

The Determination of Lattice Constants Using Low Angle Diffraction Lines

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A technique is presented whereby accurate lattice constants and interplanar spacings may be derived from low-angle reflections by using a modified camera geometry in recording the diffracted rays. Photographs thus produced require a substantially shorter exposure than those produced by conventional methods, and the technique lends itself to the elimination of the serious systematic errors which hitherto have rendered low-angle reflections unusable in lattice-constant work.

Although the study of X-ray powder diffraction patterns has been tending for some time towards greater precision, nearly all efforts in this field have dealt with obtaining lattice constants for materials which yield well defined high-angle reflections, and little has been done in an effort to obtain accurate lattice constants of other substances, even though many of these yield excellent patterns of low-angle reflections.

There are two essentially independent types of error in the low-angle region. The first embraces those errors which are related to specimen thickness, by far the most important of which is absorption. Errors of this nature may be reduced by the use of a very thin wafer of powdered specimen in place of the usual cylindrical rod. The second stems from the fact that, at low angles, an inverse relationship exists between the interplanar spacing in the crystal and the measured distance on the film. This results in a crowding together of lines from the most widely spaced crystal planes on that portion of the film where the resolution is the poorest, and where the intensity of the background radiation is greatest. The poor resolution of the circular Debye camera in the low-angle region is illustrated in Fig. 1; it will be noted that small errors in estimating the magnitude of θ result in large errors in the value of d when d is large.

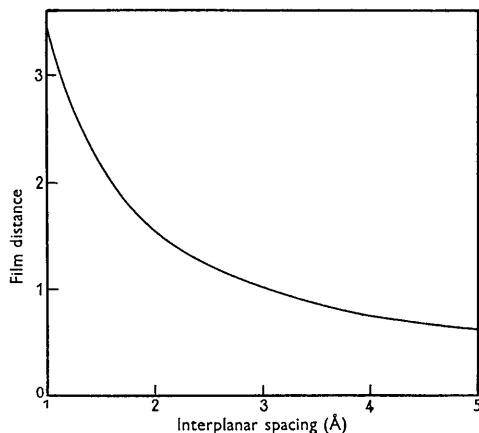


Fig. 1. Film distance versus d (Cu $K\alpha$ radiation).

Errors of this nature may be greatly reduced by altering the geometry of the camera so that the measured distance on the film is proportional to d rather than to θ , an arrangement which is difficult to achieve in practice but which can be closely approximated at low angles by arranging the film in the form of a right circular cylinder, the axis of which is coincident with the collimated X-ray beam.

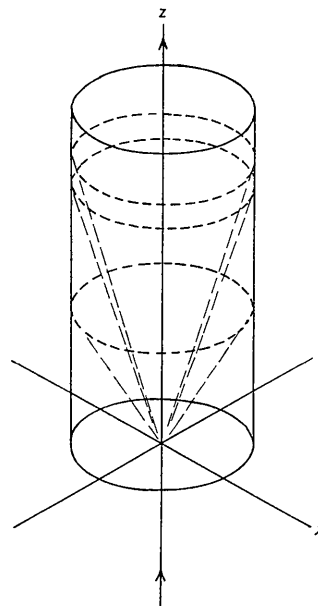


Fig. 2. The cylindrical, axially coincident geometry.

Such an arrangement is shown in Fig. 2. The specimen in this arrangement is a very thin wafer in the XY plane, and the collimated beam travels upward along the Z axis. The diffraction traces on the film are thus parallel circles, which, when the film is processed and flattened, appear as parallel straight lines.

Adapting the fundamental Bragg equation to these conditions, it is seen that

$$d/n = \lambda / \{2 \sin (\text{arc cot } Z/2)\} \quad (1)$$

where Z is the distance above the XY plane of the diffraction trace on a film of unit radius and thus $\frac{1}{2}$ arc cot Z is the θ of the Bragg equation.

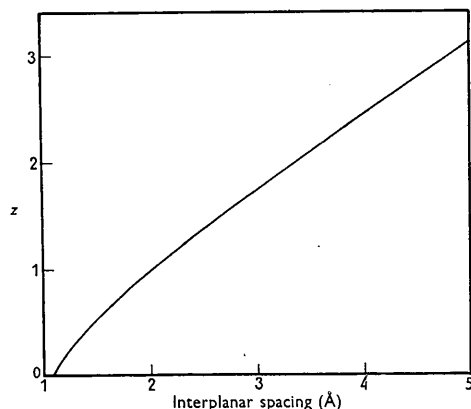


Fig. 3. d versus Z (Cu $K\alpha$ radiation).

The relationship between d and Z is shown in Fig. 3. It will be noted that, for the most part, d is very nearly a linear function of Z . Because of this, and because the use of an extremely thin specimen greatly reduces the systematic errors proportional to $\cos^2 \theta$ (Nelson & Riley, 1945) values of $\sin \theta$ and $\sin^2 \theta$ may be used directly in the simple least-squares lattice-constant derivation of Cohen (1935) rather than in the more elaborate adaptation of the least-squares method proposed by Heavens & Cheesman (1950) for low-angle lines. The general subject of the systematic errors inherent in the axially coincident geometry will be discussed elsewhere, but for the present it may be stated that these errors are small and may be recognized and corrected by noting the deviation of the diffraction traces from perfect straight lines.

By comparing Figs. 1 and 3, it will be seen that at the higher values of d the slope of the curve, and hence the resolution, is greater for the cylindrical axially-coincident camera than for the Debye camera. Furthermore, since all diffracted beams strike the film, and do so on parallel straight lines, the former system is considerably more efficient than the conventional circular arrangement, requiring less than half the exposure, despite the increased path of travel of the low-angle lines and despite the necessity for using a single rather than a double photographic emulsion. In addition, the films produced are essentially uniform in background fog, with a resulting increase in contrast for the lines at lowest angle, which in the conventional circular arrangement are frequently lost. As an illustration of the method the determination of the lattice constants of iodine at 5 °C. is described.

The camera consisted of an accurately machined copper tube, about fifteen centimeters long and five centimeters in diameter, equipped with brass end pieces, the front one carrying the collimator and specimen holder and the rear one being drilled to permit

the exit of the X-ray beam. The film was held on the inside of the copper cylinder and pressed tightly against it by spring-tensioned elliptical cams. A series of small holes was drilled in the side of the camera body in order that light passing through them should make fiducial marks on the film during the exposure for use in correcting for film shrinkage. The specimen holder was a thin annular brass disc mounted perpendicularly to the X-ray beam; the shadow cast on the film by this disc records the trace of the XY plane (Fig. 2).

The specimen itself consisted of especially purified iodine which had been stored in the presence of P_2O_5 for several weeks before use. This was mixed with an equal amount of similarly dried Pyrex glass powder. The glass-iodine mixture was then ground to an intimate dust in the absence of moisture and was sandwiched between two 0.008 cm. mica sheets, forming a layer approximately 0.004 cm. thick.

Unfiltered copper radiation was used for exposure and the temperature of the system was maintained at 5 °C. The photograph thus produced contained three series of spots—the two sets of overlapping Laue spots due to the mica supports, and the spots due to the iodine; however, since on the flattened film the Laue spots were arranged in characteristic curves and straight vertical lines whereas the iodine spots were arranged on straight horizontal lines, the identification of the iodine pattern and its subsequent indexing presented no problem.

Distances on the film from the specimen-plane shadow to the diffraction traces were measured, and, after suitable corrections for film shrinkage, temperature effects on the camera dimensions and so forth, were divided by the film radius to obtain Z . Values of $\sin \theta$ and $\sin^2 \theta$ were then obtained, by means of equation (1), from a graph of Z versus $\sin \theta$ (Table 1).

Table 1. Z versus $\sin \theta$ for θ in the range of 9° to 45° calculated for Cu $K\alpha = 1.542 \text{ \AA}$

Z	$\sin \theta$	Z	$\sin \theta$	Z	$\sin \theta$
3.078	0.1564	0.966	0.3907	0.287	0.602
2.748	0.1737	0.900	0.4067	0.249	0.616
2.475	0.1908	0.839	0.4226	0.213	0.629
2.246	0.2079	0.781	0.4384	0.176	0.642
2.050	0.2250	0.726	0.4540	0.141	0.656
1.881	0.2419	0.674	0.4695	0.105	0.669
1.732	0.2588	0.625	0.4848	0.070	0.682
1.600	0.2756	0.577	0.5000	0.035	0.695
1.483	0.2924	0.532	0.515	0	0.707
1.376	0.3090	0.488	0.530	—	—
1.280	0.3256	0.445	0.545	—	—
1.192	0.3420	0.404	0.559	—	—
1.110	0.3484	0.364	0.574	—	—
1.036	0.3746	0.324	0.588	—	—

Treatment of the data then followed the least-squares method mentioned previously, and the values obtained for the lattice constants, based upon nineteen diffraction lines having θ less than 37° are as follows,

$a=4.769\pm 0.002$, $b=7.248\pm 0.003$, $c=9.756\pm 0.005$ Å.

Straumanis' values for the iodine coefficients of expansion (Straumanis, 1943) would give

$a=4.777\pm 0.002$, $b=7.256\pm 0.003$, $c=9.761\pm 0.005$ Å
at 16 °C.

These may be compared with the values

$a = 4.7784$, $b = 7.2487$, $c = 9.7704$ Å

obtained by Straumanis using angles up to 84°.

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On the Bond Lengths of 1:14-Benzbisanthrene

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The π -bond orders of the various bonds in 1:14 benzbisanthrene are calculated by the molecular-orbital method within the π -electron approximation, the molecular orbitals being formed by linear combination of atomic orbitals (l.c.a.o.m.o.). The bond lengths are obtained from the usual curves of π -bond order *vs.* bond length and compared with experimental values. It is found that the m.o. treatment reproduces the trends in observed bond lengths, but that there is some discrepancy between these two sets of values. The effect of introducing refinements in the calculation is discussed in the light of results obtained for simple molecules like butadiene with this refinements.

Recently Trotter (1958) has determined the bond lengths in 1:14-benzbisanthrene by X-ray diffraction. His results show that the lengths of the central bonds *D*, *C*, *B*, *A* (Fig. 1) increase markedly in that order (1.40 \rightarrow 1.44 \rightarrow 1.47 \rightarrow 1.49 Å) and that the shortest bond is *V* (1.35 Å).

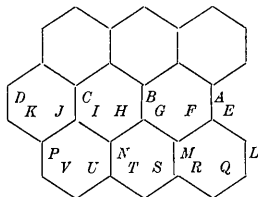


Fig. 1. 1:14-Benzbisanthrene.

Trotter also carried out a simple valence-bond calculation of the bond lengths, taking into account only the thirty unexcited structures. His calculation reproduced nicely the observed trends in the bond lengths, and the calculated values are surprisingly close to the observed. Since it is known that a simple l.c.a.o.m.o. calculation neglecting overlap also predicts

the correct bond lengths in other aromatic hydrocarbons, we were interested in comparing the success of the two methods for 1:14-benzbisanthrene. Pauncz & Berencz (1954) have calculated the π bond orders using the molecular-orbital method and have derived bond lengths. We have repeated these calculations and obtained the bond lengths from a smooth order-length curve drawn through these basic points:

	π Bond order	Bond length
Diamond corrected to sp^2 hybridization	0	1.50 Å
Graphite	0.525	1.421
Benzene	0.667	1.39
Ethylene	1.000	1.34

Our π bond orders and calculated bond lengths (which differ only slightly from those of the previous m.o. calculation) are listed in Table 1 together with the observed distances.

The figure in the third decimal place in the calculated bond lengths has no absolute significance but shows the correct order of the bonds in relation to one another. The Table shows that the trends in bond lengths are reproduced quite accurately in this cal-