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PNL-2676
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Prepared for the U.S. Department of Energy
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Pacific Northwest Laboratory
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PNL-2676

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract EY-76-C-06-1830

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Available from
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United States Department of Commerce
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Springfield, Virginia 22151

Price: Printed Copy $_____*; Microfiche $3.00

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ANNEALING OF NEUTRON DAMAGE IN GRAPHITE IRRADIATED AND STORED AT ROOM TEMPERATURE

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SUMMARY

The annealing of neutron radiation damage in graphite at the same temperature at which it was irradiated is reported here for the first time. Highly oriented pyrolytic graphite samples were irradiated to fluences in the range 0.44 to 153 x $10^{15}/cm^2$ at room temperature using three different neutron sources with average energies of 1.5, 5.5. and 15 MeV, respectively. Following these irradiations, the C_{44} elastic constants of these samples were measured several times over periods up to two years during which time sample temperatures never exceeded 30°C. The C_{44} constants were observed to slowly decrease toward their unirradiated values with up to 40% of the irradiation-induced changes eventually annealing out.

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INTRODUCTION

The value of the shear modulus, C_{44}, of Highly Oriented Pyrolytic Graphite (HOPG) has been shown to be sensitive to neutron radiation at very low fluences.[1] We have used this property to determine the relative radiation damage produced by neutrons of different energies.[2] In the process of conducting the latter experiment, the shear modulus was observed to return toward its unirradiated value over periods up to two years. This phenomenon does not appear to have been reported before, and deserves further investigation.

EXPERIMENTAL

Experimental details have been described elsewhere.[2] Briefly, three grades of HOPG were irradiated to fluences in the range 0.44 to 153 x $10^{15}/cm^2$ EFF* using the Medical Research Reactor at Brookhaven National Laboratory (BNL), the (D, Be) neutron source at the University of California at Davis, and the Rotating Target Neutron Source at Lawrence Livermore Laboratory (LLL). Neutron energies in these three sources averaged about 1.5, 5.5, and 15 MeV, respectively. Irradiation temperatures in the accelerator target rooms at Davis and LLL were not measured, but were probably about 25°C and could not have been above 35°C; temperatures in the reactor at BNL were measured to be in the range 17 to 23°C. Sample temperatures during shipment back to PNL following irradiation are unknown and were not necessarily the same for the different sets of samples. About 25 samples were irradiated in each source. The shear modulus, C_{44}, of each sample was determined by measuring the velocity, V, of a 1 MHz shear wave propagated parallel to the c-axis direction. Reproducibility of the velocity measurements was about ∿1%. Modulus and sonic velocity are related[3] by

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*Fluences used here are in terms of Equivalent Fission Fluence (EFF) for Damage in Graphite[4] using the relative damage function derived by Gray and Morgan[2] rather than the Thompson and Wright function recommended by Ref. 4.

the expression

$$E \equiv C_{44} = \rho V^2 \qquad (1)$$

where ρ is the graphite density (2260 kg/m^3).

RESULTS AND DISCUSSION

Tables I to III list moduli at various times after the end of the irradiations. Possible reasons for the observed decrease of the moduli with time include thermal (room temperature) annealing, changes induced by the sonic velocity measurements, and mechanical stresses on the samples during handling.

If thermal annealing is the primary mechanism and one assumes that a single annealing process applies, then the data should fit an equation of the form:

$$E - E_\infty = (E_0 - E_\infty)e^{-ct} \qquad (2)$$

where E is the modulus at any time, t, after irradiation, E_∞ is the value of the modulus as t become large, E_0 is the modulus at the end of irradiation, and c is a constant at any given temperature. Data for individual samples can be fitted, albeit rather crudely in some cases, to such an equation assuming that E_∞ is represented by the most recent measurements listed in the last column of Tables I to III. This assumption is justified because the decrease that has occurred between the next-to-last and last measurements is small. It is insignificant at the 95% confidence level for the LLL and Davis samples. It appears, therefore, that more time and additional measurements would produce little, if any, further decreases in the measured moduli.

As an additional test to determine whether the moduli could be further decreased, some samples were annealed at 80°C. It was feared that higher temperatures would activate additional annealing processes rather than merely assure completion of those processes already active at room temperature. Following the measurements at 396 days, two Davis samples were annealed for 22 hours at 80°C with essentially no change. Following the

TABLE 1. Shear Moduli of Samples Irradiated at LLL

Sample No.(1)	Sample Type(2)	Fluence ($10^{15}/cm^2$)	Moduli (MPa) vs. No. of Days After Irradiation(3): 21	201	290	502	704	734(4)
1	1	153	2008	1735	1738	1540	1463	1480
2	1	120	1714	1624	1621	1510	1439	1223
3	1	92.5	1535	1449	1383	1284	1239	1035
4	6	75.4	1064	937	972	916	879	850
5	1	60.8	1164	1023	983	915	891	867
11	1	36.7	828	748	728	657	643	657
12	6	31.6	680	624	609	568	550	532
13	4	28.2	667	579	592	536	516	522
14	1	24.7	728	649	619	577	549	547
15	4	22.2	558	501	493	465	453	452
16	6	17.9	559	508	515	493	473	446
17	4	13.7	439	416	411	389	371	357
18	1	12.6	526	476	464	433	405	400
19	6	11.5	443	416	423	405	385	399
20	4	7.26	354	335	333	322	308	304
21	1	6.78	394	377	372	353	349	340
22	6	6.32	396	386	366	358	336	345
23	4	2.16	284	278	283	272	266	270
24	1	2.06	311	304	302	297	280	287
25	6	1.95	317	324	329	299	310	296
6S	1	47.1	901	829	739	682		
7S	1	47.1	981	869				
8S	6	47.1	841	783	796	728	722	617
9S	6	47.1	805	749	749	699	662	609
10S	4	47.1	809	712	730	665	651	655

(1) Sample numbers followed by "S" were oriented with their basal planes parallel to the neutron beam; all others were perpendicular to the beam.

(2) Refers to width, in degrees, of the (002) x-ray diffraction peak at half-maximum intensity.

(3) Before irradiation, moduli were 264, 249, and 304 MPa for sample types 1, 4, and 6 respectively.

(4) Moduli following 80°C anneal for 260 hours.

TABLE II. Shear Moduli of Samples Irradiated At Davis

Sample No.(1)	Sample Type(2)	Fluence ($10^{15}/cm^2$)	Moduli (MPa vs. No. of Days after Irradiation(3)) 6	13	19	51	136	264	396
2	1	85.6	1501	1363	1143	1105	1051	1092	1098
3	1	68.4	1367	1091	1150	1048	1083	1086	945
4	1	42.7	930	845	829	755	736	756	680
5	4	37.5	779	751	695	658	622	646	624
6	1	33.8	825	717	712	687	670		657
7	6	30.5	666	631	601	581	565		552
8	4	28.0	647	606	598	551	541		510
9	1	24.9	677	625	586	587	551		554
10	6	22.5	573	542	535	536	492		472
11	4	20.7	536	513	496	468	449		449
12	1	7.94	428	406	371	362	349		346
13	6	7.42	388	391	391	371	354		360
14	4	7.00	349	353	332	341	314		315
15	1	2.20	307	305	300	297	287		290
16	6	2.13	337	333	329	330	323		328
17	4	2.05	278	274	280	278	271		265
18	1	0.474	281	278	276	272	265		271
19	6	0.455	310	308	308	313	304		310
20	4	0.440	265	260	262	261	251		277
1S	6	51.3	953	865	856	873	821		761
2S	4	51.3	1071	1082	969	1012	887		837
3S	1	51.3		812	824	734	753		
4S	6	51.3		828	745	767	724		723
5S	6	51.3	753	726	688	704	673		677

(1) Sample numbers followed by "S" were oriented with their basal planes parallel to the neutron beam; all others were perpendicular to the beam.

(2) Refers to widths, in degrees, of the (002) x-ray diffraction peak at half-maximum intensity.

(3) Before irradiation, moduli were 264, 249, and 304 MPa for sample types 1, 4, and 6 respectively.

TABLE III. Shear Moduli of Samples Irradiated at BNL

Sample No.	Sample Type[1]	Fluence ($10^{15}/cm^2$)	Moduli (MPa) vs. No. of Days After Irradiation[2]: 7,8[3]	14,15[3] 1st	14,15[3] 2nd	21,22[3] 1st	21,22[3] 2nd	34,35[3]	61,62[3]	194,195[3]
Capsule #1										
1	1	85.2	1292	1240	1191	1064	1101	1113	1120	991
2	1		1306	1188		1149	1120	1152	1107	1068
3	1		1115	1221	1174	1110	1052	1079	994	940
4	4		1111	1095	1078	1012	1023	1005	959	929
5	4		1073	1071	1036	993	983	975	943	933
6	4		1087	1008	983	942	905	950	883	883
7	6		1018	989		955	946	946	908	891
8	6		986	956	956	912	909	906	902	888
9	6		1002	908	911	904	907	898	872	848
Capsule #2										
1	1	36.6	800	770		762	678	711	667	675
2	1		739	627	650	666	647	606	610	610
3	1		781	803		725	683	687	682	660
4	4		706	686	677	666	627	642	613	603
5	4		649	625		641	610	613	612	609
6	4		606	639		647	628	641	616	598
7	6		662	663		664	655	647	639	618
8	6		687	663	635	632	637	619	608	622
9	6		706	668		647	647	640	584	609
Capsule #3										
1	1	4.07	318	336		324	323	322	325	302
2	1		335	332		317	323	331	325	317
3	1		366	348		333	320	329	322	330
4	4		341	305		299	291	294	288	293
5	4		317	306		304	298	300	299	304
6	4		330	329		309	307	312	316	308
7	6		367	355		347	332	347	353	346
8	6		358	350		345	352	354	349	346
9	6		349	354		352	344	358	358	359

(1) Refers to width, in degrees, of the (002) x-ray diffraction peak at half-maximum intensity.
(2) Before irradiation, moduli were 264 and 304 MPa for sample types 1 and 6 respectively; for sample type 4 they were 249 MPa for capsule #1 and 261 MPa for capsules #2 and #3.
(3) First number applies to capsules #2 and #3, second number applies to capsule #1.

measurements at 194 days, all of the 6° samples from the first BNL capsule were annealed for 113 hours at 80°C with essentially no change. Annealing data for LLL samples are shown in Table I. By discounting samples 2 and 3 which appear to be in error, the average change due to annealing at 80°C is insignificant at the 95% confidence level.

A somewhat improved fit to equation 2 was made by normalizing the data for each sample to the change at infinite time, and averaging the normalized values. In other words, equation 2 was normalized by dividing by $E_\infty - E_u$ where E_u refers to the modulus of the unirradiated sample. Thus, the quantity $(E - E_\infty)/(E_\infty - E_u)$ was calculated at each time for each sample. At low fluences, where E_∞ was only slightly larger than E_u, large uncertainties exist. Also, there may be some tendency for $(E - E_\infty)/(E_\infty - E_u)$ to be larger at lower fluences. Therefore, samples with fluences lower than $8 \times 10^{15}/cm^2$ EFF were not included in the average. Results are shown in Fig. 1. The BNL data fit quite well, and a reasonable fit occurs for the LLL data. The fit for the Davis data is not as good as for the other two sets. In fact, two straight lines, one for short times and the second for longer times, would produce a much better fit. Such behavior could be explained by two different annealing mechanisms with different time constants but this is considered unlikely because the mean neutron energy at the Davis facility was mid-way between those at the BNL and LLL facilities.

Instead of, or in addition to, thermal annealing it seemed possible that the measurements themselves might somehow be causing the moduli to decrease. A few LLL and Davis samples were measured two or three times on a given day with essentially the same results each time. Only the BNL samples were systematically checked to determine if the sonic velocity measurements had any effect. The data are shown in Table III. Most of the measurements on a given day are within experimental error of one another. Nevertheless, the second measurement usually gave the lower value and, although the average of the second measurements was only slightly lower, the difference is statistically significant. Thus, there is some indication that a change occurred during the measurements.

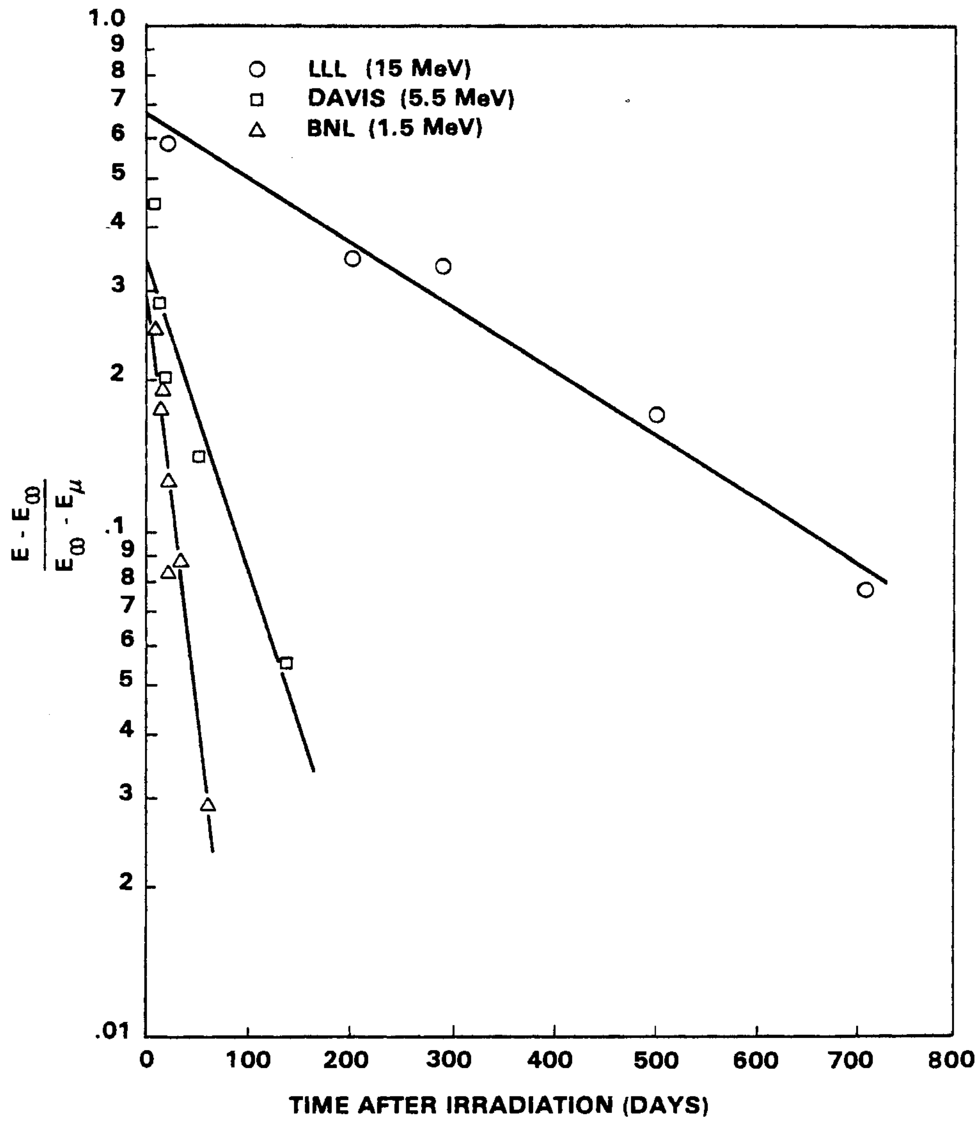

Figure 1. Change of Shear Modulus with Time.

A few samples were allowed to stand for periods up to 3 hours with the sonic waves continuously passing through them, and the measured moduli were almost exactly the same at the beginning and end of these periods. During normal measurements, waves passed through the samples for only about 5 minutes. Thus, it would appear that the energy from the sonic pulses has not caused the modulus to change.

Mechanical stress induced during handling included pressing the transducers against opposite sides of the samples together with a slight back-and-forth twisting motion to remove excess coupling agent and to make sure that a maximum signal strength was achieved (this torsional mechanical stress was sufficient to cleave about eight samples during the hundreds of measurements). Stresses of this magnitude, even when the sample was not cleaved, might have been enough to cause defect migration. To the extent that the mechanical energy supplied during preparation for a measurement was approximately the same each time, the decrease should be exponential with the number of measurements. Fig. 2 shows the same data as Fig. 1, replotted as a function of the number of measurements. The data fit a straight line relationship about equally well in both figures.

Other trends shown by the data presented in Table I to III and Figs. 1 and 2 are as follows:

- For samples irradiated in a given facility, no difference in annealing behavior was found between the three grades of graphite or between samples oriented differently relative to the neutron beam axis.
- The time constant, c, from equation 2 is much lower for the LLL samples than for the other two sample sets.
- The amount of annealing that occurred since the samples were first measured was less for the BNL samples even though they were measured more times.

There is no question that the shear moduli of all samples have decreased since the first time they were measured after irradiation, but

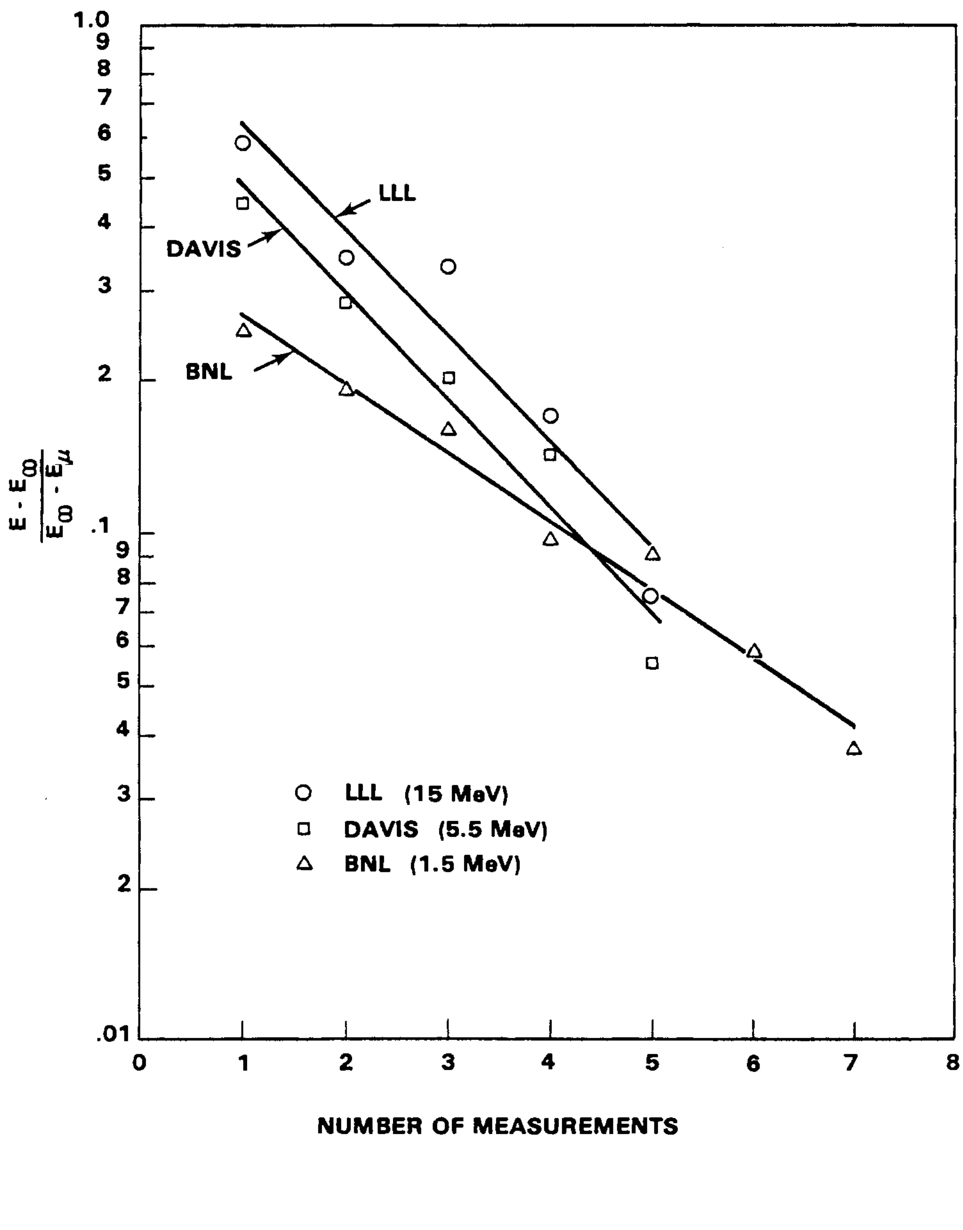

Figure 2. Change of Shear Modulus with Number of Measurements.

the cause or causes have not been firmly established. We believe that at least part of the change was due to thermal annealing. However, the case for an effect due to the measurements and/or associated handling is nearly as strong. Apparently the sonic pulses cause no change, but stresses imposed on the samples during handling may do so.

Attempts were made to observe changes with time in the defect distribution using high resolution electron microscopy. BNL samples were examined within 48 hours of their removal from the reactor and at regular intervals during the following year. Each time, the defects were observed to be small interstitial clusters $\lesssim 1.5$ nm in diameter. No differences in their character or distribution were observed. This finding is not necessarily in disagreement with the modulus measurements, however, because the defects were barely resolvable and the changes with time might have been too subtle to resolve.

ACKNOWLEDGEMENTS

The authors would like to thank F. D. Hobbs for his many arduous hours spent preparing samples and performing modulus measurements. Thanks are also due W. C. Morgan for useful discussions and help in data analysis.

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