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INTERCOMPARISON OF GRAPHITE IRRADIATIONS

par

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Intercomparison of Graphite Irradiations

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Abstract

While fast neutrons only are effective in damaging graphite, results of irradiations are more or less universally expressed in terms of thermal neutron fluxes.

This paper attempts to correlate irradiations made in different reactors, i.e., in fluxes of different spectral compositions. Those attempts are based on comparison of 1) bulk length change and volume expansion, and 2) crystalline properties (e.g., lattice parameter *C*, magnetic susceptibility, stored energy, etc.).

The methods used by various authors for determining the lattice constants of irradiated graphite are discussed.

INTRODUCTION

In all publications dealing with the modifications in the properties of graphite the doses (integrated fluxes) are usually expressed in terms of thermal neutrons.*

Since the damage is caused solely by the fast neutrons, the intercomparison of results obtained in different piles or in different localities in the same pile, is, to say the least, difficult.

We have attempted to draw some conclusions from the intercomparison of results, obtained at essentially constant temperature, pertaining to macroscopic properties and crystalline properties.

MACROSCOPIC PROPERTIES

The anisotropy of graphite restricts consideration to properties 1) on which the anisotropy has no influence, and 2) for which an independent method is available for taking account of this factor.

Amongst all the macroscopic properties measured during the irradiation of graphite the only ones compatible with these conditions are 1) the volume expansions, and 2) the linear expansions, classed in order of increasing thermal expansion coefficients.*

Table 1 presents what we believe to be an almost complete collection of the existing published values of the initial expansions, linear or volume. They relate, in general, to irradiations of several times 10^{19} to 10^{20} neutrons/cm^2 (see first footnote to Table 1).

Figures 1 and 2 show the expansions for which the coefficients of expansion were known. It is seen that the points fall reasonably well on two curves** of which the

*Very occasionally[10] calculated or experimental data concerning the fast flux and its spectral distribution are included; but unfortunately our fundamental ignorance of the effect of fast neutrons on graphite is such that, even if these data were available for all the existing graphite irradiations, we would not be able to make full use of them.

*These last have been transposed by calculation where necessary to a fixed temperature interval. Numerous measurements on graphites of varying origin have led to the ratio

$$\alpha_{-190}^{20} \Big/ \alpha_{25}^{425} = 0.88.$$

**It is surprising that the French specimens[2,3] irradiated in a neutron converter show no difference from the English specimens irradiated in BEPO. It is even more surprising to find the Canadian samples[14] falling clearly below the curve representing the values of Woods et al.;[16] but it is difficult to believe that the cause of this departure can be the ignorance in which we are left by Sheard and Pattenden[14] of the exact values of the coefficients of expansion of their samples.

Table 1

The Wigner Expansion at Low Doses, and the Coefficients of Linear Expansion

Graphites	Authors	Density, g/cm³	// Extrusion		⊥ Extrusion		Notes
			10^6 Expansion Coefficient /°C	$10^4\ \Delta l/l$ for 10^{20} n/cm²*	10^6 Expansion Coefficient /°C	$10^4\ \Delta l/l$ for 10^{20} n/cm²*	
English	Kinchin[10]	1.60			2.25 (−190+25°C)	6	(b)
Sheffield	Dunworth[4]	1.71—1.76	0.80 (−190+20°C)	1.7—3.5	2.5—3.0 (−190+20°C)	11.2—14.3	(c)
A.G.X.P.		1.56—1.57	1.05 (−190+20°C)	3.0—5.0	2.00—2.05 (−190+20°C)	8.3—11.2	
French	Delcroix [2,3]	1.67	2.10 (−190+25°C)	10	3.30 (−190 + 25°C)	16	(e)
C.S.F.	Woods [5,16,17]	—	1.1 (+25+425°C)	1.6	4.8 (+25+425°C)	7.9	(a)
T.S.G.B.F.	Woods	—	2.2 (+25+425°C)	3.7	4.2 (+25+425°C)	7.9	
W.S.G.B.F.	Woods	—	—	1.6		8.5	
C.S.G.B.F.	Woods	—	—	1.6		—	
K.C.	Woods	—	0.9 (+25+425°C)	0 (?)	5.5 (25+425°C)	10.5	
W.S.F.	Woods	—	1.4 (+25+425°C)	—	4.3 (25+425°C)	7.5	
A.G.X.P.	Sheard and Pattenden[14]	—	—	−1.7	—	2.8	(d)
Korite	Fletcher[6]	—	—	1.6	—	2.2	(f)
?	Fox[7]	—	—	≈1.6	—	—	(g)
?	Siegel et al.[15]	—	—	3.1	—	8.3	(h)
?	Hennig and Hove[9]	—	—	Volume Expansion ≈50 (?)	—	7.0	(h') (i)

*Doses in neutrons/cm². These have been taken as the various authors give them, without any attempt being made to interpret them.

(a) Hanford reactor cooled test hole, temperature = 20° to 40°C; consequently the expansions given in Figures 1 and 2 are those of Table 1 multiplied by 1.1 to bring them to 20°C; 1 Mwd/t = 6.46×10^{17} nvt. The fast flux is "several percent of the thermal flux."[17]

(b) The Harwell reactor BEPO, temperature = 20°C, fast flux up to 5 Mev. $\varphi\ (E)dE = 0.06\varphi_t dE/E$ with φ_t = thermal flux, E = energy of neutrons. This energy distribution of the flux is characteristic of the core of a natural uranium reactor with graphite moderator.

(c) The reactor, the temperature, and the energy distribution of the flux are not quoted; they are supposed identical with (b).

(d) NRX reactor at Chalk River. Irradiations made in the central thimble and in a neutron converter. 1 Mwh in the central thimble is equivalent to 1.82 Mwh at the flux maximum in the converter, the correspondence being established by resistivity variations during short irradiations. 1 Mwh in the position of the flux maximum in the converter corresponds to $1.9 \pm 0.2 \times 10^{15}$ thermal neutrons/cm² at 55°C in an experimental hole in BEPO. For this reason the expansions given by the authors[14] have been multiplied by 1.45 to convert them to 20°C before plotting them in Figures 1 and 2.

(e) Reactor E.L.2 at Saclay. Dose in thermal neutrons. Irradiation in a horizontal converter located in the reflector at a tangent to the tank. Temperature = 20°C. $\varphi_{th}/\varphi_r = 1.4$ with φ_r = fast flux measured by $S^{32}(n,p)P^{32}$ assuming an average capture cross section of 30 mb.

(f) 1 Mwhd/t = 6.5×10^{17} n/cm²-sec. The irradiation seems then to have been made at Hanford, in similar positions to those of reference 16.

(g) Brookhaven reactor. Fast flux ($\geqslant$ 1.6 Mev)/thermal flux probably $\geqslant$ 10 to 11% (reference 7, Figure 12). Expansions measured at $t \geqslant 50$°C and corrected to 20°C by extrapolation of reference 7, Figure 19.

(h) Reactor and flux spectrum not specified. Read on reference 15, Figure 6.

(h') Read on reference 15, Figure 15.

(i) It is assumed that the arbitrary units of reference 8, Figure 3 represent the percent expansion by volume. 1 Mwd/t = 5×10^{19} thermal neutrons/cm².

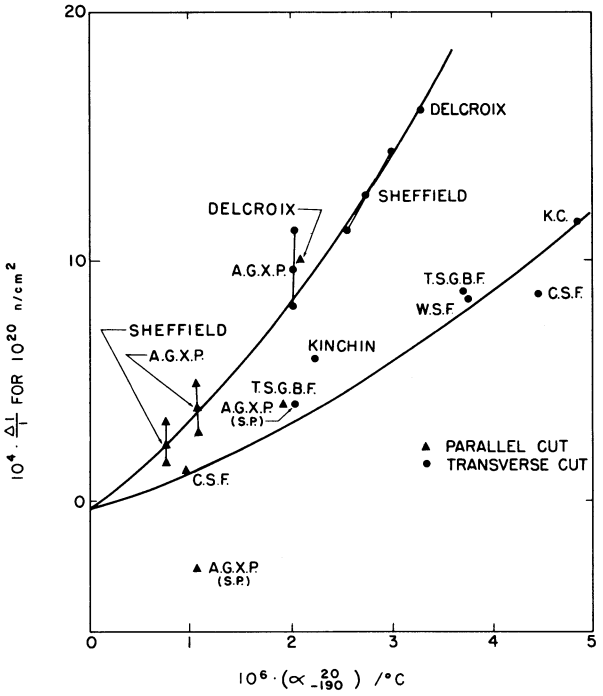

Figure 1

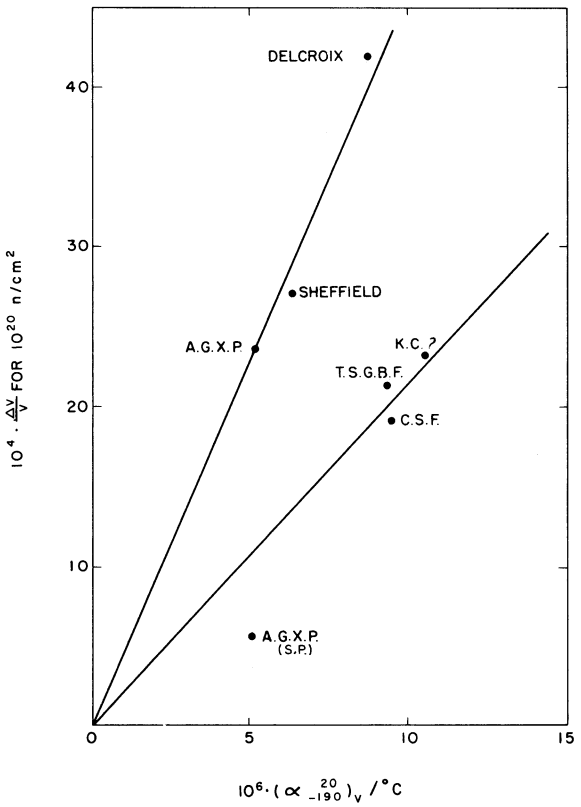

Figure 2

ratios of the ordinates are 2.35 to 2.40 for linear expansion and 2.15 for volume expansion.

The agreement between these two values is as good as the precision of the readings taken from the curves of the different authors, or even as the precision of the measurements at low doses, will allow.

CRYSTALLINE PROPERTIES

One can try to avoid the large variations affecting the macroscopic properties of industrial graphites by considering the crystallite properties, or, at any rate, those properties which are independent of the porous nature of industrial graphite.

A certain number of publications report variations 1) of the crystal parameter C, 2) of the magnetic susceptibility, and 3) of the internal energy U.*

Of these properties the first belongs strictly to the crystallite only; the second is but little influenced by that part of the carbon which is badly organized, and of which the existence cannot be excluded with certainty from industrial graphites, even those which are well crystallized; the third on the contrary must be sensitive to perturbations produced in the badly organized carbon.

Variations of the Crystal Parameter C

Depending on the authors studied, the diagrams giving $\Delta C/C$ as a function of radiation dose are either straight lines, or, on the other hand, consist of an effectively straight part followed by a curve concave towards the dose above about 5×10^{20} n/cm².

Here we shall consider only relatively low doses, not only because of the ease of dealing with a linear relationship, but also because it is for these doses only that one can give valid parameters. In fact, above 5×10^{20} n/cm²

*Woods et al.[16] and Hennig and Hove[8] also report variations in the magnetoresistivity; but the figure given by these last authors, if it is really different from Figure 25 of reference 16, is too small to be useful. Equally the lack of precision of the experimental conditions of references 16 and 8 is such that no comparison is possible with Kinchin[10] on the basis of the Hall effect.

Table 2

Variation of the Crystallographic Parameter C

Authors	C_0, Å	Irradiation Temperature	100 $\Delta C/C_0$ for 10^{20} n/cm² Observed	Corrected to 20°C	Notes
Woods	6.716	20°-40°	1.08	1.17	(a) (k)
	6.732	20°-40°	1.21	1.32	(a) (l)
Kinchin[10]	—	30°	1.3	1.4	(b) (m)
			1.2	1.3	(b) (n)
			1.0	1.1	(b) (n')
Bacon[1]	—	20°	1.15	1.15	(o)
Siegel[15]	6.70	30°	1.12	1.22	(p)
		30°	0.97	1.06	(p')
Fox[7]	6.711	50°	1.5	1.85	(q)
Hennig[8]	—	?		2.2 (?)	(r)
Perio[12]	6.710 to 6.727	20°		1.7 2.35	(e) (s) (s')

(j) For natural graphite $C_0 = 6.707$ Å.

(k) C.S.F. stock.

(l) T.S.—G.B.F. stock.

(m) Reference 10, English text, p. 8.

(n) Ibid. Figure 7.

(n') Ibid. Figure 7. See the remarks in the text concerning the parameters at high irradiation doses.

(o) From this reference we took the relationships $(\Delta C/C)_{20°}/(\Delta C/C)_{30°} = 1.09$ and $(\Delta C/C)_{20°}/(\Delta C/C)_{50°} = 1.23$.

(p) From Figure 9 of the author.

(p') From Figure 6 of the author, assuming that the abscissa values must be multiplied by 4.

(q) Uncertain extrapolation to 20° of Figure 20 of the author would give 2.0 to 2.2%/10^{20} nvt.

(r) Reference 8, Figure 3. We have arbitrarily assumed that the irradiations were made at 20°C and that the arbitrary ordinates represent percentages.

(s) Referred to thermal flux.

(s') Referred to the rapid flux measured by $S^{32}(n,p)P^{32}$.

For other notes, see Table 1.

the diffraction lines are composed of a relatively sharp and narrow peak superimposed on a strongly unsymmetrical halo of which the center of gravity is displaced, relative to the sharp line, toward the large angles. The ratio of the intensities of the sharp to the diffuse parts of the reflection decreases appreciably in going to reflections of higher order. This excludes consideration of the system as being formed of a superposition of two distinct phases. Moreover the values of the parameter taken from the maximum and from the center of gravity do not of course coincide for the same reflection; the same is true for the parameters deduced from the centers of gravity of two successive orders (in practice from 002 to 004). Under these conditions it is unreasonable to claim that the substance may be characterized by one parameter (average, or the most frequent); the model allowing an interpretation of the equivalent diffraction function remains to be discovered.

The data are summarized in Table 2. They have been brought to 20°C on the basis that for the same graphite irradiated to a given dose in a constant flux but at different temperatures the following ratios are valid:

$$\frac{\Delta C}{C^{20°}} \Big/ \frac{\Delta C}{C^{30°}} = 1.09,$$

$$\frac{\Delta C}{C^{20°}} \Big/ \frac{\Delta C}{C^{50°}} = 1.23.$$

Examination of Table 2 shows that the values of $\Delta C/C$ corrected to 20°C fall into two groups, the first being distributed around approximately 1.25% per 10^{20} n/cm², and the second consisting of values which are clearly larger. But contrary to what was found in the macroscopic expansion, the values obtained in BEPO[1,10] fall in the first group, in agreement with the fact that the irradiations were carried out in a graphite pile.

It seems normal to find the data obtained in the converter of E.L.2 amongst the group of higher values. (But they are not so clearly separated from the low value group as are the corresponding values of the linear and volume expansions.)

But it is more surprising to find there also the values obtained in the graphite pile at Brookhaven:[7] the correction necessary to convert the data from 50° to 20°C does not supply an adequate explanation for this. The absence of information about irradiation conditions in the work of Hennig and Hove[8] and the fact that these authors give their results in arbitrary values makes their presence amongst the group of high values of little significance.

Magnetic Susceptibilities, χ

Only the publications of Woods et al.[16] and of Hennig and Hove[8] present measurements of the variation of χ with dose; that of Hove and McClelland[9] simply gives the same doses in terms of neutrons of energy greater than 0.5 Mev. From the authors' figures the doses necessary to obtain variations of χ of less than 30% can only be very inexactly estimated; therefore these have not been included in Table 3.

It can be seen here that the ratios at increasing doses between the effects observed by these authors are as constant as the precision of reading the diagrams will allow. In fact Woods' text[16,p.10] leaves the impression that the two series of measurements could well be identical; no conclusion can then be drawn concerning the usefulness of magnetic susceptibility results for monitoring graphite irradiation. (Moreover, the rapid saturation of the effects limits their use to doses below 2 to 3×10^{20} n/cm².) In its favor, however, one can say that the doses corresponding to the same variation in the Hanford pile and in the central channel of the heavy water reactor E.L.2 at Saclay are certainly of the magnitude required by what one knows of the fast flux ratio. Unfortunately, interfering factors in our irradiations prevent us from putting forward at the moment more solid bases for our argument.

Table 3

Variations of the Average Magnetic Susceptibility

$-100\frac{\Delta\chi}{\chi}$	Doses in 10^{19} n/cm²		Hennig / Woods
	Woods[16](a)	Hennig[8](i)	
30	2.8	1.8	0.64
40	3.7	2.8	0.76
50	5.5	4.0	0.73
60	8.0	5.8	0.73
70	11	8.5	0.77
75	16	12.5	0.78
	Woods[16](a)	Seguin[13](t)	Seguin / Woods
13.6	1.3	3.8	3

(a) See Table 1.

(i) See Table 1.

(t) Irradiation in the central canal of E.L.2. $\varphi_r/\varphi_{th} = 0.05$ with φ_{th} = thermal flux and φ_r = fast flux measured by $S^{32}(n,p)P^{32}$.

It would be interesting to compare the variations of χ relative to those found for C. Unfortunately, the only data useful for comparison purposes are those of Woods.[16]

Stored Energy, ΔU

Table 4 shows, as a function of dose, values taken from the figures of different authors, and the ratios of these values.* Although the values differ markedly near the origin, they show a satisfactory agreement at higher doses.

*The representative curves of Woods,[16] Kinchin,[10] and Simmons[15a] are concave towards the dose axis, whereas that of Siegel[15] is a straight line above 2.5×10^{20} n/cm².

Table 4

Stored Energy, ΔU (cal/g)

Dose, 10^{20} n/cm^2	Woods[16]	Kinchin[10] Simmons[15a]	Siegel[15]	Simmons / Woods	Siegel / Woods	Siegel / Simmons
0	72*	80*	110*	1.1	1.5	1.4
1	65	80	90	1.25	1.4	1.1
	120	140	145	1.15	1.2	1.0
3	170	180	175	1.05	1.0	1.0
4	215	210	200	1.0	0.95	0.95
5	250		225		0.9	
8	340		300		0.88	
12	430		405		0.92	

At 0.2 $\times$ 10^{20} n/cm^2, ΔU = 3 cal/g [G. Mayer,[11] cf. Table 3, Note (t)].

*Initial slope $\frac{\text{cal/g}}{10^{20}\ \text{n/cm}^2}$.

This we think may be put down to the fact that, as the irradiation progresses, the part played in ΔU by those defects which heal at relatively low temperatures diminishes. It is likewise reduced by irradiation at higher temperature. Consequently, in the case of irradiations carried out under identical conditions but at two different temperatures T_1 and T_2 (with $T_2 > T_1$), ΔU must vary roughly as shown in Figure 3, giving rise to decreasing differences and perhaps eventually becoming constant.

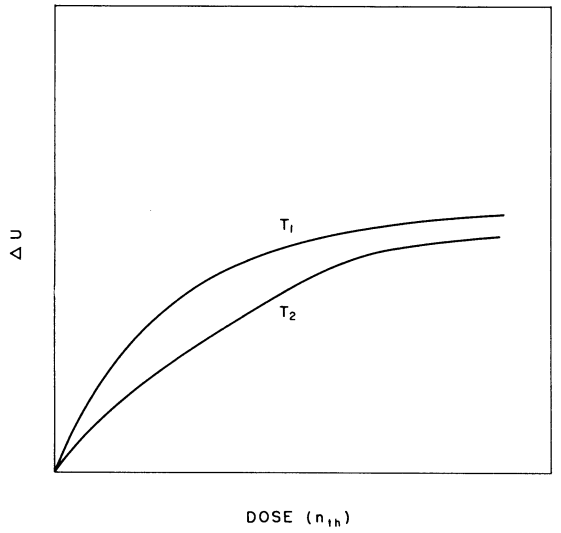

Figure 3

If the doses have been given in thermal neutrons, and if we assume that the irradiation at T_2 has been carried out in a flux richer in fast neutrons than that at T_1, then the abscissae of T_1 will be elongated with respect to those of T_2 and the two curves could intersect. It would perhaps be stretching the point too far to suggest that this is the explanation of the particular details of Table 4.

The irradiation carried out by Mayer[11] in the central channel of E.L.2 gives, on comparing the initial slope with those of other authors,

Woods/Mayer =4.8
Simmons/Mayer =5.3
Siegel/Mayer =7.3

These values are larger than the corresponding ratios for the fast fluxes in the various irradiation positions.

CONCLUSIONS

This attempted comparison leaves an impression of great confusion: we have not been able to deduce any sure terms of comparison for graphites irradiated in neutron fluxes of varied energy composition.

In particular:

1) Some contradictions exist between the crystal expansions and the macroscopic expansions, even when account is taken of the correction for the different thermal expansion coefficients of the various graphites.

2) It was impossible to establish either that the variations of crystalline properties provide a convenient dosimeter for graphite irradiation, or that those which have been considered here (the crystal parameter C and the mean magnetic susceptibility) actually varied in the same way as a function of the irradiation parameters.

3) One cannot exclude the possibility that the variation of stored energy may be too sensitive to irradiation conditions to be usefully employed.

If it is desired to deduce the parameters controlling the macroscopic behavior of graphite under irradiation, it seems necessary to us:

a) To complete, if possible, the existing data: intensity and spectral composition of the flux, irradiation temperatures, characteristics of the irradiated graphites (for instance, crystalline dimensions, fraction of poorly organized carbon, quantitative measurements on the porous structure amongst which should be included coefficients of thermal expansion).

b) To carry out comparable irradiations of the same graphites in fluxes of varied energy composition and at various temperatures; moreover, to irradiate under well established conditions various graphites whose characteristics have previously been established as completely as possible. It remains to be seen if this task, certainly no easy one, presents sufficient scientific and technological interest to justify the effort which it calls for.

Lastly, it is perhaps necessary to establish more certainly that the product flux multiplied by time can actually be considered as a unique quantity, and that it is not necessary to consider flux and time as independent variables.

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