Title
ANOMALOUS LARGE LAYER SPACINGS IN GLASSY CARBON

Authors
Henry, L.G.
Bragg, R.H.

Publication Date
1978-12-01

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

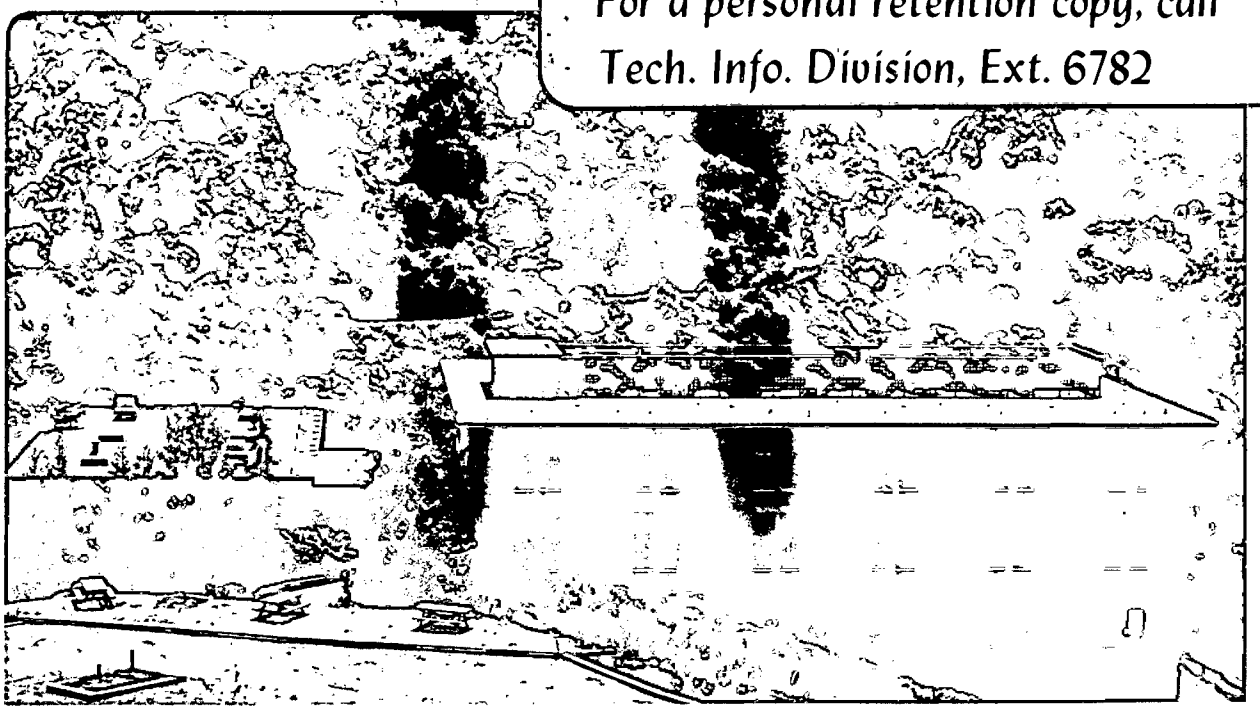
Materials & Molecular
Research Division

Presented at the 14th Biennial Conference on Carbon,
Pennsylvania State Univ., University Park, PA,
June 25-29, 1979

ANOMALOUS LARGE LAYER SPACINGS IN GLASSY CARBON

Leo G. Henry and Robert H. Bragg

December 1978



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISCLAIMER

ANOMALOUS LARGE LAYER SPACINGS IN GLASSY CARBON

Leo G. Henry and Robert H. Bragg

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Materials Science and Mineral
Engineering, University of California
Berkeley, CA 94720

ABSTRACT

Interlayer spacings greater than 0.344 nm reported for carbons are probably incorrect because of failure to correct line profiles in x-ray diffraction patterns for distortion caused by deep beam penetration and small angle scattering which overlaps Bragg reflections. In Glassy Carbon d_{002} estimated to be 0.375 nm before corrections becomes 0.344 nm when corrections are made.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

Dec. 1978

I. Introduction

In a recent publication the interlayer spacings, some greater than 0.344 nm, in Glassy Carbon (GC) heated in the range 1000°C to 2800°C were reported[1]. X-ray line profiles such as in Fig. 1 were corrected in order to obtain line profiles appropriate for analysis. The authors stated that the strong diffuse intensity below the first Bragg maximum is the high angle portion of a very strong small angle X-ray scattering, and in addition to correcting for this, the usual corrections for Compton scattering, Lorentz-polarization, and f^2 were employed. However, distortion and displacement caused by the deep penetration of the X-ray beam must also be taken into account[2,3]. The effect of these corrections is demonstrated for two specimens of GC. In this work it is shown that previously reported spacings greater than 0.344 nm are incorrect.

2. Corrections

It has been shown that if $I(2\theta)$ is the observed interference function, the intensity distribution (2θ) which would be observed in the absence of distortion due to low absorption is[2,3]

$$\frac{1}{\gamma} g(2\theta)=(h-\frac{1}{\gamma} h')_{2\theta} + |(h-\frac{1}{\gamma}h')_{2\theta+U}|\exp(-\gamma U)+ \ldots\ldots \qquad (1)$$

where $U = (2T\cos\theta/R)$, T = specimen thickness, $\gamma = 2\mu R/\sin 2\theta$, μ = linear absorption coefficient, R = source-specimen and specimen-detector slit distances, $h = \sin 2\theta I(2\theta)/AR$, A = area of beam and $h' = dh/d2\theta$. The absorption corrected data, $g(2\theta)$, is obtained prior to any other corrections. The data are next corrected for Compton scattering using measurements on single crystal HOPG in a region free of Bragg reflections to obtain a

normalization. With Compton scattering subtracted the remaining data are plotted as ln sinθ at small angles. The small angle scattering follows a $(\sin\theta)^{-n}$ law,[4] with n = 3, and with appropriate normalization its magnitude in the region,where it overlaps Bragg reflections is estimated and subtracted. The final corrections for the variation of f^2 and LP with angle are then applied.

3. Results

Uncorrected data for two GC specimens heat treated at different temperatures are shown in Fig. 2(a),replotted from Fig. 1. In Fig. 2(b) the result of correcting for low specimen absorption, Compton scattering and small angle X-ray scattering is given. It can be seen that the non-Bragg scattering, found to follow a $(\sin\theta)^{-3}$ law is merely a very strong small angle scattering. The subsequent correction for f^2 and LP, which converts Fig. 2(b) to Fig. 2(c) has produced a transformation in the shape of the profiles as well as a displacement of peak position. The d_{002} spacings estimated from peak positions is summarized in Table 1.

4. Discussion

The recognition that the small angle scattering is by far the most prominent feature of the diffraction pattern of GC came only recently.[5] It was confirmed by comparing the diffraction patterns of the same specimen in reflection and transmission. This provides an experimental basis for correcting for the small angle scattering which, when it extends into the wide angle region, is sometimes described as non-Bragg scattering without further identification[6]. Subtraction of the Compton and small angle scattering strongly affects the line profiles but has little effect on

peak positions. The largest contribution to the peak displacement in going from Fig. 2(a) to Fig. 2(b) is that from the application of Eqn. 1. Failure to make this correction caused Saxena and Bragg[1] to overestimate d_{002} in some instances by 0.005 nm. It should be noted that much of the asymmetry in the peak shape disappears when the corrections for f^2 and LP are made (Fig. 2(c)). The fully corrected line profiles constitutes the lattice interference function devoid of factors normally taken to be constant over the breadth of a Bragg reflection. These are the profiles which should be used in subsequent analyses, such as for crystallite size, strain and shape.

The implications of these results are far-reaching. It seems likely that many large d-spacings reported for carbons or other disordered porous materials are over estimated. In GC it is probable that d_{002} spacings larger than 0.344 nm do not occur. That is, the range of structural disorder in hard carbons is very similar to that in soft carbons and these in these materials the degree of graphitization attained for a given heat treatment is usually greater than that estimated from uncorrected line profiles.

5. Conclusion

In order to obtain meaningful d-spacings the X-ray line profiles of Glassy Carbon must be corrected for small angle scattering and low specimen absorption in additon to the usual sources of line profile distortion. The range of structural disorder in GC characterized by interlayer spacings is probably 0.344 nm to 0.335 nm as in soft carbons.

Acknowledgment

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

References

1. R. R. Saxena and R. H. Bragg, "Kinetics and Graphitization in GC," Carbon, 16, 373 (1978).

2. D. T. Keating and B. E. Warren, Rev. Sci. Instr., 23, 519 (1952).

3. Bragg, R. H., Packer, C.M., Rev. Sci. Instr. 34, #11, 1207 (1963).

4. Guiner, A. et al., "Small Angle Scattering of X-Rays," Chap. 3, John Wiley & Sons, N.Y., 1955.

5. Bragg, R.H. and Hammond, M.L., Seventh Biennial Carbon Conference, Cleveland, June 1965, also Carbon 3, 340 (1965).

6. R. R. Chianelli, E. B. Prestridge, T. A. Pecoraro and J. P. De Neufrille, Science, 203, 1105 (1979).

Table 1

Sample	d_{002} Uncorrected (a)	First Correction (b)	Total Correction (c)
GC 1000-1	0.375 nm	0.370 nm	0.344 nm
GC 2700-2	0.349 nm	0.347 nm	0.343 nm

Figure Captions

Fig. 1 Uncorrected line profiles of Glassy Carbon.

Fig. 2. Effect of corrections on Glassy Carbon Line Profiles.

Fig. 3. Interlayer spacings in Heat-treated GC.

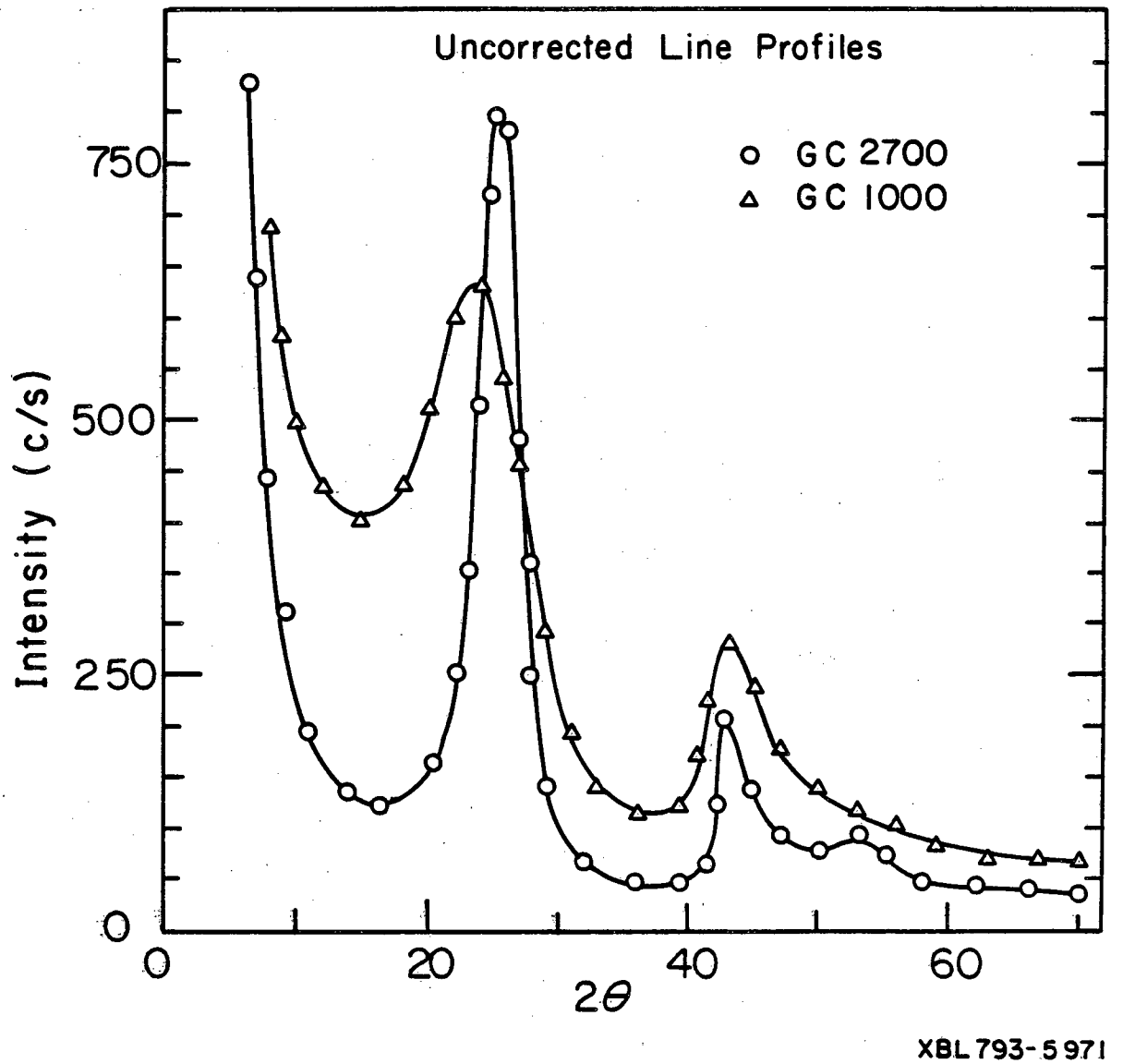

Uncorrected Line Profiles
GC 2700
GC 1000
Intensity (c/s)
750
500
250
0
0
20
40
60
2θ
XBL 793-5971

Fig. 1

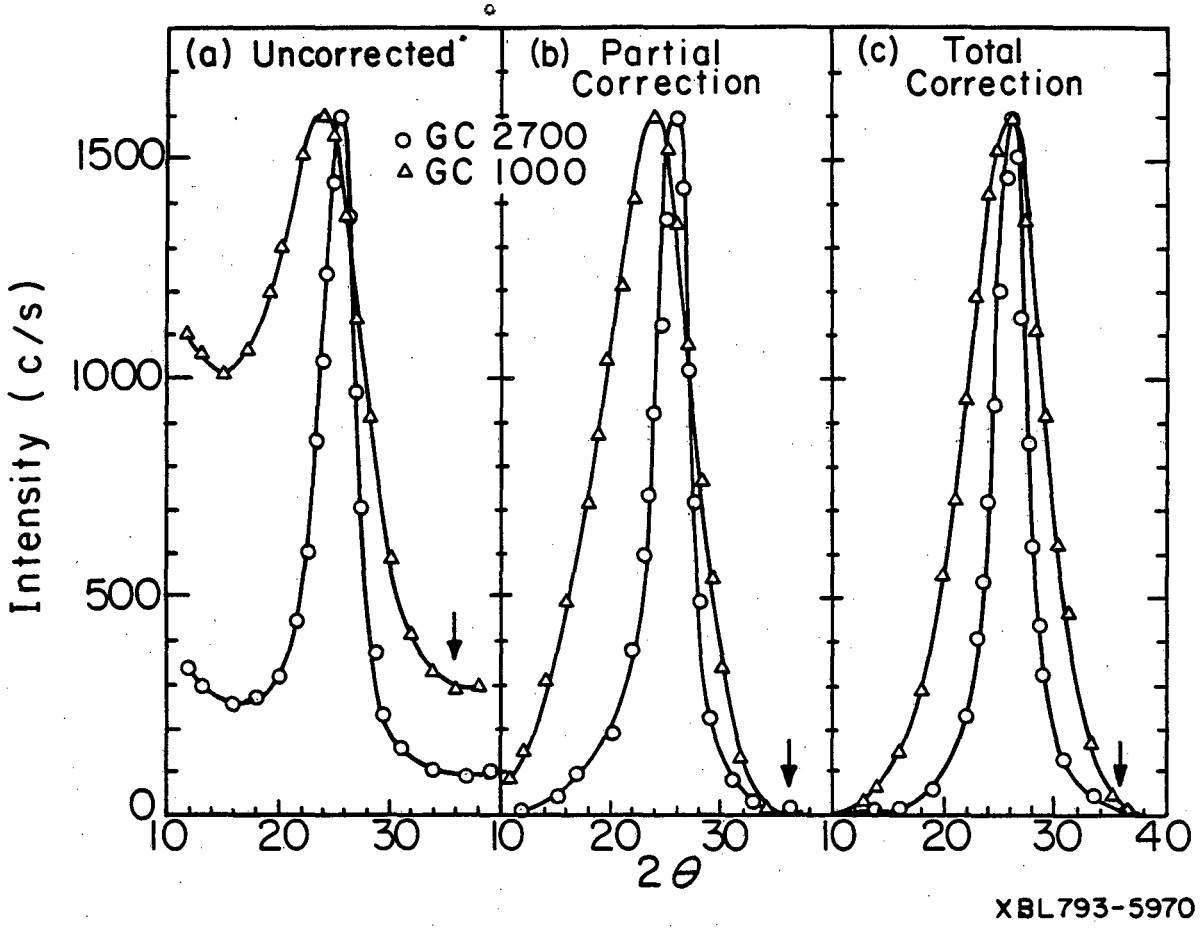

(a) Uncorrected
(b) Partial Correction
(c) Total Correction
o GC 2700
Δ GC 1000
Intensity (c/s)
1500
1000
500
0
10
20
30
40
2θ
XBL793-5970

Fig. 2

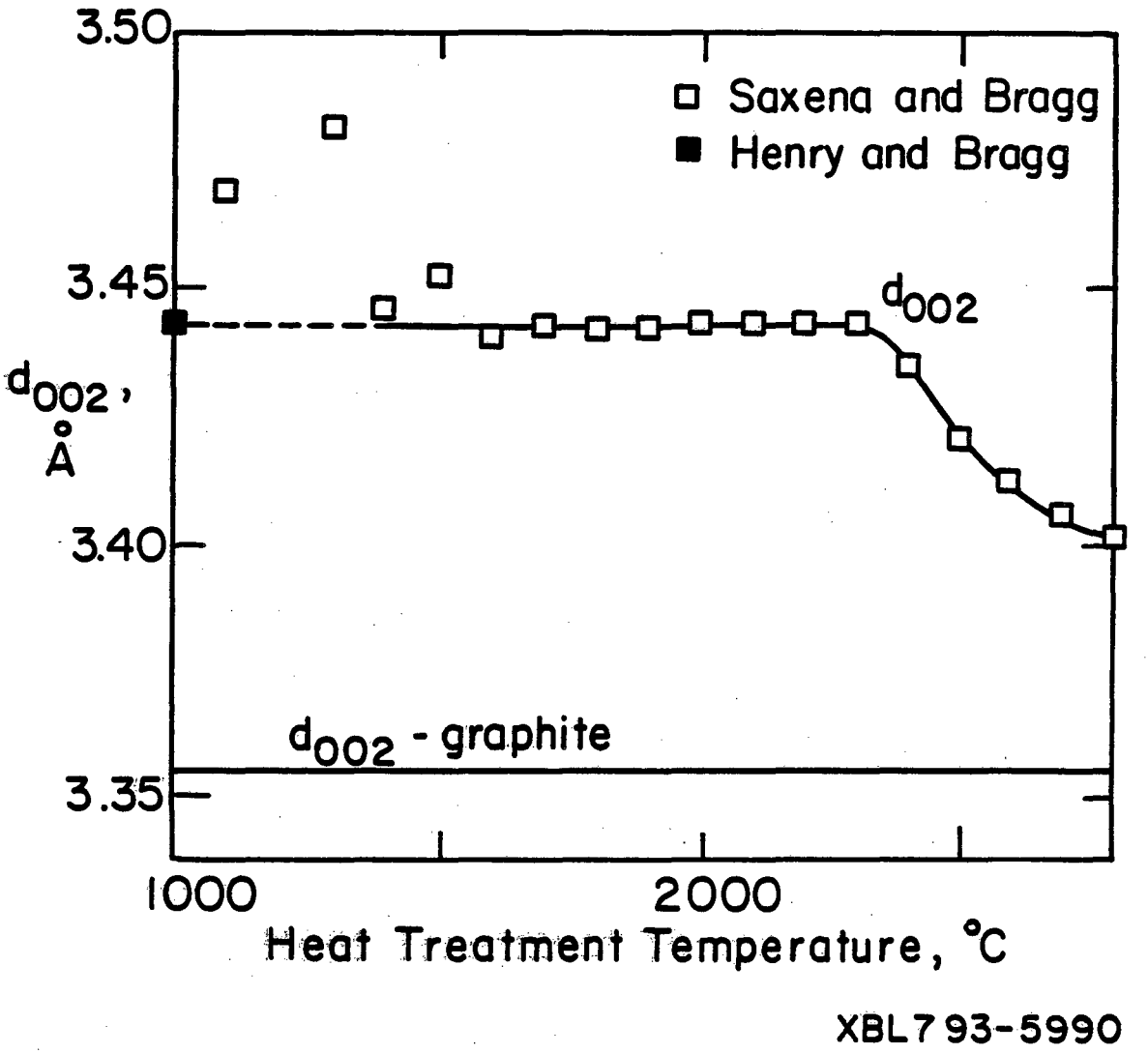

3.50
3.45
3.40
3.35
d_{002}, Å
Saxena and Bragg
Henry and Bragg
d_{002}
d_{002} - graphite
1000
2000
Heat Treatment Temperature, °C
XBL793-5990

Fig. 3

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720