

## Lattice Constants of Graphite at Low Temperatures\*

Y. BASKIN AND L. MEYER

*Institute for the Study of Metals, University of Chicago, Chicago, Illinois*

(Received May 2, 1955)

The lattice constants of a graphite single crystal, natural graphite powder, and artificial graphite powder have been measured at 297°K, 78°K, and 4.2°K. The *a*-spacing does not change in this temperature range within the error of  $\pm 0.0005$  Å. The material with the greatest *c*-spacing showed between 297° and 78° the greatest change of *c*-spacing and the smallest change below 78°. The *c*-spacing of the artificial powder did not return to its original value at 297° after a thermal cycle, demonstrating irreversible deformation.

THE measurements at low temperatures of the physical properties of graphite such as electrical conductivity are usually slightly irreproducible.<sup>1,2</sup> Carbon thermometers used in the liquid helium temperature range generally have to be recalibrated each time they are used. It was suspected that this effect is due to the unusually large anisotropy of the thermal expansion of graphite which can cause mechanical deformation in every thermal cycle. In order to test this hypothesis precision measurements were made of the lattice constants of a single crystal of graphite (from Ticonderoga, New York), spectroscopically pure natural graphite powder (National Carbon Corporation No. SP 1) and spectroscopically pure artificial graphite (National Carbon Corporation No. SP 2) at room temperature (297°K), liquid nitrogen temperature (78°K), and liquid helium temperature (4.2°K). The measurements were performed in the low-temperature precision x-ray spectrometer developed in this laboratory and described elsewhere.<sup>3</sup>

The *c*-axis spacing was derived by the method of Nelson and Riley<sup>4</sup> from the maxima of the 002, 004, 006, and 008 peaks produced by Ni-filtered Cu radiation; each peak was scanned at intervals of one minute of arc. The *a*-axis spacing was derived from the 110

peak only. The accuracy with which the peaks were determined is  $\pm 0.005^\circ$  yielding an accuracy for the spacing of  $\pm 0.0005$  Å. The temperature was known to  $\pm 0.3^\circ$ K. Table I contains a summary of the results for the *c*-spacing.

The change of interlayer spacing with temperature depends strongly on the nature of the sample: The material with the largest interlayer spacing showed the greatest change of spacing, between 297° and 78° and the smallest change below 78°. A large *c*-spacing is usually considered to be a sign of less perfect crystallites.<sup>5</sup> Since anisotropic changes of volume, especially in polycrystalline material, are often accompanied by plastic deformation, it does not seem surprising that a temperature exists at which the thermal forces trying to contract the specimen are balanced by the opposing mechanical strain from surrounding crystallites, and that this temperature depends on the size and the quality of the crystals. At the lowest temperatures the single crystal which had the smallest fraction of imperfections among the specimens showed the greatest amount of contraction with the lowering of the temperature.

The irreversible changes possible during a thermal cycle are demonstrated by the fact that the *c*-spacing of the artificial graphite did not return to its original value at 297°K after being cooled to 4.2°K.

As Walker *et al.*<sup>6</sup> found a practically linear variation of interlayer spacing with temperature down to 78°K, an average thermal expansion coefficient  $\alpha$  defined by

$$d_T = d_{T_0} + \alpha(T - T_0),$$

$d_T$  being the interlayer spacing at the temperature  $T$ , and calculated between 297° and 78°, is given in the bottom row of Table I. The value of  $\alpha$  for the artificial powder agrees with that found by Walker *et al.*; the  $\alpha$  values for the natural powder and the single crystal are distinctly lower.

The *a*-axis spacing was found to be  $2.4589 \pm 0.0005$  Å at 297°K, changing less than 0.0005 Å when the specimen was cooled to 78°K.

TABLE I. Interlayer spacing of graphite as a function of temperature.

T°K	Single crystal A	Natural powder SP 1 A	Artificial powder SP 2 A
297°	3.3538	3.3542	3.3600
78°	3.3378	3.3378	3.3392
4.2°	3.3360	3.3367	3.3388
297° after cooling	3.3538	3.3542	3.3590
Expansion coefficient 78°-297°K	$7.34 \cdot 10^{-5}$	$7.59 \cdot 10^{-5}$	$9.52 \cdot 10^{-5}$

\* Supported in part by U. S. Atomic Energy Commission.

<sup>1</sup> Meyer, Picus, and Johnston, National Bureau of Standards Circular No. 519, October, 1952, p. 249.

<sup>2</sup> W. Primak and L. H. Fuchs, Phys. Rev. **95**, 22 (1954).

<sup>3</sup> Barrett, Long, Meyer, and Walker (to be published).

<sup>4</sup> J. B. Nelson and D. P. Riley, Proc. Phys. Soc. (London) **57**, 477 (1945).

<sup>5</sup> R. E. Franklin, Acta Cryst. **4**, 253 (1951).

<sup>6</sup> Walker, McKinstry, and Wright, Ind. Eng. Chem. **45**, 1711 (1953).