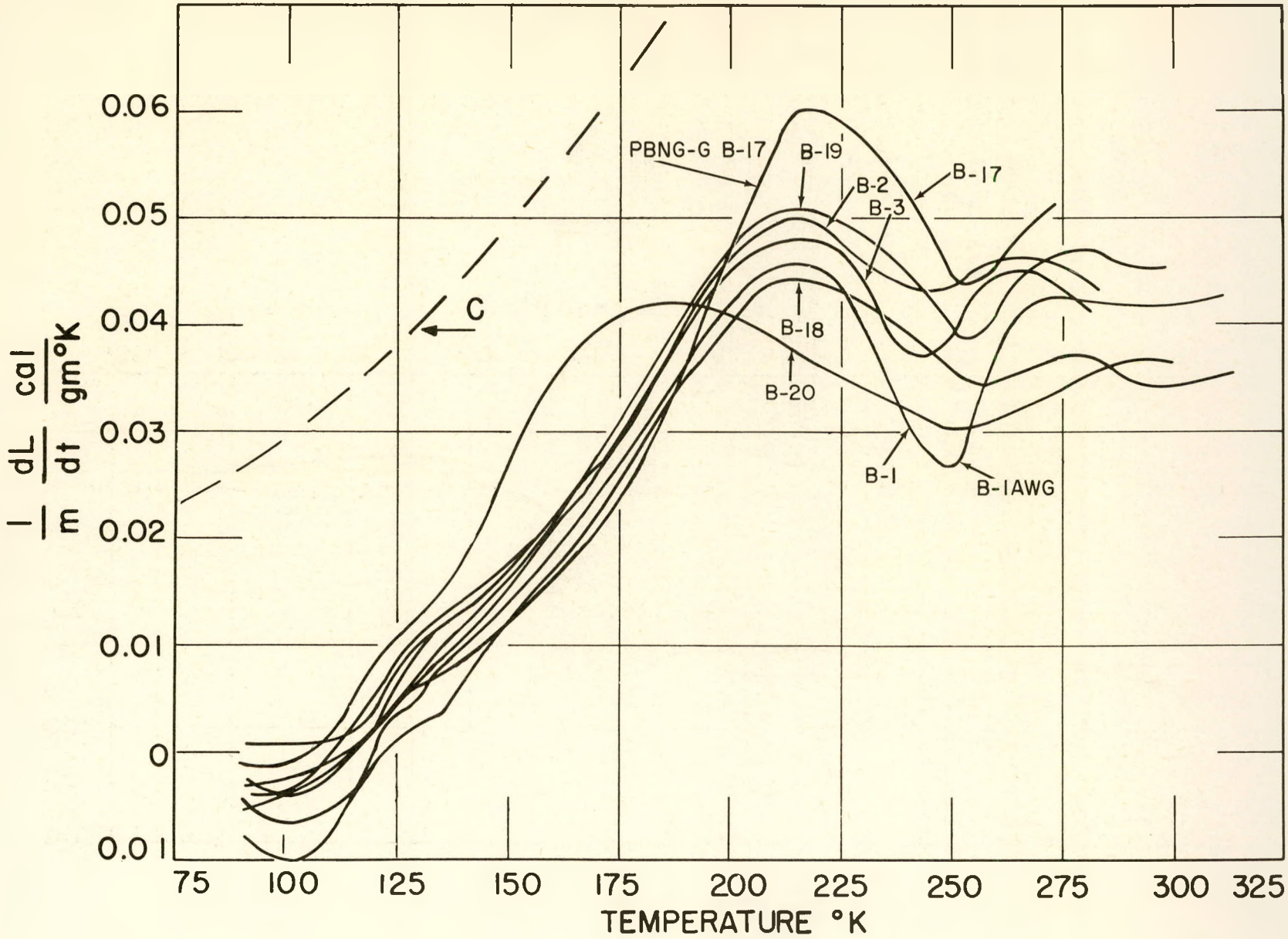

Fig. 8. Spectral Anneal. 5,915 Mwh Irradiation

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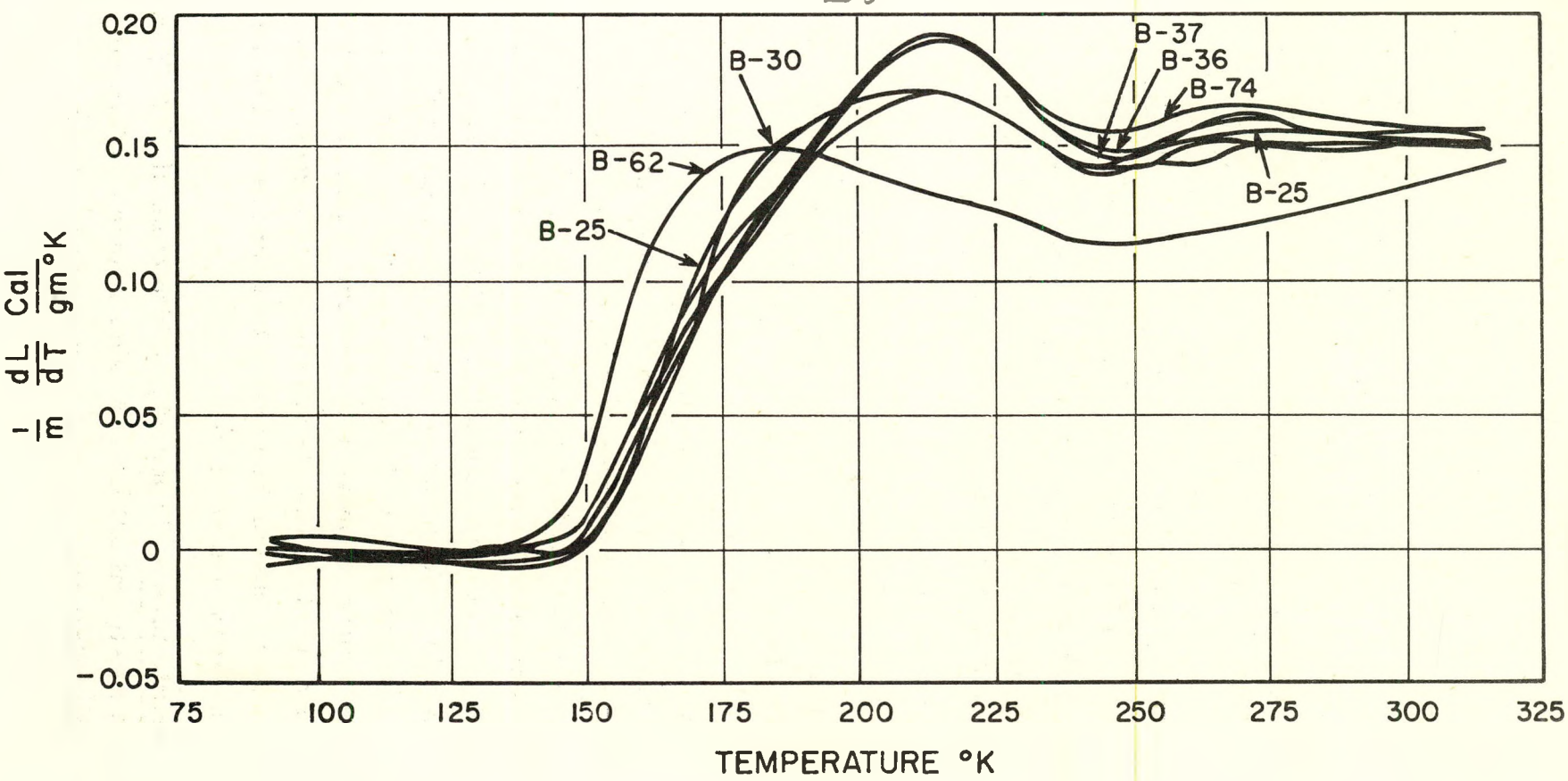

Fig. 9. Spectral Anneal. Irradiation to 22,293 Mwh

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B. ANNEALING RATES

1. Shape of Spectral Energy Release - The annealing spectra derived from intermediate and long irradiation tests are quite similar in shape. The general features will be considered first, followed by a more detailed discussion. The spectra for the low irradiation tests are not exactly similar, probably because the derived values of stored energy release are small relative to the experimental and data reduction errors. The most prominent features of the curves are the peaks which appear at 185-215° K and at approximately 275° K. Previous data [6, 3] show that an annealing peak occurs at about 475° K, so that, unless the 275° K peak shown in this report merges with the 475° K peak, there are three peaks in the spectrum of stored energy release, each probably involving unrelated types of annealing mechanisms. The breadth of the low-temperature peak should be noted; it will be referred to again later.

The initial portion of the curves in Figs. 7, 8, and 9 show an apparent negative stored energy release. Although the effect is small, and variable in magnitude, the direction of displacements of the curves are consistent with only a few exceptions. In many cases the magnitude of the effect is beyond the reproducibility limit of 1 per cent and therefore is probably real as shown in the figures. A probable explanation for this, having interesting implications lies in the following interpretation. In the low temperature region of each annealing spectrum i. e., below the annealing temperature, there is no releasable stored energy. Furthermore the negative stored energy release can be considered as an increase in the true specific heat as a result of irradiation. The liklihood of this will be explored further in a later section. It is also possible that some sort of irreversible chemical reaction related to the preceding irradiation may be responsible. In order to evaluate these various considerations it will be necessary to make careful specific heat measurements at temperatures well below the irradiation temperature, where one can be certain that irreversible changes do not occur during the course of the experiment.

2. Effect of Crystallite Size - Types of graphite other than AWG were used in these studies to permit a determination of the importance of grain size in the annealing process. It is possible that if grain boundaries do play a role in the

basic mechanism of damage and annealing, then it could be most easily observed in the low-temperature regions. Presumably, the grain boundaries would serve as defect traps in either of two ways, i. e.

a. To trap carbon atoms as they are driven from the lattice during irradiation. These trapped atoms might then move back into the lattice during thermal annealing.

b. To provide a sink for interstitial atoms diffusing through the crystallite lattice during thermal annealing. In this instance it is presumed that the vacancies do not move, since Dienes has shown that the activation energies for vacancy migration are relatively high.[11]

Other mechanisms might be proposed by which crystallite size could influence activation energies. For example, the potential fields inside the crystal lattice might be sensitive to the proximity of the crystallite boundaries. A close boundary could then lower activation energies of diffusion and allow defects to migrate more easily and thus facilitate annealing at lower temperatures.

In Figs. 8 and 9 the spectral anneal curves are shown for SA-25, composed of very small crystallites; AWG graphite, composed of intermediate-sized crystallites; and for Ceylon natural and pitch bonded natural (PBNG-G) graphite, the latter two being composed of very large crystallites. In the figures it may be observed that the SA-25 has a broad peak at about 183° K while the Ceylon and PBNG-G have a sharp and much higher peak at about 215° K. The curve for AWG lies somewhere between these two extremes.

This dependency on graphite type can be explained if it is assumed that interstitial defects, initially distributed uniformly, diffuse during annealing to sinks at crystallite boundaries. Preliminary computations for annealing rates based on this model and using estimated crystallite sizes of 300Å average diameter for SA-25 and 3000Å for AWG graphite, show a temperature shift in the annealing peak position which is in good agreement with the experiment. The activation energy of defect diffusion was found from these computations to be approximately 0.4 ev. The breadth of the annealing peak, as previously mentioned, may be attributed to either a range of activation energy or a range of crystallite sizes within a particular specimen, or both.

C. SPECIFIC HEAT

An increase in specific heat has been reported[7] for a sample of graphite which received a high irradiation in the Hanford reactor resulting in a stored energy content of 475 cal/gm at room pile temperature. At 13° K, the reported specific heat for the same sample was double the normal specific heat, and the excess increased in magnitude to 0.075 cal/gm-atom° K, or about 3.5 per cent of the normal value at room temperature. There are also other instances of increase of specific heat reported in the literature.[8]

The increase observed in the present experiment occurs for a much lower irradiation than that referred to above, presumably because of the retention of certain types of damage at low temperatures, which do not survive at higher temperatures. It is possible to explain this increase in terms of isolated interstitial atoms, using theoretically reasonable physical constants.

Let us consider an isolated interstitial which might be expected to act as an Einstein Oscillator with fairly low characteristic temperature for motion in the "a" direction, and estimate the contribution of an isolated Einstein oscillator as follows: Assume the interstitial vibrates in a parabolic potential well with a potential barrier of 0.6 ev[11] at half the inter-atomic spacing (a) in the lattice; the restoring force then would be, $1.3\ 10^{4}$ dyne cm^{-1}, and the frequency of oscillation would be 0.52×10^{13} / sec. This yields a characteristic temperature of $\theta_E = h\nu/k \simeq 200°$ K where h is the Planck constant, ν the frequency, and k the Boltzmann constant. The average energy of a group of such two-dimensional oscillators would then be[9]:

$$\overline{E} = 2N_i \left(\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \right), \qquad \ldots (9)$$

where N_i is the number of interstitial atoms per unit volume. The specific heat derived from this is

$$C^E \simeq C_v{}^E = \frac{d\overline{E}}{dT} = \frac{2N_i k e^{\theta_{E/T}}}{\left(C^{\theta_{E/T}} - 1\right)^2} \left(\frac{\theta_E}{T}^2 \right). \qquad \ldots (10)$$

Then, at 50° K, the specific heat due to the isolated interstial atoms would be

$$C^E = 0.608\, N_i k \quad . \qquad \ldots(11)$$

At 50° K, the normal specific heat of graphite is[10]

$$C^n = Nk\ 14.4 \left(\frac{T}{\theta}\right)^2 \qquad \ldots(12)$$

where N is the number of atoms per unit volume in the normal lattice and θ = 900° K.[10] For the specific heat to be doubled at 50° K by isolated interstitial atoms, the relative density would have to be

$$C^n = C^E \qquad \ldots(13)$$

then,

$$\frac{N_i}{N} = \frac{0.0436}{0.608} = 7.2 \text{ per cent} \qquad \ldots(14)$$

Hence a density of 7.2 per cent interstitial carbon atoms could cause the observed specific heat to be double that of normal graphite at 50° K. From the scattering experiments of Antal, et al., we can estimate roughly that the above density corresponds to 10^{21} nvt. This very rough calculation shows that if interstitials can survive as lattice defects at low temperatures, they can contribute a large amount of excess specific heat, and therefore be responsible for the observed "negative" stored energy release.

The excess specific heat, which appears at lower temperatures than release of stored energy, appears to anneal out at relatively low temperatures, although the data indicating this is rather tentative. Two specimens B-4 and B-5 were annealed to 193° K (dry ice temperature) and immediately cooled again to 78° K for the post-anneal run. In both cases, the specific heat after anneal to 193° K, was identical to that obtained after the samples had been annealed to room temperature or higher. An incidental observation was that the release of stored energy started at a temperature of approximately 35 degrees higher for the long term than for the intermediate term irradiations. A knowledge of the precise temperature history of the samples during irradiations might yield an explanation for this phenomena. Since both the short and long term irradiations show no release of stored energy

below 150° K, and since they were handled together during and after irradiation, it is possible that an unintended anneal to 150° K occurred following irradiation. It was also observed that the excess specific heat at low temperature for the long-term irradiation was somewhat lower than for the intermediate irradiation. An obvious interpretation therefore is that the lattice defects contributing to the excess specific heat annealed to more stable positions at between 115° K and 150° K. In Fig. 8, there appears a small but reproducible peak at about 125° K superimposed on the much larger main peak. It is quite plausible, in view of the preceding discussion, to credit this small hump as being due to the energy released when the isolated interstitial atoms migrate to more stable lattice positions; and to think that these isolated interstitials contribute to most, if not all, the excess specific heat measured at the lower temperatures. In this picture the loss of isolated interstitials at 125° K is accompanied by a very small release of energy and therefore the original density of such atoms was either quite small or the new metastable state has only slightly less potential energy than the original had.

Since these considerations are based in part on incidental and speculative data, the data should be confirmed by refined methods of measuring the specific heat. If it can be demonstrated that the increase is due to isolated interstitial atoms, specific heat measurement may well prove to be an important tool in detecting and measuring small-scale atomic rearrangements, not only in graphite, but in other crystalline materials as well.

In the same sense that the increase in specific heat can be tentatively explained in terms of isolated interstitials, interstitial clusters of atoms may contribute to an increase in specific heat, but to a lesser extent due to the tighter binding forces holding the cluster together. This may in part account for the increase of specific heat observed in specimens heavily irradiated at room temperature, but other effects undoubtedly contribute due to the much higher disruption of the crystal lattice with heavy irradiation.

D. ISOTHERMAL ANNEAL

Isothermal anneals were performed on four samples B-6, B-7, B-8 and B-9 at temperatures corresponding more or less with those of peak annealing

rates as demonstrated by the spectral anneal data. These four specimens were type AWG graphite exposed to the intermediate Brookhaven irradiation.

The rates of stored energy release during isothermal anneal are shown as a function of time and integrated energy release in Figs. 10 to 14. Zero on the abscissa of each of these figures represents the instant during the anneal that the specimen temperature had risen to 5° C below the block temperature. Since the maximum overshoot of specimen temperature was less than 2° C in all cases, the graphs represent very nearly ideal isothermal anneals. The isothermal temperature of each of the anneals are shown on the graphs.

The data from the isothermal anneals have not been examined analytically for annealing kinetics. However, qualitative examination indicates that the curves agree in character with the diffusion mechanism previously referred to. In such a mechanism, defect migration to the crystallite boundaries would continue in the large crystallites even after the bulk of annealing had virtually ceased in the smaller ones. Thus, in a sample composed of a range of crystallite sizes stored energy would continue to be released for longer periods of time than extrapolation of the early portion of the annealing curve would indicate. Such annealing behavior is demonstrated by the isothermal data.

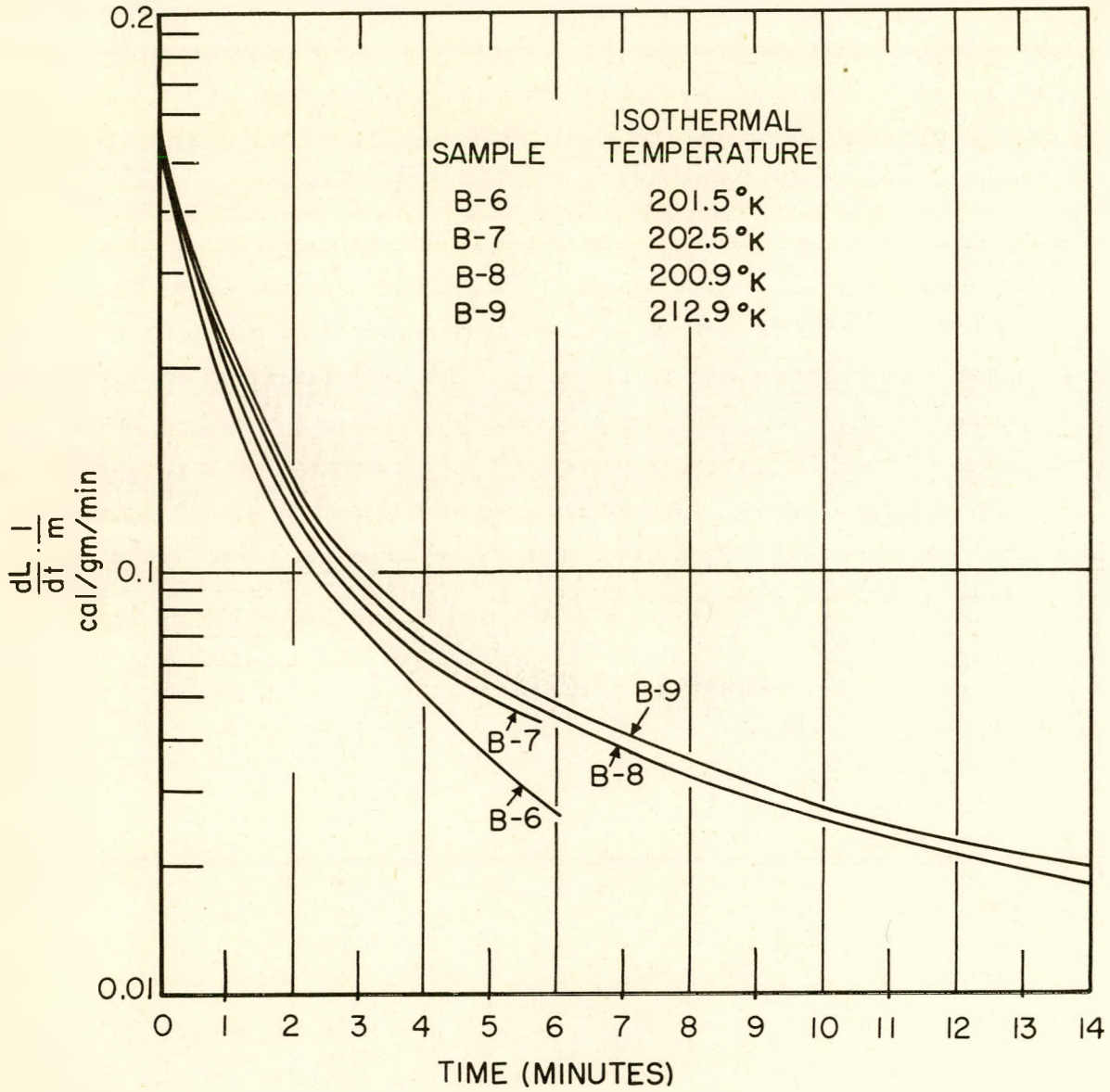

Fig. 10. Isothermal Anneal for AWG Specimens Between 200° K and 213° K

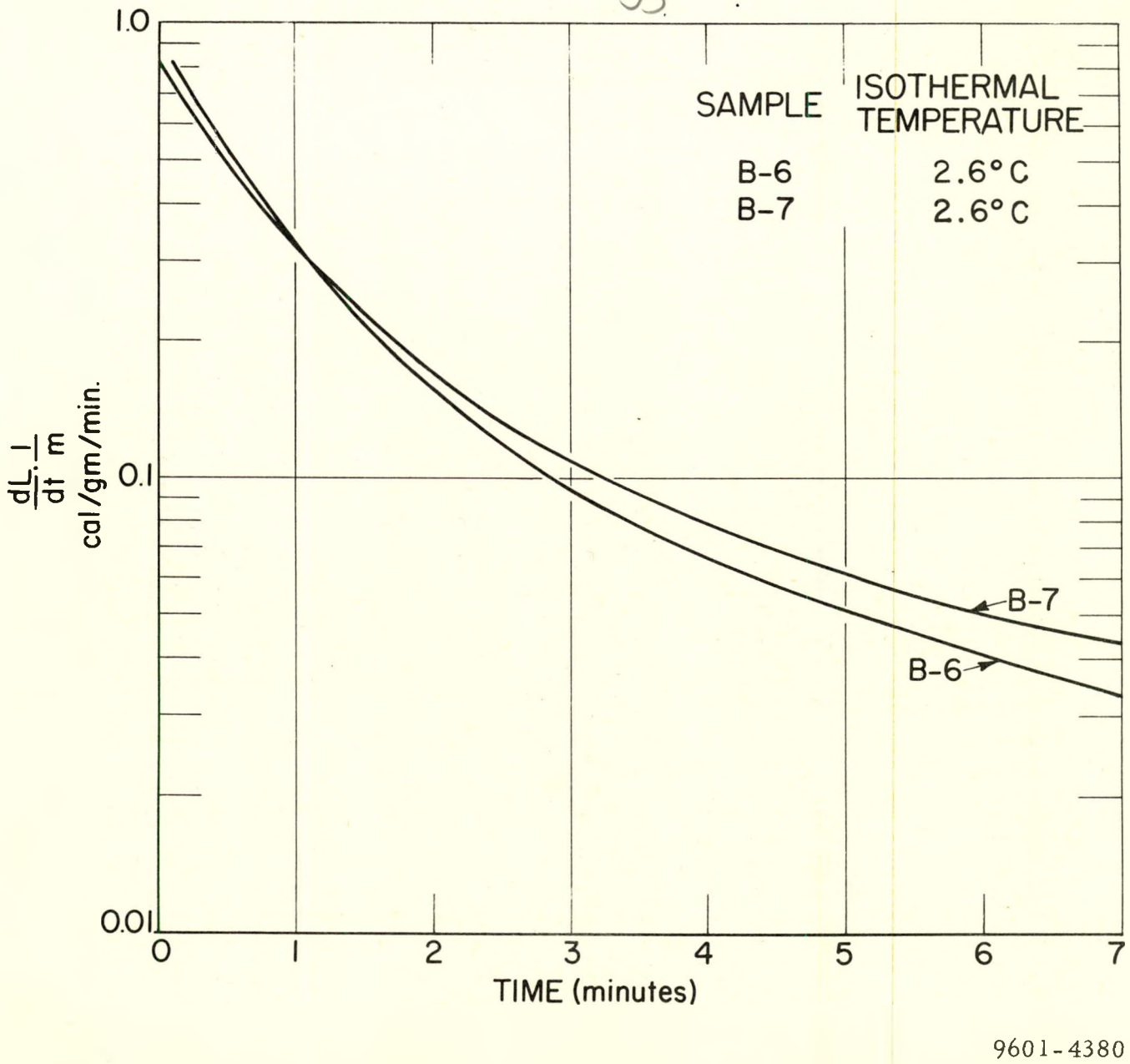

Fig. 11. Isothermal Anneal for AWG Specimens at 2.6° C

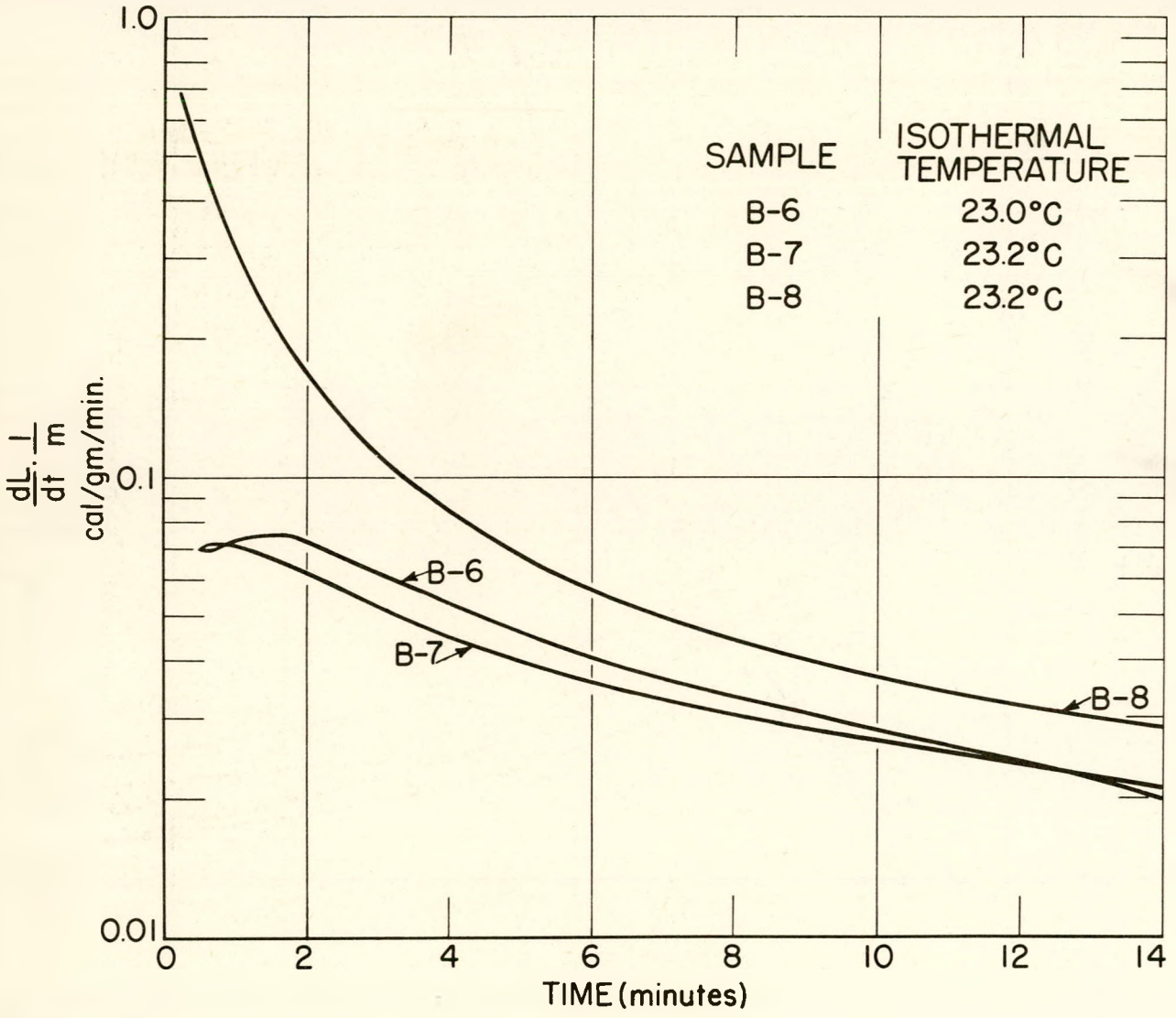

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Fig. 12. Isothermal Anneal for AWG Specimens at 23.0° C and 23.2° C

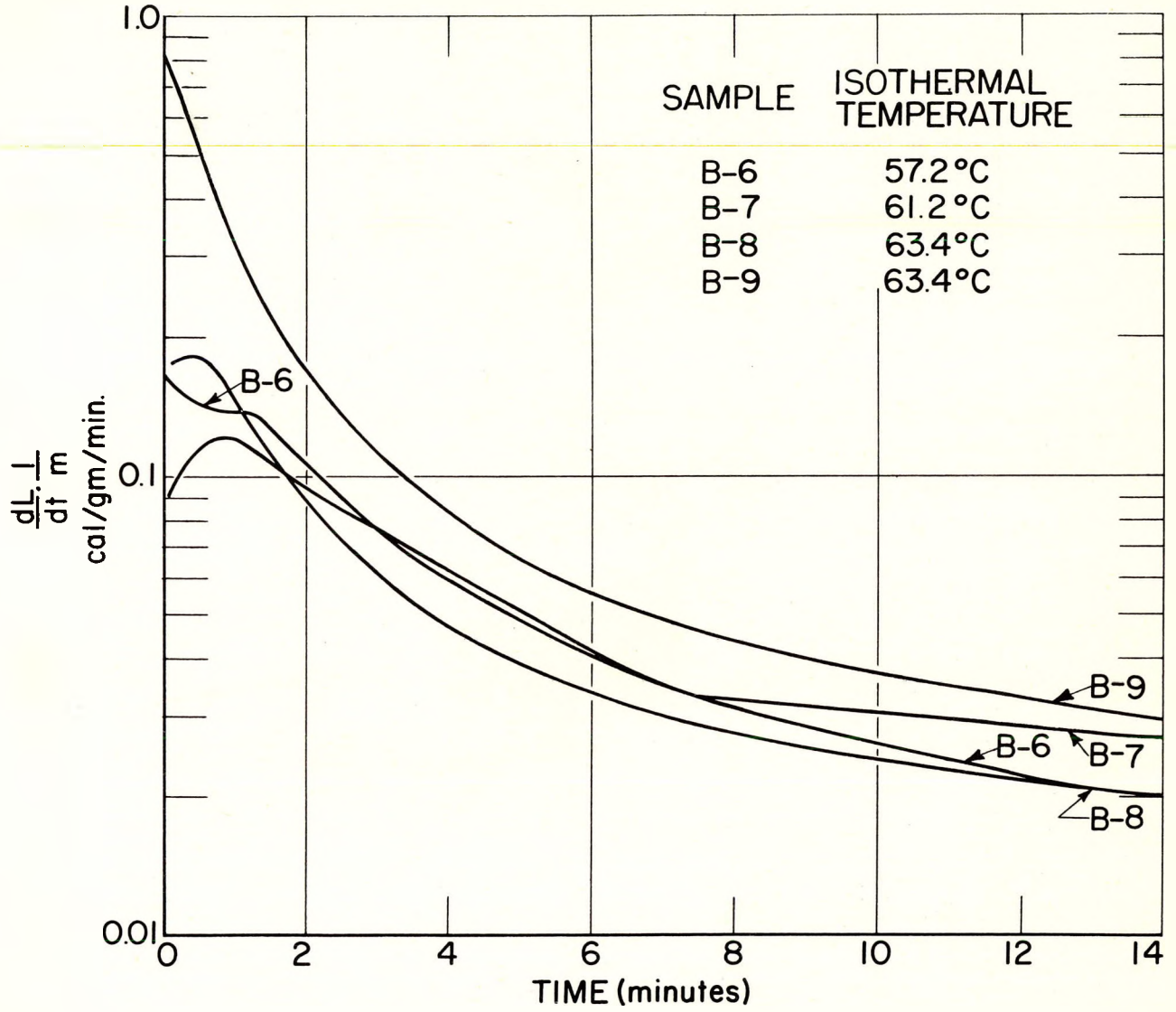

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Fig. 13. Isothermal Anneal for AWG Specimens Between 57.2° C and 63.4° C

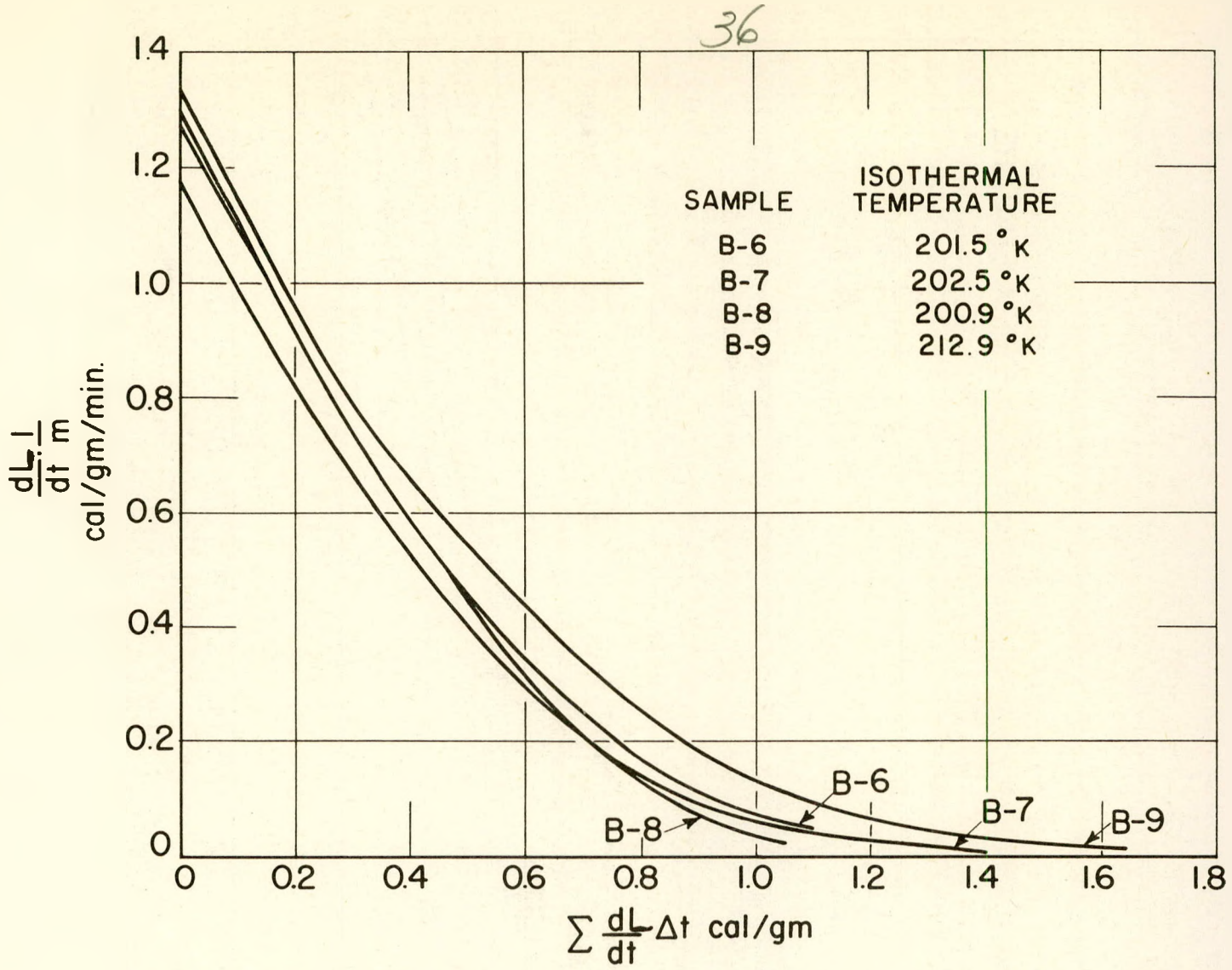

Fig. 14. Isothermal Annealing Rate as a Function of Stored Energy Released at 200-213° K

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