

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/253038849>

# Improved crystallographic data for graphite

Article · June 2003

DOI: 10.1154/1.1536926

---

CITATIONS

35

---

READS

1,989

4 authors, including:



Jane Howe

University of Toronto

202 PUBLICATIONS 4,809 CITATIONS

SEE PROFILE



C. J. Rawn

University of Tennessee

132 PUBLICATIONS 2,748 CITATIONS

SEE PROFILE



Hooisweng Ow

Cornell University

19 PUBLICATIONS 2,577 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:



Soot oxidation in an Enviromental TEM [View project](#)



Adomian decomposition method [View project](#)

# Improved crystallographic data for graphite

J. Y. Howe<sup>a)</sup>

*School of Ceramic Engineering and Materials Science, Alfred University, Alfred, New York 14802*

C. J. Rawn

*High Temperature Materials Laboratory, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831*

L. E. Jones and H. Ow<sup>b)</sup>

*School of Ceramic Engineering and Materials Science, Alfred University, Alfred, New York 14802*

(Received 10 June 2002; accepted 15 November 2002)

Powder diffraction pattern of SP-1 graphite has been obtained using synchrotron X-ray diffraction. Unit cell dimensions were calculated using a least-squares analysis that refined to a  $|\Delta 2\theta^\circ|$  of no more than 0.007. A hexagonal cell was determined with a space group of  $P6_3/mmc$  (194),  $a=2.4617(2)$  and  $c=6.7106(4)$  Å. The Smith/Snyder figure of merit is 167 based upon 11 peaks, which indicates that the quality of this data set is superior to the existing PDF card for graphite, 41-1487. It is also emphasized that the interlayer spacing of graphite should be 3.355(1) Å. Using GAS and EXPGUI codes, a new set of calculated powder diffraction data based upon the interlayer spacing of 3.555 Å is generated. A comparison with the current calculated card, 75-1621, has also been made. © 2003 International Centre for Diffraction Data. [DOI: 10.1154/1.1536926]

Key words: graphite, powder diffraction, synchrotron X-ray

## I. INTRODUCTION

The objective of this work was to produce a set of cell refinement data based upon a high-quality graphite to replace the current PDF cards of measured pattern (PDF41-1487) and calculated pattern (PDF75-1621).

SP-1 is a commercially available single-crystal graphite with an interlayer spacing of 3.3553 Å. It has been frequently referenced by carbon researchers and industry as a standard for well-crystallized graphitic material. It is well accepted that the interlayer spacing of graphitic carbon ( $d_{002}$ ) decreases as the degree of crystallinity increases (Franklin, 1951; Oberlin, 1989; Ruland, 1968). The most highly graphitized carbon materials have an interlayer spacing of 3.355(1) Å (Franklin, 1951; Oberlin, 1989; Ruland, 1968; Trucano and Chen, 1975; Walker, Jr. *et al.*, 1965). However, the current PDF reference for graphite is based upon a material with  $d_{002}$  of 3.3756 Å (PDF 41-1487). This is an appreciable difference from that of SP-1 graphite (3.3553 Å). Material with an interlayer spacing of 3.3756 Å is merely a graphitic carbon, not crystalline graphite. Consequently, it is imperative that a set of excellent cell refinement data be collected from SP-1 graphite to serve as the new standard.

The current calculated pattern on graphite, Card 75-1621 was also under scrutiny. Lattice parameters used to generate this pattern ( $d_{002}=3.395$  Å) were cited from Hassel and Mark's study in 1924 (Hassel and Mark, 1924). Using a Laue camera, Hassel and Mark did four measurements of the  $c$  axis of the graphite 4H on single crystal graphite. They reported the values to be 6.78, 6.60, 6.78, and 6.81 Å. For reasons not mentioned in their paper, they rejected the value of 6.60 Å. Taking the average from the three higher values, they determined the  $c$  axis of graphite to be 6.79 Å, which

gave a  $d$  spacing of 3.395 Å. Obviously, Hassel and Mark's coarse measurement on the lattice parameters was due to the rudimentary instrumentation at the time. Later in the 1950s, Franklin first gave a clear definition of graphite and graphitic carbon. Her accurate measurements of interlayer spacing (3.354 Å) became the standard, still being widely accepted among carbon researchers and industries (Franklin, 1951). In 1975, Trucano and Chen published their study on the crystallography of graphite using neutron diffraction (Trucano and Chen, 1975). They confirmed that the spacing group of graphite 4H is  $P6_3/mmc$ . Even more important, they reported the anisotropic temperature factors for this highly anisotropic material. Now that more accurate, reliable data such as those from Trucano and Chen are readily available, Hassel and Mark's data should not be used for pattern simulation any longer.

Obtaining high quality data on graphite using X-ray powder diffraction is difficult. Carbon has a very low mass absorption coefficient for X-rays, which contributes to errors associated with displacement and peak broadening. Also, due to its layered structure it is difficult to prepare a graphite sample that is not highly textured. In order to circumvent these problems, we chose to collect data at a synchrotron facility equipped with a rotated, horizontally mounted capillary (normal transmission) and an analyzer crystal. The high intensity of synchrotron radiation allows the use of a horizontally mounted rotating capillary which minimizes preferred orientation effects caused by the platelet shape of the graphite crystals (McCusker *et al.*, 1999). The high intensity beam also permits the use of an analyzer crystal in place of a simple receiving slit. Acting like a slit with a very narrow angular acceptance, the analyzer crystal accepts only the reflected parallel beam. The parallel nature of the beam thus eliminates problems associated with sample displacement and aberrations caused by a flat sample (Baerlocher and McCusker, 1994).

<sup>a)</sup> Present address: Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831; electronic mail: howej@ornl.gov

<sup>b)</sup> Present address: Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853.

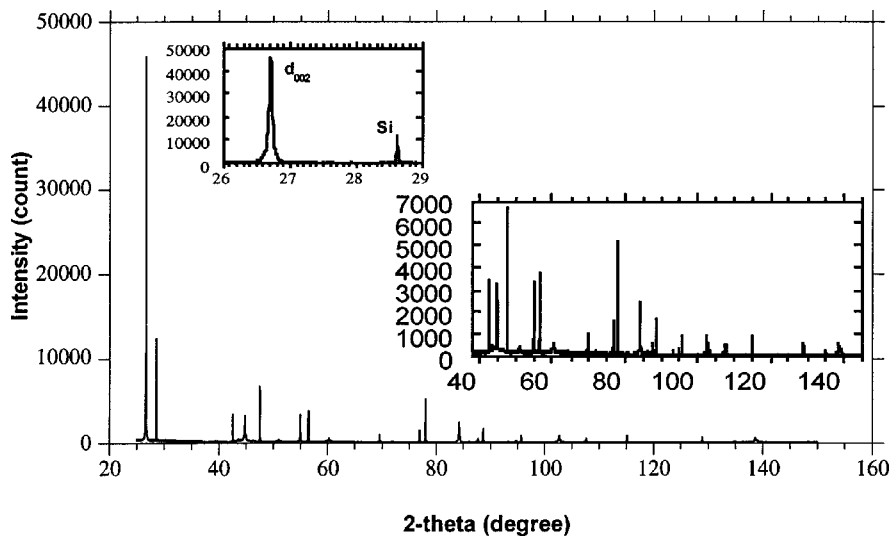


Figure 1. Synchrotron X-ray diffraction pattern of SP-1 graphite with SRM 640 silicon standard. Wavelength  $\lambda = 1.550\ 04\ \text{\AA}$ .

## II. MATERIALS AND EXPERIMENTAL

### A. Material

As-received SP-1 is a flaky material processed from purified natural graphite flake by Union Carbide Corporation, with a mean diameter of  $30\ \mu\text{m}$ . The total impurity is less than 6 ppm (Ranish, 1984). The total surface area is  $1.8\ \text{m}^2/\text{g}$  (BET, Ar, 77 K) (Allardice and Walker, Jr., 1970). Walker, Jr., Austin, and Tietjen report that the SP-1 crystals contain a minimum number of stacking faults between the layer planes (Walker, Jr. *et al.*, 1965). They also state that the select area electron diffraction study indicates that, in most cases, each flake of SP-1 has a single crystal form of graphite. SP-1 has the highest measured density among all the graphitic materials, which is  $2.265 \pm 0.001\ \text{g}/\text{cm}^3$  (Ismail, 2001). This value is quite close to the theoretical density of graphite,  $2.269\ \text{g}/\text{cm}^3$  (Walker, Jr. *et al.*, 1965). For these reasons, SP-1 has been considered highly crystalline and frequently cited as a reference for graphite.

### B. Experimental procedures

The SP-1 was ground in acetone using agate mortar and pestle, and sieved through a 500-mesh sieve ( $<25\ \mu\text{m}$ ). The powder was then mixed with 6 wt. % NIST SRM 640b silicon for internal calibration. X-ray powder diffraction data were collected on the high resolution powder diffraction beamline X14A at the National Synchrotron Light Source (located at Brookhaven National Laboratory, Upton, NY). The incident beam was vertically focused by a cylindrical mirror and horizontally focused by a ribbed and curved Si(111) crystal. A Ge (111) analyzer crystal was used between the sample and the Ar/CO<sub>2</sub>-filled proportional counter. The wavelength of  $1.550\ 04\ \text{\AA}$  was determined by refining on LaB<sub>6</sub> (NIST SRM 660) (PDF34-427). Additional verification of the wavelength was performed by using Si (NIST SRM 640b) as an internal standard (PDF27-1402). The sample was loaded into a 1-mm-diam thin walled glass capillary and continually rotated. This served to reduce systematic errors attributable to preferred orientation and inadequate powder averaging.

The diffraction pattern was collected from  $25^\circ$  to  $150^\circ$   $2\theta$ , with a step size of  $0.005^\circ$   $2\theta$ , and 50 000 counts/step at

room temperature. The intensity of the graphite  $d_{002}$  peak initially exceeded 40 000 counts/step, a count rate beyond which the detector and associated electronics were no longer linear. In order to reduce the diffraction intensity, the first portion of the diffraction pattern, from  $25^\circ$  to  $50^\circ$   $2\theta$ , was collected with  $75\ \mu\text{m}$  of aluminum foil placed in front of the detector. The remainder of the pattern, from  $40^\circ$  to  $150^\circ$   $2\theta$ , was collected without attenuation. The full diffraction pattern, Figure 1, from  $25^\circ$  to  $150^\circ$   $2\theta$ , was obtained by adjusting the intensity according to the intensity ratio of the overlap, from  $40^\circ$  to  $50^\circ$   $2\theta$  of the two patterns.

$I/I_c$  is the intensity ratio of the highest intensity reflection versus the corundum (104) reflection. To determine  $I/I_c$ , the specimen was prepared by mixing corundum (Linde C) with SP-1 graphite at 1:1 wt. ratio and loaded in a side-drifted holder. The  $I/I_c$  data were collected using a vertical Siemens D500  $\theta$ - $2\theta$  diffractometer equipped with a  $1^\circ$  divergence slit, a  $0.05^\circ$  receiving slit, a graphite diffracted-beam monochromator, and a scintillation detector. Cu  $K\alpha$  radiation was used at 30 mA and 40 kV. The diffraction pattern was collected as a step scan from  $25^\circ$  to  $45^\circ$   $2\theta$ , with a step size of  $0.02^\circ$   $2\theta$  and a dwell time of 10 s/step.

### C. Simulation procedures

Using the lattice parameters derived from SP-1 graphite and anisotropic thermal constants from Trucano and Chen (1975), a diffraction pattern of graphite was calculated using GSAS and EXPGUI (Larson and Von Dreele, 2000; Toby, 2001). The simulated pattern ranged from  $20^\circ$  to  $160^\circ$  of  $2\theta$  using Cu  $K\alpha$  wavelength of  $1.540\ 52\ \text{\AA}$ , with a step size of  $0.002^\circ$   $2\theta$ . All the intensities are determined from the maximum of the reflection (peak height).  $I/I_c$  was derived by simulating the phases of graphite and corundum at 1:1 weight ratio. The lattice parameters of the corundum phase were cited from PDF card 46-1212 and the paper of Huang *et al.* (1990) (PDF46-1212).

## III. RESULTS AND DISCUSSIONS

Using the convention that designates the polymorphs of silicon carbide, Holcombe denotes the unit cell of an ideal

TABLE I. Peak list report of SP-1 graphite.<sup>a</sup>

<i>hkl</i>	$2\theta$ (cal)	$2\theta$ (obs)	$\Delta 2\theta$	<i>d</i> (cal)	<i>d</i> (obs)	$\Delta d$	<i>I/I</i> <sub>0</sub>
002	26.710	26.710	0.000	3.3553	3.3553	0.0000	100
100	42.635	42.635	0.000	2.1319	2.1319	0.0000	7.0
101	44.846	44.849	-0.003	2.0318	2.0317	0.0001	6.3
102	51.025	51.032	-0.007	1.7994	1.7992	0.0002	0.4
004	55.028	55.027	0.001	1.6777	1.6777	0.0000	7.1
103	60.291	60.299	-0.008	1.5433	1.5431	0.0002	0.7
110	78.050	78.052	-0.002	1.2309	1.2308	0.0001	11.7
112	84.241	84.241	0.000	1.1556	1.1555	0.0001	5.0
006	87.728	87.726	0.002	1.1184	1.1185	-0.0001	1.1
201	94.815	94.821	-0.006	1.0527	1.0527	0.0000	0.4
114	102.696	102.703	-0.007	0.9924	0.9924	0.0000	1.8

<sup>a</sup>The  $2\theta$  values are given based upon the synchrotron wavelength of 1.550 04 Å; space group:  $P6_3/mmc$ ;  $a=2.4617(2)$  and  $c=6.7106(4)$  Å; color: metallic black; calculated density by XRD: 2.265 g/cm<sup>3</sup>; measured density: 2.265 g/cm<sup>3</sup>.

form of hexagonal graphite as 4H-G (Holcombe, 1973). Holcombe's work is also documented in PDF card 25-284 (PDF25-284). According to Holcombe, the notation 4H designates a hexagonal (H) unit cell with four carbon atoms. The space group of graphite-4H is  $P6_3/mmc$  (full notation is  $P6_3/m\ 2/m\ 2/c$ ) (Oberlin, 2000; Ruland, 1968). PDF card 41-1487 reports the space group is  $P6_3/mmc$  and a 2H notation for graphite. The notation 2H is incorrect because there are four carbon atoms per unit cell, not two.

The powder diffraction pattern of SP-1 graphite along with the NIST silicon standard is shown in Figure 1. The interlayer spacing of SP-1 is measured to be 3.3553 Å, which suggests that the material is indeed a well-crystallized graphite. The reflections listed in Table I, are indexed based upon the space group  $P6_3/mmc$ ,  $a=2.4617(2)$ ,  $c=6.7106(4)$  Å. The density calculated from the diffraction data is 2.265 g/cm<sup>3</sup>, which agrees well with the measured density of 2.265 g/cm<sup>3</sup>, provided by Ismail (2001).

The peak list report of the calculated pattern is tabulated in Table II. There are a total of 25 reflections at less than 160°  $2\theta$ . Some of them are rather weak reflections. *I/I*<sub>c</sub> value of 2.36 agrees well with the value reported on Card 75-1621, which is 2.37. In general, the peak intensities are in good agreement with Holcombe's calculation (PDF25-284) and Card 75-1621.

TABLE II. Calculated pattern of graphite.<sup>a</sup>

Peaks	<i>hkl</i>	<i>d</i> spacing (Å)	$2\theta$	Relative intensity
1	002	3.3553	26.543	100.0
2	100	2.1319	42.360	3.5
3	101	2.0318	44.555	16.7
4	102	1.7994	50.689	3.0
5	004	1.6777	54.661	5.4
6	103	1.5433	59.882	4.5
7	104	1.3184	71.498	0.7
8	110	1.2309	77.480	5.0
9	112	1.1556	83.605	7.3
10	105	1.1358	85.400	1.0
11	006	1.1184	87.052	0.7
12	200	1.0659	92.539	0.1
13	201	1.0527	94.051	1.0
14	202	1.0159	98.609	0.3
15	114	0.9924	101.818	4.1
16	106	0.9904	102.102	2.0
17	203	0.9623	106.346	0.8
18	204	0.8997	117.767	0.2
19	107	0.8743	123.518	0.4
20	008	0.8388	133.343	0.3
21	205	0.8347	134.670	0.6
22	116	0.8277	137.037	2.7
23	210	0.8058	145.844	0.3
24	211	0.8000	148.634	1.5
25	212	0.7835	158.893	0.5

<sup>a</sup>The  $2\theta$  values are given based upon the Cu  $K\alpha$  wavelength of 1.540 52 Å; lattice parameters:  $a=2.4617$  Å and  $c=6.7106$  Å; space group:  $P6_3/mmc$ .

A comparison of the relative intensity as well as the *d* spacing of SP-1 and the PDF 41-1487 is given in Table III. It shows that the reflections of SP-1 have higher relative intensity at low *d*-spacing regions. The reduced preferred orientation is also reflected in a smaller value of *I/I*<sub>c</sub>. The *I/I*<sub>c</sub> of SP-1 is  $5.5\pm 0.5$  as compared with that of 7.78 of the current card. The lower the *I/I*<sub>c</sub> value, the better the agreement of the experimental data to the theoretical calculations.

There is a significant improvement of the data quality as indicated by the figure of merit (FOM). The Smith/Snyder FOM is 167 based upon 11 peaks, which is an order of magnitude higher than the FOM of PDF 41-1487 (F(10)=18.4).

Due to the geometry and setup of the sample holder, as well as the high intensity and parallel nature of synchrotron

TABLE III. Comparison of *d* spacing and relative intensity of SP-1 graphite and PDF 41-1487.<sup>a</sup>

<i>hkl</i>	<i>d</i> spacing (Å)			Relative intensity ( <i>I/I</i> <sub>0</sub> )		
	SP-1 graphite	PDF 41-1487	$\Delta d$	Calc.	SP-1 graphite	PDF 41-1487
002	3.3553	3.3756	0.0203	100	100.0	100
100	2.1319	2.1386	0.0067	3.5	7.0	2
101	2.0317	2.0390	0.0073	16.7	6.3	6
102	1.7992	1.8074	0.0082	3.0	0.4	1
004	1.6777	1.6811	0.0034	5.4	7.1	4
103	1.5431	1.5478	0.0047	4.5	0.7	1
110	1.2308	1.2341	0.0033	5.0	11.7	3
112	1.1555	1.1604	0.0049	7.3	5.0	3
006	1.1185	1.1208	0.0023	0.7	1.1	1
201	1.0527	1.0567	0.0040	1.0	0.4	1
114	0.9924	n/a	n/a	4.1	1.8	n/a

<sup>a</sup>The calculated data (listed in column "Calc.") are cited from Table II.

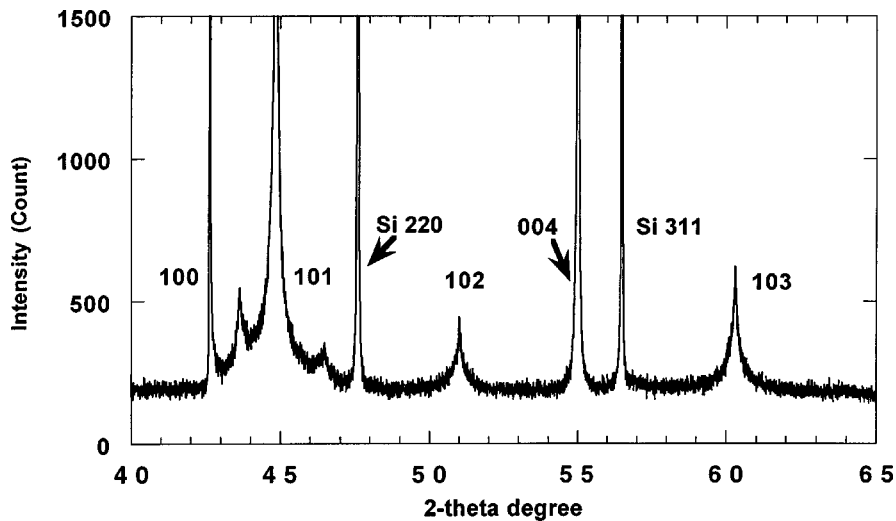


Figure 2. Synchrotron X-ray diffraction pattern of SP-1 graphite with SRM 640 silicon standard from 40 to 65° of  $2\theta$  (wavelength  $\lambda = 1.550\ 04\ \text{\AA}$ ). Graphite peaks (101), (102), and (103) are systematically broadened due to stacking faults.

radiation, there is minimal peak broadening, which allows a close examination of the peak broadening due to the nature of the crystallites. It is noted that there is a systematic peak broadening of graphite  $(10l)$  peaks, i.e., (101), (102) and (103). Peak broadening is also observed at  $(11l)$  peaks ( $l \neq 0$ ). Figure 2 is an X-ray diffraction (XRD) pattern of SP-1 from 40 to 65° of  $2\theta$  where the  $(10l)$  peaks are included. The full width at half-maximum (FWHM) and peak positions in  $2\theta$  of selected peaks are given in Table IV. Because the  $(00l)$  peaks and (110) peak are not affected by stacking faults, they can be used as a guideline to evaluate peak broadening.

Since peak width increases with diffraction angle (for instance, a peak at 20° is inherently broader than a peak at 80°), a comparison of peak widths should be undertaken between peaks at the similar  $2\theta$  angles. Listed in Table IV, the FWHM of (002), (004), and (006) peaks are 0.065, 0.088, and 0.123°  $2\theta$ , and is 0.060° for the (110) peak. Comparing peaks at similar  $2\theta$  regions, the  $(10l)$  peaks are more than two times wider. The FWHM of (101), (102), and (103) peaks are 0.165°, 0.268°, and 0.266°  $2\theta$ , respectively. The (102) and (114) peaks also broaden noticeably, with FWHM of 0.194° and 0.340°  $2\theta$ , respectively. Many researchers, including Franklin, Ruland, and Oberlin, attribute this to the presence of stacking faults (Franklin, 1951; Ruland, 1968). Grinding is the main source of stacking faults in this material, in which a mechanical deformation of the hexagonal lattice involves a selective and cumulative gliding of pairs of planes (Ruland, 1968). A similar peak broadening is observed in neutron diffraction patterns of a graphite rod by Chakoumakos (2000).

TABLE IV. FWHM of graphite  $(10l)$ ,  $(11l)$ , and  $(00l)$  peaks.

$(10l)$ and (110)	FWHM (degree $2\theta$ )	Peak position	FWHM (degree $2\theta$ )	Peak position
(101)	0.165	44.849	(002)	0.065
(102)	0.268	51.032	(004)	0.088
(103)	0.266	60.299	(006)	0.123
(110)	0.060	78.052		
(112)	0.194	84.241		
(114)	0.340	102.703		

#### IV. SUMMARY

A set of high quality diffraction data of graphite was generated using synchrotron X-ray radiation on SP-1 graphite powder. Apparently, stacking faults introduced by the mechanical working of hand-grinding caused peak broadening observed in the  $(10l)$  and  $(11l)$  ( $l \neq 0$ ) peaks. A calculated XRD pattern is also produced using the experimental data from SP-1 graphite.

#### ACKNOWLEDGMENTS

This work was sponsored by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the High Temperature Materials Laboratory User Program, Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725. We thank Dr. A. Oberlin and Dr. Scott Speakman for their helpful discussions. We are grateful that Dr. Jianming Bai assisted with the synchrotron XRD experiments at the X14A beam line.

- Allardice, D. J. and Walker, Jr., P. L. (1970). "The Effect of Substitutional Boron on the Kinetics of the Carbon-Oxygen Reaction," *Carbon* **8**, 375–385.
- Baerlocher, C. and McCusker, L. B. (1994). "Practical Aspects of Powder Diffraction Data Analysis," *Stud. Surf. Sci. Catal.* **85**, 391–427.
- Chakoumakos, B. (2000). Oak Ridge National Laboratory, Oak Ridge, TN (private communication).
- Franklin, R. E. (1951). "The Structure of Graphitic Carbons," *Acta Crystallogr.* **4**, 253–261.
- Hassel, O. and Mark, H. (1924). "Über die Kristallstruktur des Graphis," *Z. Phys.* **25**, 317–337.
- Holcombe, C. E. (1973). USAEC Oak Ridge Y-12 Plant, Report Y 1887.
- Huang, T. C., Parrish, W., Masciocchi, N., and Wang, P. W. (1990). "Derivation of d-Values from Digitized X-ray and Synchrotron Diffraction Data," *Adv. X-Ray Anal.* **33**, 295–303.
- Ismail, I. M. K. (2001). Air Force Research Laboratory, Edwards AFB, CA (private communication).
- Larson, A. C. and Von Dreele, R. B. (2000). "General Structure Analysis System (GSAS)," Los Alamos National Laboratory Report No. LAUR 86-748.
- McCusker, L. B., Von Dreele, R. B., Cox, D. E., Louer, D., and Scardi,

- P. (1999). "Rietveld Refinement Guidelines," *J. Appl. Crystallogr.* **32**, 36–50.
- Oberlin, A. (1989). In *Chemistry and Physics of Carbon*, edited by P. A. Thrower (Marcel Dekker, New York), Vol. 22, pp. 133–135.
- Oberlin, A. (2000). CNRS-Orleans University, France (private communication).
- PDF 25-284, International Centre for Diffraction Data, Newtown Square, PA, 2001.
- PDF 27-1402, International Centre for Diffraction Data, Newtown Square, PA, 2001.
- PDF 34-427, International Centre for Diffraction Data, Newtown Square, PA, 2001.
- PDF 41-1487, International Centre for Diffraction Data, Newtown Square, PA, 2001.
- PDF 46-1212, International Centre for Diffraction Data, Newtown Square, PA, 2001.
- PDF 75-1621, International Centre for Diffraction Data, Newtown Square, PA, 2001.
- Ranish, J. M. (1984). Ph.D. thesis, The Pennsylvania State University.
- Ruland, W. (1968). In *Chemistry and Physics of Carbon*, edited by P. L. Walker, Jr. (Dekker, New York), Vol. 4, pp. 28–33.
- Toby, B. H. (2001). "EXPGUI, a graphical user interface for GSAS," *J. Appl. Crystallogr.* **34**, 210–213.
- Trucano, P. and Chen, R. (1975). "Structure of Graphite by Neutron Diffraction," *Nature (London)* **258**, 136–137.
- Walker, Jr., P. L., Austin, L., and Tietjen, J. (1965). In *Chemistry and Physics of Carbon*, edited by P. L. Walker, Jr. (Dekker, New York), Vol. 1, pp. 342–343.