Title
SMALL ANGLE X-RAY SCATTERING FROM ORIENTED ELLIPSOIDAL VOIDS IN PYROLYTIC GRAPHITE

Author
Bose, S.

Publication Date
1977-09-01

Submitted to Journal of Applied Physics

UC-25
LBL-6655
Preprint

SMALL ANGLE X-RAY SCATTERING FROM ORIENTED ELLIPSOIDAL VOIDS IN PYROLYTIC GRAPHITE

S. Bose and R. H. Bragg

September 1977

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

DISCLAIMER

0 0 0 0 4 8 0 5 5 7 4

LBL-6655

SMALL ANGLE X-RAY SCATTERING FROM ORIENTED ELLIPSOIDAL VOIDS IN PYROLYTIC GRAPHITE

S. Bose and R. H. Bragg

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

ABSTRACT

Small angle x-ray scattering from oriented voids in pyrolytic graphite has been studied. The scattering is found equivalent to that from a dilute dispersion of ellipsoids of revolution called "Guinier Spheres" of radius of gyration

$$R = (\tfrac{3}{5}H)^{1/2} = [\tfrac{3}{5}\,(a^2 \mathrm{Sin}^2\gamma + b^2 \mathrm{Cos}^2\gamma)]^{1/2}$$

where γ is the angle between the common axis of revolution (semi-minor axis b) and the scattering vector $\bar{h}$. Analysis of the data using Hamzeh and Bragg's theory provides values of a, b and a/b from the 'Guinier' and the 'Porod' regions independently with good agreement. The theoretically predicted angular dependence of H using "best fit" values of a and b is in good agreement with the experimentally determined value of H, γ varying from 0° to 180°.

I. INTRODUCTION

Pyrolytic graphite is a carbon material prepared by thermal decomposition of methane on a graphite mandrel. Optical microscopy and wide range x-ray diffraction studies show that it has a strong (002) texture, i.e., slightly wrinkled but highly oriented graphite-like layers approximately parallel to the plane of deposition. However, the density of pyrolytic graphite is typically 2.10 g/cm^3 compared to 2.25 g/cm^3 for ideal graphite, indicating a porosity of five percent.

An orientation dependent small angle scattering from pyrolytic graphite was first reported by Bragg, et al[1]. These authors suggested an interpretation in terms of a dilute monodisperse collection of oblate ellipsoids of revolution with a common semi-minor axis approximately normal to the deposition plane.

Hamzeh and Bragg subsequently treated the SAXS by oriented ellipsoids of revolution[2]. They showed that the scattering has the form of Rayleigh scattering by a "Guinier Sphere" whose radius depends upon the orientation of the ellipsoid relative to the plane of observation. In the present work the orientation dependence of the scattering by voids in pyrolytic graphite is reported.

II. THEORY

A theoretical analysis to predict the small angle x-ray scattering (SAXS) from a dilute dispersion of oriented ellipsoids of revolution was made by Hamzeh and Bragg[2]. The calculated intensity depends on the size and orientation of the ellipsoids through the relation

$$I(hH) = NI_e(\rho V)^2\ 9\left(\frac{\mathrm{Sin}(hH) - hH\ \mathrm{Cos}\ (hH)}{(hH)^3}\right)^2$$

where

$H^2 = a^2 \mathrm{Sin}^2\gamma + b^2 \mathrm{Cos}^2\gamma$

b = axis of revolution of the ellipsoid and is the semi-minor axis

$|h| = 4\pi \mathrm{Sin}\theta/\lambda$

2θ = angle of scattering

λ = wavelength of x-rays

N = number of ellipsoids irradiated

ρ = electron density of the ellipsoids with respect to the surrounding matrix

V = volume of each ellipsoid

I_e = intensity scattered by a single electron at small angles

γ = angle between $\bar{b}$ and $\bar{h}$

For $h \to 0$ we have the "Guinier approximation"

$$\underset{h\to 0}{I(hH)} = NI_e(\rho V)^2 \exp\ [-\ 1/3h^2(3/5H^2)]$$

wherefrom the "Guinier radius" becomes $(3/5)^{1/2}H$.

For large h, however, we have the "Porod approximation"

$$\underset{h\to\infty}{I(hH)} = NI_e \frac{\rho^2}{h^4}\frac{9V^2}{2H^4}$$

which, in the infinitely long and narrow slit arrangement[3] becomes

$$I(hH) = \frac{\text{constant}}{h^3 H^4}.$$

Thus

$$[h^3 I(hH)]^{-1/2} = \text{constant}\ \{(a^2-b^2)\text{Sin}^2\gamma + b^2\}$$

A plot of $[h^3 I]^{-1/2}$ vs $\text{Sin}^2\gamma$ should, therefore, give a straight line with the ratio between intercept at $\gamma = 0$ and the slope equal to $b^2/(a^2-b^2)$.

The foregoing analysis provides the basic theory to characterize anisotropic SAXS from materials with oriented inhomogeneities whose shape approximates ellipsoids of revolution.

III. EXPERIMENT

Measurements were made on specimens cut as shown in Fig. 1(a) from a specially prepared block of PG about 2.5 cms thick (supplied by Pfizer Inc.). Both the Bonse-Hart type apparatus[4] and a conventional x-ray diffractometer with a modified slit arrangement were used to collect data using CuK_α radiation. The mode of preparation of PG clearly indicates that it is isotropic in a plane parallel to the deposition surface Fig. 1(b) with the common axis of revolution b normal to it.

IV. RESULTS

The scattering from a specimen of orientation, Fig. 1(b), was found to be independent of the angle of rotation ϕ of the sample about the incident beam, as shown in Fig. 2. A direct measurement of 2a was made from Guinier plots of data used to obtain Fig. 2. This gave a value

2a = 214A°. The orientation dependence for a plane normal to the deposition surface, Fig. 1(c), was studied by rotating the specimen about the direct beam to vary γ. For each value of γ, intensity was measured as a function of h. From the 'Guinier plots' of Log I vs h^2 for each value of γ, H was determined. Since the number of voids is of the order of $6 \times 10^{15}/cm^3$ their average separation exceeds 500A°, much larger than the void size. Thus, for all practical purposes the influence of the interparticle interference on the Guinier radius may be neglected. In Fig. 3 is shown the observed γ dependence of H along with the calculated least square fit curve using 2a = 228A° and 2b = 152A°.

The Porod region provides an additional check. In this asymptotic region the intensity measured with an effectively infinite slit geometry has been found to follow the relation $[h^3 I]$ = constant, the constant differing for each value of γ as shown in Fig. 4. As predicted by the theory, the data of Fig. 5 fall on a straight line. The ratio of the intercept to slope is found to be 0.77, in good agreement with $b^2/(a^2-b^2) = 0.80$ calculated using the values of a and b obtained from the Guinier plots. A departure of $[h^3 I]^{-1/2}$ vs $\sin^2\gamma$ from a straight line at large values of $\sin^2\gamma$ may be due to the slit smearing of the anisotropic intensity distribution.

V. DISCUSSION

The isotropic scattering (Fig. 2) obtained for material in the orientation of Fig. 1(b) is consistent with the mode of preparation of the pyrolytic graphite. That is, one expects the normal to the deposition plane to be an axis of rotational symmetry, and thus the average cross section of the voids parallel to the deposition plane is approximately circular. The good agreement between the data of Fig. 3 strongly support a model of the void structure as a dilute dispersion of oriented ellipsoids of revolution with the semiminor axis b approximately normal to the deposition plane. An additional confirmation is afforded by the fact that the dimension 2a is obtained independently from analysis of the scattering from orientations, Fig. 1(b) and also Fig. 1(c), for $\gamma = 0$. These values 214A and 228A are again in reasonable agreement.

A striking demonstration of the asymmetry of the small angle scattering is shown in Figs. 6 and 7. The data are computer printouts of two dimensional SAXS data obtained from our pyrolytic graphite samples by Hendricks and Lin[5] using the ORNL 10 meter Small Angle Scattering Facility. The connected curves are isointensity contours. While no attempt was made to analyze the data in detail, the data show clearly that in orientation 1(b) the scattering is approximately isotropic, i.e., circular across sections on the average, and the isointensity contours are approximately elliptical for 1(c).

Despite the foregoing consistency it cannot be concluded that the voids are ellipsoidal. It is well known that diffraction pattern of an asymmetric object will have a center of symmetry.[6] Thus it is possible, even likely, considering the growth cone structure of pyrolytic graphite, the the voids have shapes closer to hemispherical shells than true ellipsoids.

VI. CONCLUSION

Inhomogeneities that can be represented as ellipsoids of revolution scatter x-rays in the small angle region as if they were spheres of radius that depend on the dimension of the ellipsoids as well as on the orientation. Pyrolytic graphite provides a good vehicle to test the theory since it has oriented voids that may be approximated to ellipsoids of revolution. However the analysis has the general limitation of any diffraction experiment that it cannot detect the absence of a center of symmetry.

ACKNOWLEDGEMENT

This work was supported by the U. S. Energy Research and Development Administration through the Molecular and Materials Research Division, Lawrence Berkeley Laboratory.

REFERENCES

1. R. H. Bragg, M. L. Hammond, J. C. Robinson and P. L. Anderson, Nature 200, 557 (1963).
2. F. M. Hamzeh and R. H. Bragg, J. Appl. Phys. 45(7), 3189 (1974).
3. A. Guinier and G. Fournet, Small Angle Scattering of X-rays, J. Wiley and Sons, New York (1955)
4. V. Bonse and M. Hart, Appl. Phys. Letters, 7, 288 (1965).
5. Hendricks, R. W., Private Communication
6. G. Harburn, C. A. Taylor and T. R. Welberry, Atlas of Optical Transforms, Cornell University Press, Ithaca, New York (1975) Plate 2 and 31.

FIGURE CAPTIONS

Fig. 1. (a) Block of pyrolytic graphite

(b) Voids project as circles

(c) Voids project as ellipses

(d) Geometry of voids in scattering measurements.

Fig. 2. Isotropic scattering from specimen cut parallel to the deposition surface.

Fig. 3. Dependence of "Guinier Sphere" radius on orientation.

Fig. 4. Verification of Porods Law at larger values of h.

Fig. 5. Linear relationship between $(h^3 I)^{-1/2}$ and $\sin^2\gamma$.

Fig. 6. Circular symmetry of scattering from specimen cut parallel to deposition surface.

Fig. 7. Elliptical symmetry of scattering from specimen cut normal to deposition surface.

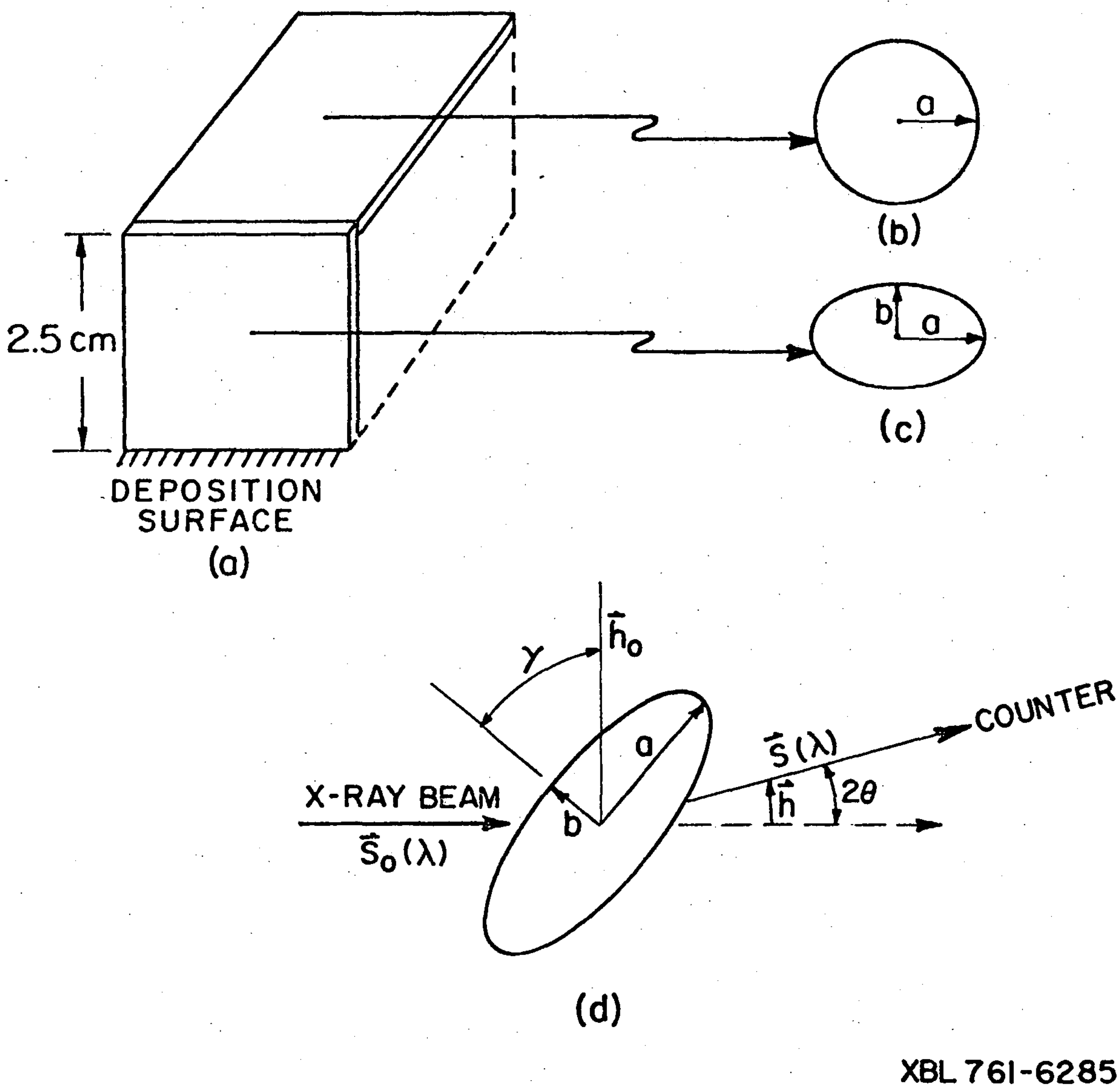

2.5 cm
DEPOSITION
SURFACE
(a)
a
(b)
b
a
(c)
$\vec{h}_o$
γ
a
COUNTER
$\vec{s}(\lambda)$
X-RAY BEAM
$\vec{s}_o(\lambda)$
b
$\vec{h}$
2θ
(d)
XBL 761-6285

Fig. 1

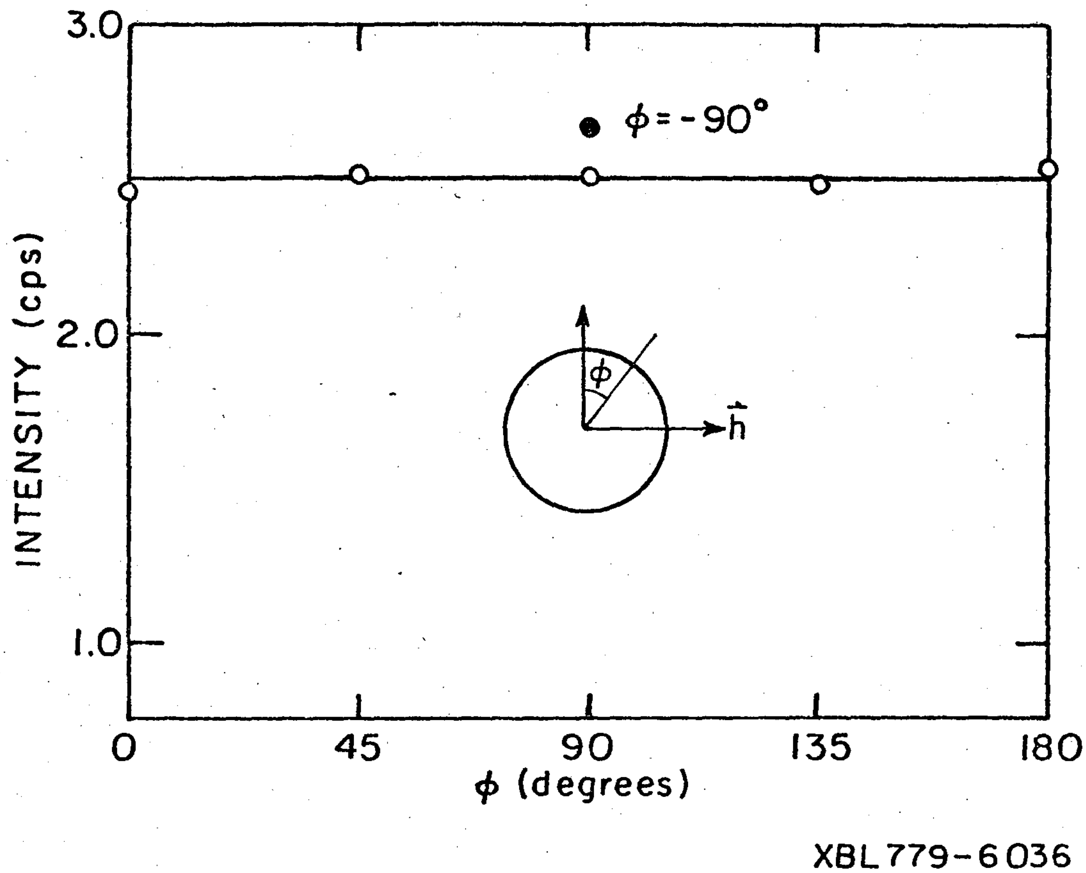

3.0
2.0
1.0
INTENSITY (cps)
φ = -90°
φ
h
0
45
90
135
180
φ (degrees)
XBL 779-6036

Fig. 2

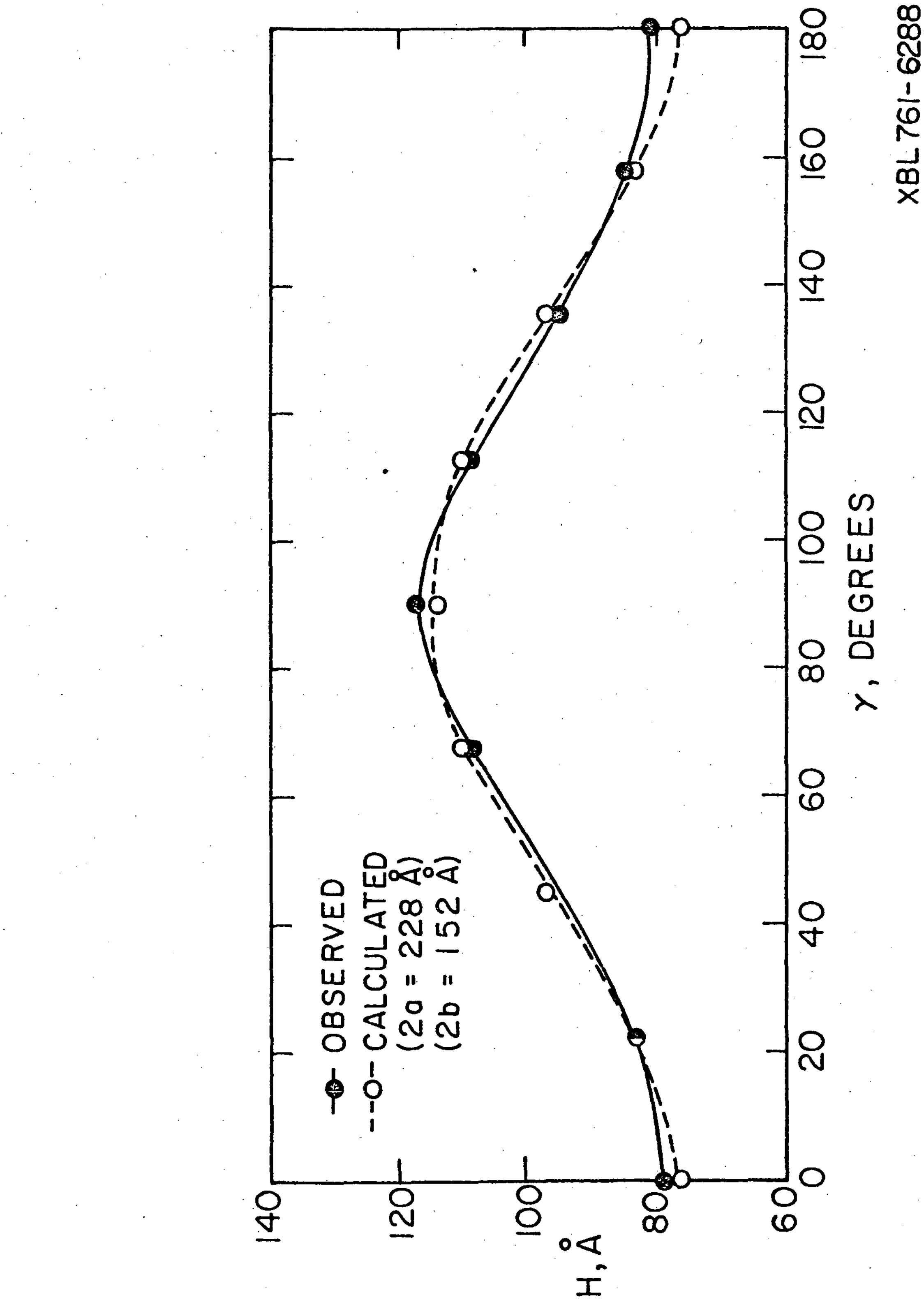

OBSERVED
CALCULATED
(2a = 228 Å)
(2b = 152 Å)
H, Å
γ, DEGREES
XBL 761-6288

Fig. 3

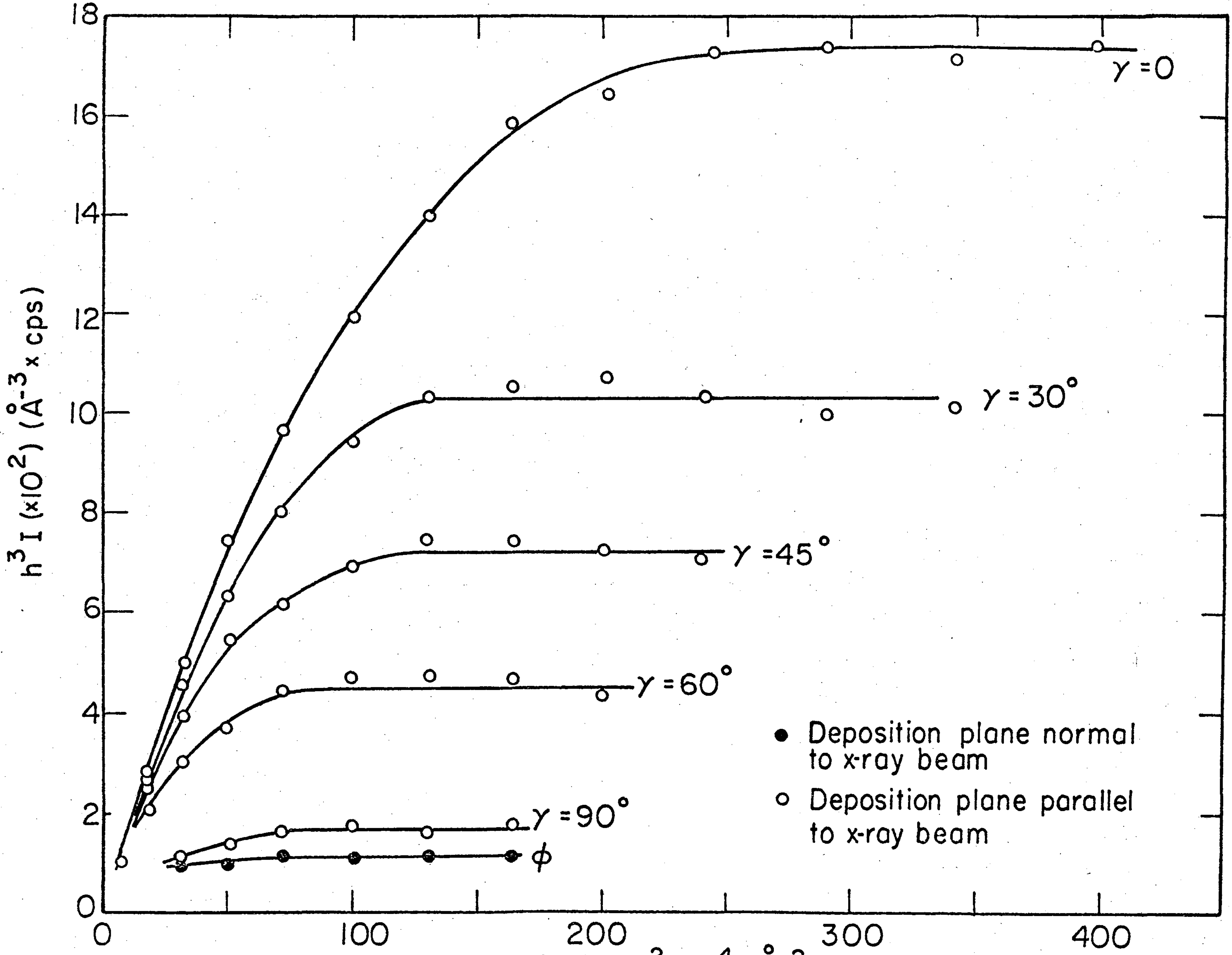

$h^3 I$ (x10^2) (Å^{-3} x cps)
γ = 0
γ = 30°
γ = 45°
γ = 60°
γ = 90°
ϕ
Deposition plane normal to x-ray beam
Deposition plane parallel to x-ray beam
h^2 x 10^4 (Å^{-2})

Fig. 4

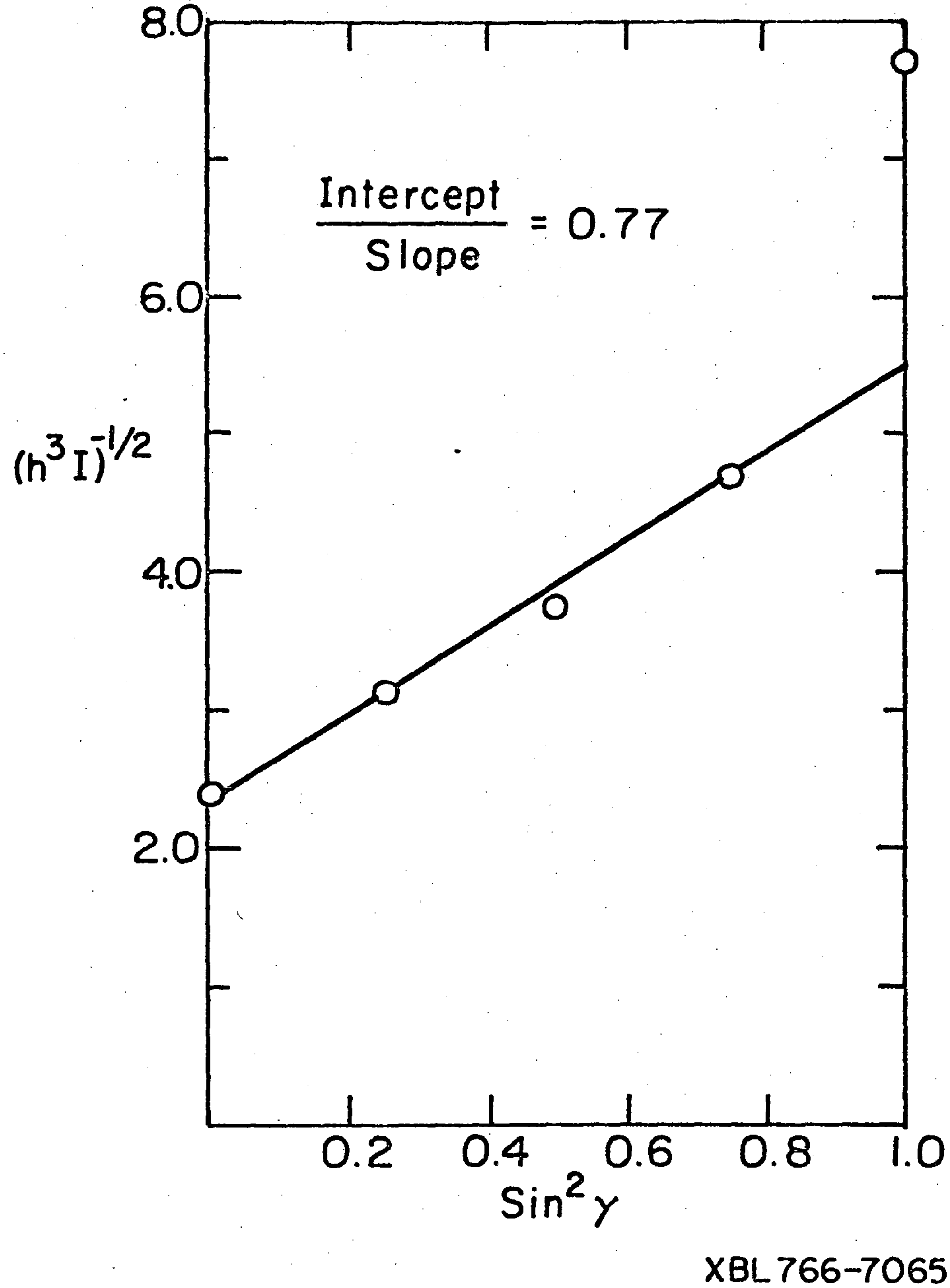
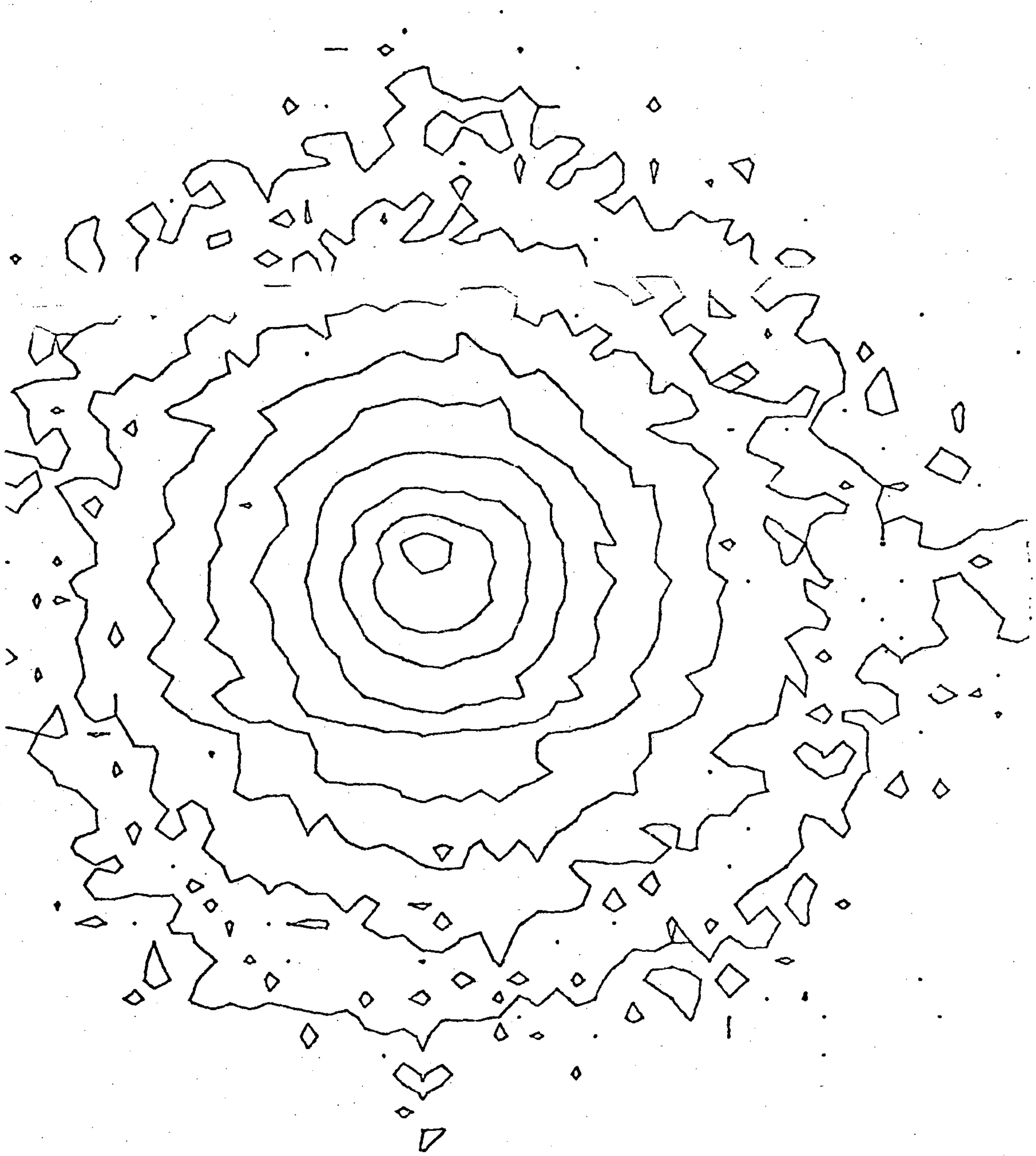
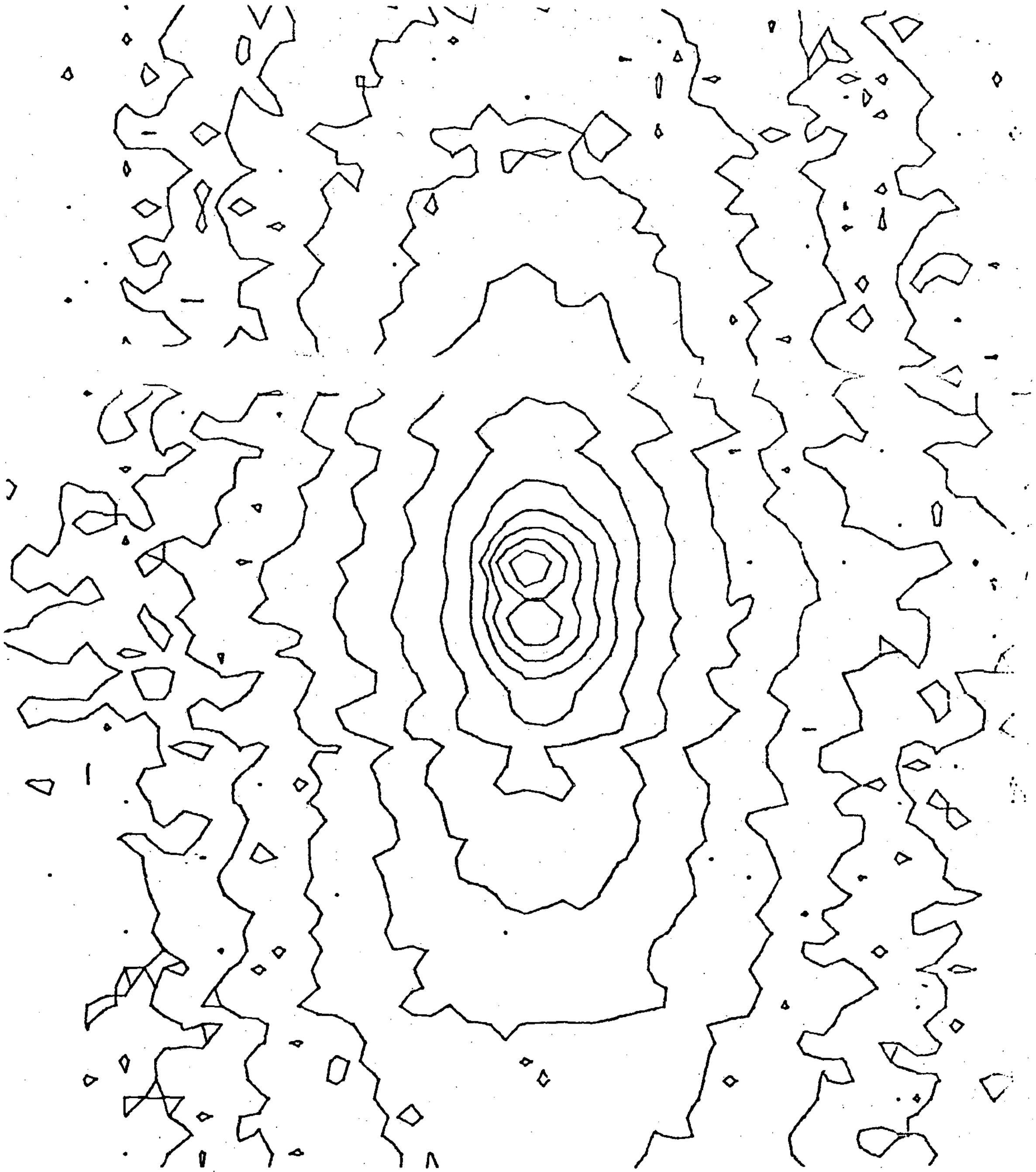

8.0
6.0
4.0
2.0
$(h^3 I)^{-1/2}$
$\frac{\text{Intercept}}{\text{Slope}} = 0.77$
0.2
0.4
0.6
0.8
1.0
$\sin^2 \gamma$
XBL 766-7065

Fig. 5



XBL 779-2477

Fig. 6



XBL 779-2476

Fig. 7

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