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Unit-Cell Dimensions of Graphite

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It is shown that the variation with particle size of the *c* dimension of the graphite unit cell, often reported for small crystallites, can be followed through the range of relatively well-crystallized specimens. The value of *c* is found to be a linear function of the reciprocal of the number of carbon layers in the crystallite. The *a* dimension remains constant over this range, although there are small displacements of the *hki*0 lines, probably on account of admixture of a proportion of turbostratic material.

Introduction

In the course of determinations of the unit-cell dimensions of various types of graphite further data have been obtained concerning the variations of these dimensions with crystallite size. Earlier measurements, such as those of Hofmann & Wilm (1936), have shown the difference between normal graphite and graphites with very small particles. The present measurements show that there is a continuous variation of the *c* dimension of the unit cell through the range of relatively well crystallized specimens (both natural and artificial), the value tending to a limit for the best crystallized samples available. Over the same range the *a* dimension is found to remain constant, although there are apparent changes when measurements are based on *hki*0 lines, due presumably to superposition of a displaced maximum from a proportion of turbostratic material.

Experimental details

The spacing measurements were made by the method described by the writer (1948). Extruded specimens of powdered graphite mixed with a little NaCl were employed, using Cu $K\alpha$ radiation in a 19 cm. camera. All the spacing values were taken as the mean of those found from four or more pairs of films. For determination of the *c* dimension the 0008 reflexion at $\theta = 67°$ was measured in the case of the samples with fairly large crystallites, but with decrease of cystallite size the 0008 reflexion becomes too diffuse for accurate measurement and in these cases 0006 at 44° was used. Using this relatively low-angle reflexion it was shown that there was no significant error due to orientation by extrusion, of the type described by Nelson & Riley (1945*a*), this being established by subsidiary experiments in which small cylinders, 0·05 cm. in diameter, were turned in a lathe from a large uniform block of graphite and mounted directly in the camera. Measurement was made of the angular difference between the $11\bar{2}0$ and 0006 reflexions. These lines have θ values differing by only 4·8°, and their measured angular separation will be little influenced by absorption corrections. Moreover, the $11\bar{2}0$ line will be uninfluenced by orientation and serves therefore as a constant reference position. It was found that the separation measured was the same, to 0·0001 A., as that for the extruded specimens containing NaCl. A similar experiment established the reliability of the 0008 reflexion, when it could be employed, measurement being made of the angular separation between the 0008 and $12\bar{3}0$ reflexions.

For the *a* dimension the main measurements were of the $12\bar{3}0$ and $12\bar{3}1$ reflexions, which occur at $\theta = 73$ and 74° respectively. Calculation shows that the position of the latter is influenced very little by the precise value chosen for *c*. The $11\bar{2}0$ line at 39° was also measured.

The crystallite sizes of the samples were determined from the X-ray line widths, which were interpreted on the graphite model proposed by Hofmann & Wilm (1936). This model explains the particular characteristic of the graphite photograph, namely *hkil* lines which become increasingly broad with increase of the *l* index, except for the 000*l* lines which are sharp. This is explained by assuming that the carbon planes are stacked regularly for an average thickness *t*, at successive intervals of which there is a random twist about the

c axis, although parallelism of the planes is maintained over a considerably greater distance H. Thus the line widths for $10\bar{1}3$, $11\bar{2}2$, $11\bar{2}4$, $11\bar{2}6$, etc., are determined by a thin plate crystallite of thickness t, whereas the line widths for 0004, 0006 and 0008 are determined by the greater height H. For the samples examined, the dimensions in the plane of the layers are estimated from the $11\bar{2}0$ and $12\bar{3}0$ reflexions to range from about 700 to a few thousand Ångström units, but are too great to measure accurately. The dimension t can be calculated fairly accurately in all cases, but H is too large for accurate estimation in the samples with large crystallites. Where it could be measured a value of about seven times t was obtained.

The line-width measurements were made using the mixture method described by Jones (1937). For samples with large particles the high-angle lines $12\bar{3}1$, $11\bar{2}4$ and $11\bar{2}6$ were measured, annealed tungsten being chosen as the most suitable standard substance which would avoid overlapping of lines. For the samples with smaller particle sizes the lines 0004, 0006, $10\bar{1}3$, $11\bar{2}2$ and $11\bar{2}4$ were measured, and in this case copper was the most convenient standard substance. In all cases the lines were resolved into their α_1, α_2 components by the graphical method discussed by Pease (1948). If the carbon layers are assumed to be of infinite horizontal extension it can be shown, by a simple application of the formula (2) given by Stokes & Wilson (1942), that the line widths, β, for the $hkil$ reflexions are given by

$$\beta=\frac{\lambda\sin\alpha}{t\cos\theta},$$

where α is the inclination to the horizontal of the normal to the $hkil$ planes. Consequently, a plot of $\beta\cos\theta$ against $\sin\alpha$ gives the value of t.

Discussion of results

The results obtained for the c dimension are shown in curve (1) of Fig. 1 for four samples of graphite, three of them (A_1, A_2 and A_3) artificial and the fourth a sample of Ceylon graphite. The values are given at 15° C. in Ångström units, assuming λ for Cu $K\alpha_1=1{\cdot}54050$ A., and are plotted against the values found for t. The value of H, when it could be measured, is also indicated. The areas drawn around the points on the curve indicate the estimated accuracy of the results. For comparison the value for c given by Nelson & Riley (1945*b*) for Ceylon graphite is also given, with the experimental error quoted, after conversion from kX. to Ångström units. It is seen from the curve that with increase of t, and H, there is a gradual decrease of c dimension, the value tending to a limit at large t. In order to check that no appreciable variation of c was due to adsorbed gases, samples were heated for an hour at 850° C., but no changes outside the experimental error of the measurements were found.

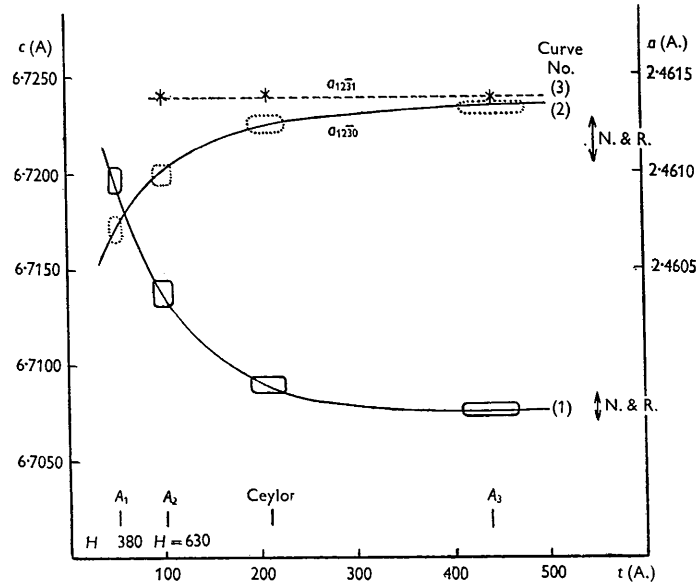

Fig. 1. Variation of c and a dimensions with crystallite thickness.

If the c dimension is plotted against $1/t$ or $1/H$, a linear relation is found to hold. The slopes of the lines obtained are such as to suggest that the linear relation holds right down to the small crystallites having H values of about 15 A. measured by Hofmann & Wilm. Moreover, the variations are of the same order as estimated theoretically by Lennard-Jones (1930) for small crystallites. It is intended to make further measurements to examine these agreements.

The values of the a dimension, as determined from measurements of the $12\bar{3}0$ reflexion, which is a well-resolved line for all the samples, are shown in curve (2) of Fig. 1. The value of a given by Nelson & Riley for Ceylon graphite is also shown. There is a regular decrease of a, from the limiting value, with decrease of crystallite size. Measurements of the low-angle $11\bar{2}0$ line at 39°, which was resolved graphically into its α_1, α_2 components, also suggested a variation of a, a difference of $0{\cdot}0007 \pm 0{\cdot}0002$ A. being obtained between samples A_1 and A_3. At first sight this variation is a genuine effect, since if each sample were composed entirely of regular blocks of thickness t the $hki0$ reflexions would be pure three-dimensional reflexions and not subject to change of shape and displacement to larger θ values, as described for turbostratic material by Warren (1941) and discussed by Taylor (1942). The conclusion of the latter paper is that there is no genuine change of the a dimension for carbon layers having widths greater than a few tens of Ångström units, but the accuracy of the measurements considered is not sufficient for this paper alone to discount the genuineness of the relatively small variation shown in our curve (2). However, the theoretical work of Bradburn, Coulson & Rushbrooke (1948) does suggest that variations of this magnitude will not be found amongst particles as large as those under consideration. Measurements were made therefore of the position of the $12\bar{3}1$ line, which is a well resolved line for all but the first sample, A_1. It is necessary to assume a value of c in order to determine a from this line, but the result is very insensitive to the precise value chosen, since in the formula for calculating the spacing of this line the term involving c is less than 2 % of the a term; an error of 0·01 A. would be necessary in c in order to give an error of 0·00005 A. in a. The values obtained are shown in curve (3) of the figure and are constant to a few hundred-thousandths of an Ångström unit. With A_3, the sample with the largest particles, the mean value of a from $12\bar{3}0$ is still slightly below the value obtained from $12\bar{3}1$, but the difference here is within the estimated experimental error. Unfortunately, with A_1, the sample showing the smallest layer planes, the $12\bar{3}1$ reflexion is too diffuse for accurate measurement, on account of the simultaneous reduction of t, so that it is not possible to investigate by this method over what further range a remains constant.

From curve (3) it is concluded that the apparent displacements of the $hki0$ maxima, such as $11\bar{2}0$ and $12\bar{3}0$, are due to the increasing effect of the superposition of a two-dimensional maximum, from a proportion of turbostratic material, on what is mainly a three-dimensional reflexion. The resultant error in a would depend not only on the values of the layer dimensions and $1/\sin\theta$ (Taylor, 1942) but also on the proportions and the relative magnitudes of the structure factor for two and three-dimensional reflexions for the particular $hki0$ line. It is hoped that evidence may be obtained from intensity measurements to decide whether the actual magnitude of the displacements found can be accounted for.

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The Crystal Structure of 'Gammexane', γ-$C_6H_6Cl_6$

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The crystal structure of the γ-isomer of benzene hexachloride, the insecticide 'Gammexane', has been determined by X-ray analysis (Weissenberg diagrams) in the usual way by trial and error, starting from Patterson data and supported by repeated Fourier syntheses.

Introduction

Gammexane (m.p. 112° C.), γ-$C_6H_6Cl_6$, is monoclinic prismatic with

$$a=8{\cdot}52,\quad b=10{\cdot}27,\quad c=13{\cdot}94\ \text{A.},\quad \beta=121^\circ\,16'.$$

Cell volume 1042·6 A.^{3}. Four molecules per unit cell. Measured density = 1·85 g.cm.$^{-3}$; calculated density = 1·852 g.cm.$^{-3}$. Absent spectra: $(h0l)$ when l is odd; $(0k0)$ when k is odd. Space group $P2_1/c$. Equivalent points: (x,y,z); $(\bar{x},\bar{y},\bar{z})$; $(x,\bar{y}+\frac{1}{2},z+\frac{1}{2})$; $(\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2})$. Most crystals have well-developed diamond-shaped $(\bar{1}02)$ planes with diagonals [201] and [010]; also the planes