is of interest to note that anomalously small values of a can be accounted for in this way, even when three-dimensional order is, as in this case, relatively highly developed.

This note is published with the approval of the Director of the Atomic Energy Research Establishment.

References

BACON, G. E. (1950). *Acta Cryst.* **3**, 137.
BACON, G. E. (1951). *Acta Cryst.* **4**, 558.
BRADBURN, M., COULSON, C. A. & RUSHBROOKE, G. S. (1948). *Proc. Roy. Soc. Edinb.* **62**, 336.
FRANKLIN, R. E. (1951). *Acta Cryst.* **4**, 253.
WARREN, B. E. (1941). *Phys. Rev.* **59**, 693.

Acta Cryst. (1951). **4**, 562

The determination of interplanar spacings and cell dimensions from powder photographs using an internal standard.

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A method for the determination of the unit-cell dimensions of non-cubic substances has been described by Bacon (1948). The object of this communication is to draw attention to some more general applications of the same simple principles which have been in use in this laboratory.

I. The simplest way of obtaining corrected interplanar spacings of a non-cubic substance is to mix it with a suitable cubic standard. Whatever method of extrapolation is employed for the cubic lattice spacings, the extrapolation curve can be used directly to give the correction to be placed on the values obtained for the interplanar spacings of the intervening non-cubic lines. From these spacings the unit-cell dimensions may be calculated as suggested by Bacon (1948).

II. An extension of this simple procedure was suggested by Jay (1942) who showed that, provided the reflected rays come from the outer layers of the specimen (thus necessitating the use of a thicker and denser specimen for materials of lower absorption), a very nearly linear extrapolation could be obtained by plotting cubic lattice spacings against $\cos^2\theta/\sin\theta$. This function gives extrapolations which are, in effect, practically indistinguishable from those obtained with the function

$$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$$

as suggested by Nelson & Riley (1945) and by Taylor & Sinclair (1945). These functions, on extrapolation, tend to infinity as $\theta \to 0$, and direct use for correcting low-angle spacings, especially at values of θ lower than that for the cubic line of lowest spacing on the film, is limited. If, however, $(\Delta a/a) \times 100 \times \sin\theta$, where $\Delta a = a_0 - a$, is plotted against $\cos^2\theta$, as indicated in Fig. 1, a curve, A, is obtained which reaches a finite value at $\cos^2\theta = 1$. From this curve a 'percentage correction' curve, B, is deduced by dividing the ordinate for selected points on A by the value of $\sin\theta$ for these points, which are themselves conveniently chosen so that $\sin\theta = 0{\cdot}1$, $0{\cdot}2$, $0{\cdot}3$, etc. (i.e. $\cos^2\theta = 0{\cdot}99$, $0{\cdot}96$, $0{\cdot}91$, etc.). The curve A also provides a check on the accuracy of the preliminary cubic extrapolation, and is often very nearly linear.

III. Occasionally the 'internal standard' is one of the components of a mixture, and is not cubic. In this case the interplanar spacings of the standard substance can be used to obtain a curve of $(\Delta d/d)\sin\theta$ plotted against $\cos^2\theta$.

IV. If the curve of $(\Delta d/d)\sin\theta$ is obtained for some non-cubic substances and it does not pass through the origin but intersects the vertical axis above or below zero, at $\cos^2\theta = 0$, this result may be useful for estimating solid-solution effects in compounds where the interplanar spacings for the pure compound are known to a sufficient degree of accuracy. Thus $\Delta d/d = \Delta d_1/d + \Delta d_2/d$ and the intercept represented by $\Delta d_1/d$ is the magnitude of the solid-solution effect, whilst $(\Delta d_2/d)\sin\theta$ would give an almost linear curve through the origin if plotted against $\cos^2\theta$. Small amounts of solid solution have been estimated in rhombohedral oxides and calcites by this method, although it is not suitable if there are marked axial-ratio changes.

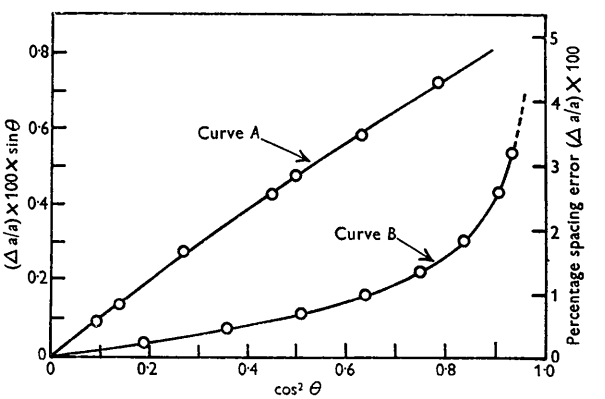

Fig. 1. Curve A: the relationship of $(\Delta a/a) \times 100 \times \sin\theta$ to $\cos^2\theta$ for a specimen containing MgO. Curve B: the curve of percentage spacing error against $\cos^2\theta$ derived from curve A. The individual points correspond to $\sin\theta = 0{\cdot}2$, $0{\cdot}3$, $0{\cdot}4$, etc. (i.e. $\cos^2\theta = 0{\cdot}96$, $0{\cdot}91$, $0{\cdot}84$, $0{\cdot}75$, etc.).

V. In cases where only low- to medium-angle reflexions are suitable for measurements a correction can be applied by another simple procedure. The line separation is multiplied by the interplanar spacing for each of the standard lines and the product is plotted against the separation distance itself, as in Fig. 2. Interplanar spacings corresponding to the intervening lines are found by reading the value of the product, distance × spacing, and dividing the product by the distance.

VI. A similar method frequently used for flat films, but of general application, is to draw a graph of the re-

ciprocals of the interplanar spacings of the internal standard against distance along the film. This should be nearly linear, and the values of $1/d$ for the substance being investigated can be readily interpolated.

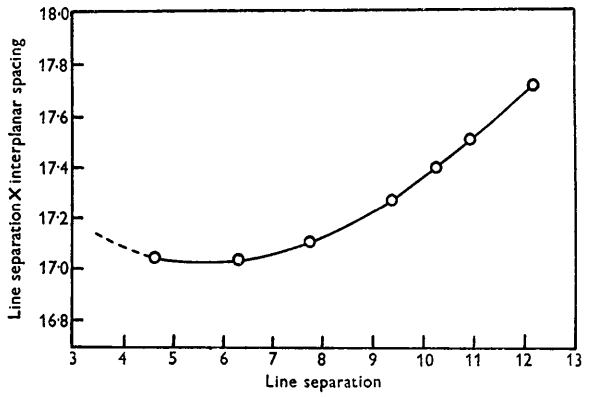

Fig. 2.

All of these methods have been applied to the identification of constituents of mixtures with an added standard substance or with a cubic or other substance already present in the mixture. The first two methods have been occasionally applied to the determination of unit-cell dimensions, whilst the last two in particular are only suitable for the approximate determination of cell dimensions, the accuracy being relatively low.

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References

BACON, G. E. (1948). *Acta Cryst.* **1**, 337.

JAY, A. H. (1942). Unpublished work. (Referred to at Conferences of the X-ray Analysis Group (Institute of Physics) 1942, and in 1948.)

NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc. Lond.* **57**, 160.

TAYLOR, A. & SINCLAIR, H. (1945). *Proc. Phys. Soc. Lond.* **57**, 126.

Acta Cryst. (1951). **4**, 563

Suggested device for the production of a monochromatic divergent beam.

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The appearance of absorption conics on divergent-beam photographs (e.g. Lonsdale, 1947) is in accordance with the expected *increase* of absorption of X-rays in the Bragg position. It has been shown, however (Borrmann, 1950), that for highly perfect crystals of quartz and calcite, *dark* conics are observed instead of light absorption

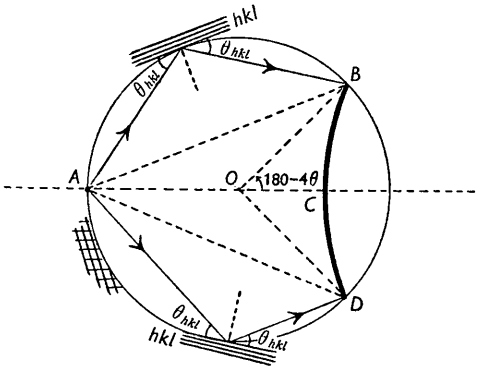

Fig. 1. General case. The monochromatic component of the X-rays diverging from a point on the circumference of a hollow sphere of polycrystalline material in which a form of planes $\{hkl\}$ has Bragg angle θ_{hkl}, are focused on the circle BCD defined by $\angle\ BOC = 180° - 4\theta$.

conics, indicating a *decrease* of absorption in the Bragg position. This discovery accentuates the importance of quantitative measurements of absorption and extinction, and these could usefully be made by divergent-beam methods if a monochromatic divergent beam could be produced.

No method of producing such a beam appears to have been published hitherto, but it does not seem to be impossible, and the principle on which it could be done is given below.

This principle (Fig. 1) makes use of an integrating sphere. A polychromatic divergent beam containing a strong monochromatic component—such as can be generated from a wide-angle tube—diverging from a point on the surface of a polycrystalline sphere would produce

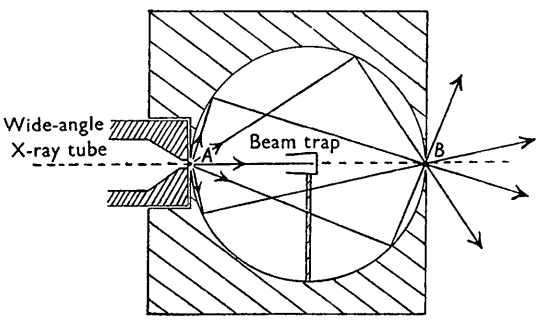

Fig. 2. Special case. When $\theta = 45°$, then $\angle\ BOC = 0$, and a monochromatic component of the original polychromatic beam diverging from A is focused at B, which thus becomes the origin of a monochromatic divergent beam.

a ring of monochromatic radiation on the surface of the sphere for each form of planes $\{hkl\}$ present in the polycrystalline sphere. When the Bragg angle is 45° for such a form of planes, this ring degenerates into a point and a divergent monochromatic beam will be generated with its apparent origin at this point, B (Fig. 2). Since $\theta = 45°$, each component of the new beam will be completely plane polarized, but, as the components come from all