atomic steps were present on the substrate surface or if silicon diffused below the surface.

In conclusion, approximate crystallographic match between the three pairs of atomic planes (110)/(11$\bar{2}$0), {100}/(01$\bar{1}$2), and {111}/(0001) in non-isomorphous silicon and sapphire has been found by systematic analysis of their lattice structures. The latter two matches agree with those of Nolder & Cadoff (1965). The same two matches have been experimentally verified by Manasevit *et al.* (1965). Parallelism between (110) silicon and (11$\bar{2}$0) sapphire has been experimentally verified by Manasevit & Simpson (1964) and by Joyce *et al.* (1965), but the first authors used a substrate which was not cut parallel to (11$\bar{2}$0), and the second authors reported no atomic fit between these two planes. Preliminary work in this laboratory, however, indicated epitaxy between (110) silicon and (11$\bar{2}$0) sapphire when sapphire was cut parallel to (11$\bar{2}$0).

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The Shape of Two-Dimensional Carbon Black Reflections*

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A rigorous derivation is given for the shape of a two-dimensional *hk* reflection for a turbostratic structure in which the layers are considered to be disks of radius R. An average disk dimension is defined as $L_a=(\pi/2)R$, and this dimension is obtained from the half maximum breadth of an *hk* reflection by $L_a=1{\cdot}77\lambda/(B\cos\theta_0)$. The constant differs by only 4 % from that obtained in an earlier approximate treatment. This definition of an average dimension differs by 17 % from that which has been used in recent treatments of carbon black patterns by the general Debye scattering equation.

Introduction

Carbon black is a common example of a turbostratic structure. Parallel layer groups are built up out of graphite layers, arranged parallel to one another, but with random orientation about the normal to the layers. Except for crystalline 00*l* reflections, the random orientations of the layers prevent the appearance of the general *hkl* reflections. The individual layers diffract independently, and we have two-dimensional *hk* reflections. For such a turbostratic structure, the reciprocal lattice comprises 00*l* points and continuous *hk* rods. In a powder pattern, the 00*l* points give the usual powder pattern peaks, and the *hk* rods give peaks which rise sharply on the small angle side and tail off slowly on the high angle side. From the shape of such a two-dimensional reflection, it is possible to obtain the size of the individual layers.

The problem of a two-dimensional powder pattern reflection from carbon black has been treated by Warren (1941). The graphite layers were assumed to be parallelograms of edges N_1a_1 and N_2a_2, where a_1 and a_2 are the usual graphite axes. An average dimension L_a was defined in such a way that for $N_1a_1=N_2a_2=Na$, the dimension is given by $L_a=(\sqrt{3}/2)\,Na$. Approximating functions of the type $\sin^2 Nx/\sin^2 x$ by Gaussian functions, the layer dimension L_a was expressed in terms of the breadth at half maximum intensity by the relation

$$L_a=\frac{1{\cdot}84\lambda}{B(\frac{1}{2},2\theta)\cos\theta_0}. \qquad (1)$$

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Although this relation has had considerable use in the determination of the L_a dimension in carbon blacks, it can be criticized on several points. It is uncertain how much error is caused by the Gaussian approximation, a disk shaped layer would be more realistic than the parallellogram which was used, and a peak breadth at two-thirds of the maximum intensity would be less influenced by the 004 reflection which occurs on the high angle side of 10.

A treatment of this problem which avoids making the Gaussian approximation, and which covers layers of any simple shape, has been given by Wilson (1949). Although the method is completely general, the work was not carried to the point of obtaining quantitative relations which could be used for determining layer sizes. The most realistic shape for the graphite layers is a disk, and for this shape there is another method for treating the problem rigorously which leads to the same result as the method of Wilson (1949), and for which the final numerical integration is simpler.

Profile of a two-dimensional reflection

We assume graphite layers which are disks of radius R. In terms of the two-atom structure factor F, the amplitude from one layer is given in electron units by

$$A(eu)=F\sum_m \exp\left[2\pi i\left(\frac{\mathbf{S}-\mathbf{S}_0}{\lambda}\right)\cdot(m_1\mathbf{a}_1+m_2\mathbf{a}_2)\right]$$

where $\mathbf{S}$ and $\mathbf{S}_0$ are unit vectors in the directions of the scattered and primary beams. We represent the diffraction vector in terms of the reciprocal vectors $\mathbf{b}_1\mathbf{b}_2\mathbf{b}_3$ and the continuous variables $h_1h_2h_3$. $(\mathbf{S}-\mathbf{S}_0)/\lambda=(h+h_1)\mathbf{b}_1+(k+h_2)\mathbf{b}_2+h_3\mathbf{b}_3=\mathbf{H}+\mathbf{q}+h_3\mathbf{b}_3$, where $\mathbf{H}=h\mathbf{b}_1+k\mathbf{b}_2$ is the vector to the $hk0$ position on the hk rod, and $\mathbf{q}=h_1\mathbf{b}_1+h_2\mathbf{b}_2$ is a vector from the center line of the hk rod. Let $\boldsymbol{\varrho}_m=m_1\mathbf{a}_1+m_2\mathbf{a}_2$ where $\boldsymbol{\varrho}_m$ is measured from the center of the disk. Since the intensity is appreciable only for small values of q, the sum can be replaced by an integral, and we obtain for the amplitude

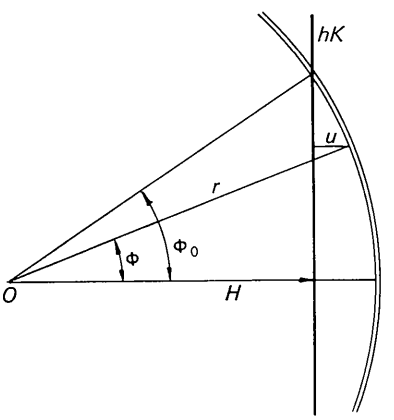

Fig. 1. The reciprocal space geometry involving an hk rod and the sphere of radius r.

$$A(eu)=F\sum_m \exp\left[2\pi i\mathbf{q}\cdot\boldsymbol{\varrho}_m\right]=\frac{F}{A_a}\int_0^R\int_0^{2\pi}\exp\left[2\pi iq\varrho\cos\alpha\right]$$

$$\varrho d\varrho d\alpha=\frac{2\pi F}{A_a}\int_0^R J_0(2\pi q\varrho)\varrho d\varrho=\frac{F\pi R^2}{A_a}\left[\frac{2J_1(2\pi qR)}{2\pi qR}\right]$$

where $A_a=a^2\sqrt{3}/2$ is the area of the two-atom unit cell. The intensity per layer is then given by

$$I(eu)=F^2\left(\frac{\pi R^2}{A_a}\right)^2\left[\frac{2J_1(2\pi qR)}{2\pi qR^2}\right]^2. \qquad (2)$$

Let M be the number of randomly oriented disks in the sample, D the distance to the receiving surface, and dV a volume element in reciprocal space. The power P arriving at the receiving surface is then given by the powder pattern power theorem (Warren, 1959):

$$P=\frac{MD^2\lambda^3}{4}\iiint\frac{I_{eu}(h_1h_2h_3)}{\sin\theta}dV. \qquad (3)$$

In reciprocal space, we introduce a spherical shell of radii r and $r+dr$, where $r=2\sin\theta/\lambda$, as shown by Fig. 1. If dS is an element of area on the surface of the spherical shell, $dV=dSdr=dSd(2\theta)\cos\theta/\lambda$. Incorporating this in equation (3),

$$P=\int P_{2\theta}d(2\theta)=\frac{MD^2\lambda^3}{4}\iiint\frac{I_{eu}(h_1h_2h_3)}{\sin\theta}\frac{\cos\theta}{\lambda}dSd(2\theta).$$

Omitting the integration with respect to $d(2\theta)$, and dividing by $2\pi D\sin 2\theta$, we obtain $P'_{2\theta}$, the measured power distribution per unit length of diffraction circle:

$$P'_{2\theta}=\frac{MD\lambda^2}{16\pi\sin^2\theta}\iint I_{eu}(h_1h_2h_3)dS. \qquad (4)$$

Using $I(eu)$ from equation (2), and introducing a multiplicity $m(hk)$ to include the contribution from all equivalent hk rods, we obtain the observable powder pattern profile $P'_{hk}(2\theta)$:

$$P'_{hk}(2\theta)=\frac{mMD\lambda^2F^2}{16\pi\sin^2\theta}\left(\frac{\pi R^2}{A_a}\right)^2\iint\left[\frac{2J_1(2\pi qR)}{2\pi qR}\right]^2dS. \qquad (5)$$

Since the intensity differs from zero only for positions close to the hk rod (q small), we can replace the sphere by the tangent cylinder of radius r. Let $q^2=u^2+v^2$ where, on Fig. 1, u is in the plane of the paper and v is perpendicular to the paper. The element of area is then represented by $dS=rd\varphi dv$. Let $(2\pi qR)^2=a^2+z^2$ where $a=2\pi uR$ and $z=2\pi vR$.

$$\iint\left[\frac{2J_1(2\pi qR)}{2\pi qR}\right]^2dS=2\int_0^\pi = rd\varphi\frac{2}{2\pi R}\int_0^\infty\left[\frac{2J_1(\sqrt{a^2+z^2})}{\sqrt{a^2+z^2}}\right]^2dz.$$

$$\text{Let } Q(a)=\int_0^\infty\left[\frac{2J_1(\sqrt{a^2+z^2})}{\sqrt{a^2+z^2}}\right]^2dz=\frac{2}{a^2}H_1(2a) \qquad (6)$$

where $H_1(x)$ is the Struve function, defined and tabulated in Watson (1952). With this abbreviation,

$$P'_{hk}(2\theta) = \frac{mMD\lambda^2F^2}{16\pi \sin^2\theta}\left(\frac{\pi R^2}{A_a}\right)^2 \frac{2r}{\pi R}\int_0^{\pi} Q(2\pi uR)d\varphi \,. \quad (7)$$

Referring to Fig. 1,

$$u = r\cos\varphi - H = (r-H) - 2r\sin^2\varphi/2 \,.$$

Let $2\pi uR = \pi\gamma - x^2$, where $\gamma = 2R(r-H)$, $x = 2(\pi Rr)^{\frac{1}{2}} \sin\varphi/2$, and $dx = (\pi Rr)^{\frac{1}{2}}\cos\varphi/2 d\varphi$. Since there is an appreciable contribution only when φ is close to φ_0, we replace $\cos\varphi/2$ by $\cos\varphi_0/2$ and take it outside of the integral. The value is given by $\cos\varphi_0/2 = [(\sin\theta + \sin\theta_0)/2\sin\theta]^{\frac{1}{2}}$ where $\sin\theta_0 = \lambda H/2$.

With the abbreviation

$$X(\gamma) = \sqrt{\pi}/2\int_0^{\infty} Q(|\pi\gamma - x^2|)dx \quad (8)$$

we obtain a final expression for the intensity profile

$$P'_{hk}(2\theta) = \frac{mMD\lambda^{3/2}R^{5/2}F^2X(\gamma)}{2\pi A_a^2 \sin\theta\,(\sin\theta + \sin\theta_0)^{\frac{1}{2}}} \quad (9)$$

where

$$\gamma = \frac{4R}{\lambda}(\sin\theta - \sin\theta_0) \,. \quad (10)$$

The function $X(\gamma)$ is readily evaluated from equation (8), making use of equation (6) to express $Q(|\pi\gamma - x^2|)$ in terms of the tabulated Struve function. The values obtained in this way are shown by Fig. 2. For large values of γ ($\gamma > 2$), $X(\gamma)$ can be evaluated by direct integration, and we obtain $X(\gamma) = \pi/(4\gamma)^{\frac{1}{2}}$.

If the problem is carried through by the method of Wilson (1949) we obtain

$$P'_{hk}(2\theta) = \frac{mMD\lambda^{3/2}R^{5/2}F^2Y(\gamma)}{2\pi A_a^2 \sin\theta\,(\sin\theta + \sin\theta_0)^{\frac{1}{2}}} \quad (11)$$

where

$$Y(\gamma) = \int_0^1 \left\{\frac{\cos^{-1}S - S\sqrt{1-S^2}}{\sqrt{S}}\right\}(\cos 2\pi\gamma S + \sin 2\pi\gamma S)dS \quad (12)$$

and, as before, $\gamma = (4R/\lambda)(\sin\theta - \sin\theta_0)$. Although equation (12) is a little more complicated than equation (8), it is readily programmed, and the values of $Y(\gamma)$ are shown by Fig. 2. In spite of the difference in appearance, $X(\gamma)$ and $Y(\gamma)$ are identical, and the two treatments lead to the same profile.

Conclusions

From Fig. 2, the width of the $X(\gamma)$ curve at half maximum is $\Delta\gamma = 2{\cdot}25$. In terms of equation (10), $\Delta\gamma = (2R/\lambda)\cos\theta_0 B(\frac{1}{2}, 2\theta)$. For a disk, it is reasonable to define an average dimension by

$$L_a = \pi R^2/2R = (\pi/2)R \,. \quad (13)$$

Combining these expressions, the average dimension is given in terms of the measured breadth at half intensity by

$$L_a = \frac{1{\cdot}77\lambda}{B(\frac{1}{2}, 2\theta)\cos\theta_0} \quad (14)$$

The numerical constant differs by only 4% from that of equation (1). However, the two treatments refer to average dimensions L_a defined for differently shaped layers. Relating L_a to the area of the layer

Equation (1) $A = (2/\sqrt{3})L_a^2$ $L_a = 0{\cdot}93\,A^{\frac{1}{2}}$.
Equation (14) $A = (4/\pi)L_a^2$ $L_a = 0{\cdot}89\,A^{\frac{1}{2}}$. (15)

In terms of the area of the layer, equations (1) and (14) lead to almost identical values. Since a disk shape is the more realistic, it is preferable to use equation (14), recognizing that the value obtained is $L_a = (\pi/2)R$ where R is the radius of the disk.

Because of the fact that the 004 reflection occurs on the high angle side of 10, it may be preferable to measure the breadth at two-thirds of the maximum intensity since this gets a little farther away from 004. From Fig. 2 $\Delta\gamma = 1{\cdot}20$ and the average dimension is given by

$$L_a = \frac{0{\cdot}94\lambda}{B(2/3, 2\theta)\cos\theta_0} \,. \quad (16)$$

If there is a variation in size, the larger layers contribute more to the upper part of the peak, and equation (16) will give a larger value of L_a than equation (14). It has been suggested by Clarke (1964) that the slope of the small angle side of 10 would be more nearly free from the influence of (004). If $\Delta(2\theta, \frac{1}{4}-\frac{3}{4})$ is the difference between positions at $\frac{1}{4}$ and $\frac{3}{4}$ of maximum,

$$L_a = \frac{0{\cdot}38\lambda}{\Delta(2\theta, \frac{1}{4}-\frac{3}{4})\cos\theta_0} \,. \quad (17)$$

The drawback to the use of equation (17) is, of course, that it requires measuring a very small $\Delta(2\theta)$ for which the instrumental corrections may be very important.

The peak of the $X(\gamma)$ curve occurs at $\gamma = 0{\cdot}35$. This represents a shift toward large angle from the position where an $hk0$ graphite reflection would occur.

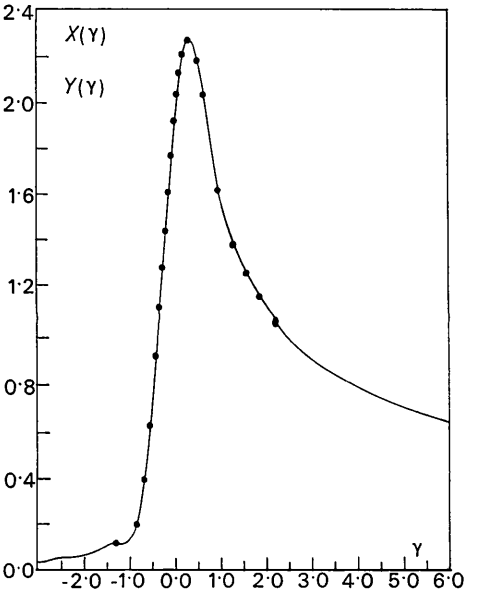

Fig. 2. The functions $X(\gamma)$ and $Y(\gamma)$ as a function of γ. $X(\gamma)$ is shown by the points, and $Y(\gamma)$ by the continuous curve.

$$\Delta(\sin\theta)=0{\cdot}35\lambda/4R=0{\cdot}14\lambda/L_a\,. \qquad (18)$$

This is close to the same peak shift obtained previously by Warren (1941).

The results obtained here are rigorous within the conditions assumed. We have postulated disk shaped graphite layers all of one size, with no allowance for a size distribution. The results are applicable only for graphite layers which are large enough to give well developed *hk* reflections for which it is possible to make a breadth measurement which is not influenced by neighboring peaks. It is also postulated that the layers have random orientation about the layer normal, with no modulations in the peak due to neighboring layers assuming the graphite orientation.

For samples in which the layers are very small, it is necessary to develop the diffraction pattern from the general Debye scattering equation. The problem has been treated in this way by Diamond (1957) and Warren & Bodenstein (1965). Both of these treatments follow Diamond's convention, which in terms of areas of disks, amounts to defining an $L_a=1{\cdot}9R$. This differs from the average dimension $L_a=(\pi/2)R$ used in this paper. The difference is about 17%, and it must be kept in mind in comparing results from the two treatments.

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Correlation of Observations in the Least-Squares Calculation for the Analysis of Gas Electron Diffraction Data

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In an ordinary least-squares analysis of gas electron diffraction, the standard deviation for the most probable value of a parameter for a molecule depends on the interval of measurements Δs on a microphotometer recording, that is, on the number of observed points on an intensity curve.

It is shown that a reasonable estimate of the standard deviation of a parameter can be obtained by taking into account the effect of 'correlation' among the points of observations. A general method and its simplified form for dealing with the correlation are developed by introducing off-diagonal elements into the weight matrix used in the least-squares fit of the observed values. The simplified method is applied, as an example, to the electron-diffraction data of silicon tetrachloride, and it is shown that the standard deviation of the most probable value estimated by using an infinite number of observations does not approach zero. At the same time, it is shown that when a diagonal weight matrix is used for simplicity there is an optimum interval for measurements in order to get a correct standard deviation. The optimum interval in the example given was about $\Delta s=\pi/10$.

Introduction

In a usual method of least squares, the standard deviation for the most probable value is approximately proportional to the inverse of the square root of the number of observed points used in the calculation. Since an arbitrary number of points can be chosen on a continuous curve, such as the microphotometer trace obtained by experiments of gas electron diffraction, the standard deviation for a parameter estimated by the least-squares analysis can be made unlimitedly small if the number of observations is infinitely increased. Such an argument, however, is based on a wrong assumption that all observed points remain mutually independent even when the interval of measurements becomes small. It would thus be desirable to have a