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# ON THE DETERMINATION OF LATTICE PARAMETERS BY THE DEBYE-SCHERRER METHOD

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*ABSTRACT.* The types of systematic error arising in the determination of lattice parameters by the use of Debye-Scherrer powder diagrams are discussed. The various extrapolation methods are reviewed, and it is shown how a consideration of the absorption factor and geometry of the focal spot lead to the most satisfactory forms of extrapolation curve. It is shown how the absence of specimen eccentricity enables perfectly linear extrapolation curves to be drawn, thus allowing fullest use to be made of low-angle reflexions, whereby the very highest accuracy in parameter determination may be achieved.

## § 1. THE DETERMINATION OF LATTICE PARAMETERS

CIRCULAR Debye-Scherrer powder cameras are most conveniently used in the identification of compounds and alloy phases. When the structures have relatively high symmetry, powder photographs may also be employed for the elucidation of their atomic arrangements. At some stage of the work, particularly in the case of alloys when the course of a phase boundary is being followed, it becomes necessary to make precision measurements on the dimensions of the unit cell. If the Debye-Scherrer camera has been satisfactorily designed, it is possible to record diffraction spectra at Bragg angles in the region of 85 to 86°. It is then possible to achieve an accuracy in lattice-parameter measurement comparable with that yielded by flat-film back-reflexion cameras recording only a limited portion of the diffraction pattern.

All parameter determinations by x-ray methods involve the derivation of the Bragg angle $\theta$ for a given set of reflecting planes from measurements on the peak positions of the diffraction spectra. These peak positions are very sensitive to the experimental conditions, which introduce various systematic errors into the parameter determinations. In our discussion, we shall consider only cubic crystals, and thus confine ourselves to one lattice parameter, although the methods under consideration can, in many cases, be applied to more complicated unit cells.

For a cubic crystal, the lattice parameter $a$ is related to the wave-length within the crystal of the radiation $\lambda$, the Bragg angle $\theta$, and the indices of reflexion $hkl$, by the equation

$$a=\frac{\lambda}{2}\frac{\sqrt{h^2+k^2+l^2}}{\sin\theta}. \qquad \ldots\ldots(1)$$

The fractional error in $a$, caused by errors in measuring $\theta$, is obtained by differentiating equation (1), and is

$$\frac{da}{a}=-\cot\theta\, d\theta. \qquad \ldots\ldots(2)$$

Thus in the region where $\theta$ approaches 90°, $\cot\theta$ tends to zero, and any error in measuring $\theta$ produces only a small variation in the lattice parameter. In aiming at the highest accuracy in parameter determination, it is thus essential to design a camera which will record as high a Bragg angle as possible, and to choose a radiation which will give spectra at a high Bragg angle.

If $R$ is the camera radius and $S$ the distance between corresponding reflexions on each side of the incident ray,

$$S = 4R\theta, \quad \text{so that} \quad dS = 4Rd\theta.$$

Hence

$$\frac{da}{a} = -\frac{\cot\theta}{4R}\,dS. \qquad \ldots\ldots(3)$$

The errors $dS$ which arise from the experimental conditions may be classified under the following headings :—

(*a*) Finite length of specimen irradiated by the beam.
(*b*) Film shrinkage.
(*c*) Refractive index of the crystal for x rays.
(*d*) Eccentricity of the specimen.
(*e*) Absorption of the beam within the specimen.

A. J. Bradley and A. H. Jay (1932) have shown that the error in lattice parameter caused by (*a*) is negligibly small. They eliminate the effects of (uniform) film shrinkage by fitting the camera with knife-edges which subtend a standard angle $\theta_k$ in the region of $\theta = 90°$. $\theta_k$ is obtained by measuring the camera directly or by taking a photograph of a standard material such as rock-salt or quartz for which the angles of reflexion are known to a very high accuracy (Bradley and Jay, 1933; Wilson and Lipson, 1941). The angle $\theta$ of any pair of lines on the film is related to $S$, the distance between the lines, by the relation $\theta/\theta_k = S/S_k$, where $S_k$ is the distance apart of the fiducial marks on the film produced by the knife-edge shadows.

The correction for refractive index is very small, being of the order of one part in 50,000. This is added to the final value of the lattice parameter (Weigle, 1934 ; Jette and Foote, 1935).

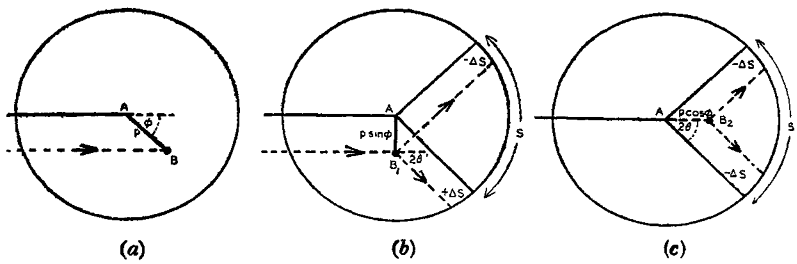
The errors in lattice parameter introduced by the eccentricity of the specimen and by absorption are most easily eliminated by extrapolation methods making use of high-angle reflexions where the resolving power of the powder photograph is greatest and errors in $\theta$ least. The simplest of these methods was described by G. Kettman (1929), who plotted values of lattice parameter $a$ calculated for each line on the film against corresponding values of Bragg angle $\theta$. A smooth curve was drawn through the points, and by extrapolating to $\theta = 90°$, a value of $a$ was obtained largely freed from experimental error. A similar process is described by Bradley and Jay, who plot values of $a$ against the corresponding values of $\cos^2\theta$ and extrapolate to $\cos^2\theta = 0$. Extrapolations may also be carried out against $\cot\theta$ or $(\pi/2 - \theta)\cot\theta$, as pointed out by Buerger (1942).

All these methods of graphical extrapolation yield slightly different values of $a$. The source of the differences lies in not really knowing the exact equation of the function plotted and trying to eliminate the effects of absorption and eccentricity with one and the same extrapolation curve. Although the errors vanish when $\theta = 90°$, and, therefore, when $\cos^2\theta$, $\cot\theta$ and $(\pi/2-\theta)\cot\theta = 0$, the highest angle at which a line can be measured is set by the geometry of the camera and the wave-length of the radiation, and this angle is in the region of 80 to 85°. Because the extrapolation curves have different shapes, and the distances over which the extrapolations are carried out differ greatly, they cut the $a$-parameter axis in different places. To decide which form of the extrapolation curve we should take we must see how the line-contours and the eccentricity of the specimen influence the peak positions.

## §2. ERRORS PRODUCED BY ECCENTRICITY AND ABSORPTION

### (a) *Errors produced by eccentricity*

In ($a$) of figure 1 the specimen B is displaced from the centre of the camera A through the distance $p$ at an angle $\phi$ with respect to the incident beam. Bradley and Jay (1932) have shown that the displacement may be considered as a vector split into the two components $p\sin\phi$ and $p\cos\phi$, as shown in ($b$) and ($c$) of figure 1.




($a$) ($b$) ($c$)

Figure 1. Effect of specimen eccentricity on line position. (After A. J. Bradley and A. H. Jay, *Proc. Phys. Soc.* **44**, 563, 1932.)

The former displacement produces a change in $S$ of $-\Delta S + \Delta S = 0$, while the latter produces a net change of $-\Delta S - \Delta S = -\Delta S_{ecc} = 2p\cos\phi\sin 2\theta$ in the value of $S$. Thus, in considering the errors introduced by the eccentricity of the specimen, we find that only displacements along the line of the undeviated incident beam have any effect.

### (b) *Errors produced by absorption*

In a previous communication (1945) we showed how absorption displaced the peaks of the lines in the direction of greater $\theta$ by an amount which depended on the experimental conditions. If $\Delta r$ is the shift of a diffraction line due to absorption alone, the error in $S$ must be $\Delta S_a = 2\Delta r$, considering the two symmetrical portions of the film lying on each side of the incident ray. Hence the total line displacement due to absorption and eccentricity is

$$\begin{aligned}\Delta S &= \Delta S_a + \Delta S_{ecc} \\ &= 2\Delta r - 2p\cos\phi\sin 2\theta. \qquad \ldots\ldots(4)\end{aligned}$$

The corresponding error in lattice parameter is, therefore,

$$\begin{aligned}\frac{da}{a} &= -\frac{dS}{4R}\cot\theta \\ &= -\frac{1}{4R}(2\Delta r - 2p\cos\phi\sin 2\theta)\cot\theta \\ &= -\frac{\Delta r}{2R}\cot\theta + \frac{p\cos\phi}{R}\cos^2\theta. \qquad \ldots\ldots(5)\end{aligned}$$

Thus when $\theta$ tends to 90°, $\cot\theta$, $\cos^2\theta$, and also $\Delta r$, all tend to zero, and, therefore, at $\theta = 90°$, $da/a = 0$. To determine the most satisfactory form of extrapolation curve, we must obtain an expression for the variation of $\Delta r$ with $\theta$.

## § 3. FORMS OF EXTRAPOLATION CURVE

### (a) *The Bradley and Jay $\cos^2\theta$ extrapolation*

In figure 2 we show curves of $\Delta r$ for different types of tube focus covering the range from $\theta = 0$ to 90°. They have been drawn for a Debye-Scherrer camera of radius $R = 95{\cdot}0$ mm. and a distance AX of 150 mm. between the specimen

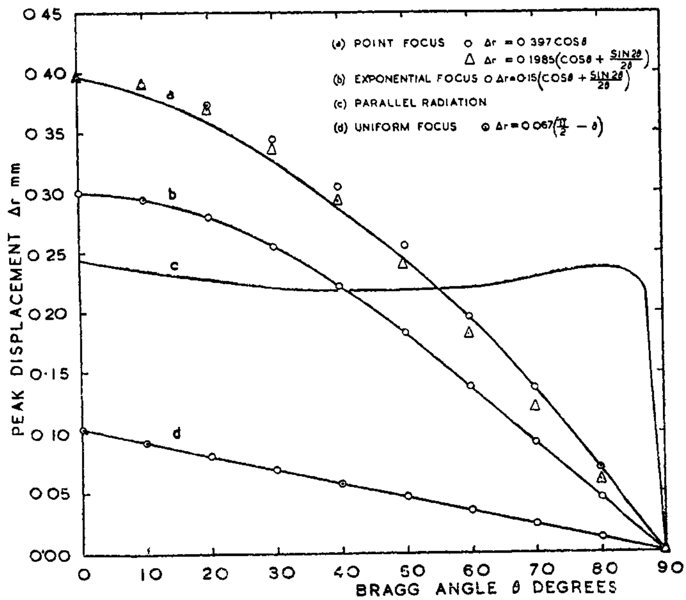



Figure 2. Values of $\Delta r$ for different types of focus.

Full curves are those obtained from the line contours calculated for camera radius $R = 95{\cdot}0$ mm., specimen-focus distance AX = 150·0 mm., specimen radius $r = 0{\cdot}25$ mm., $\mu r = 2{\cdot}0$. Points are values obtained by empirical formulae.

and focus. The radius of the specimen, $r$, was taken to be 0·25 mm., a figure quite close to the one occurring in practice. The value $\mu r = 2{\cdot}0$ was taken, the line-contours for this case being the ones most accurately determined. It should be borne in mind that $\Delta r$ does not vary a great deal between the values $\mu r = 1{\cdot}0$

and $\mu r = \infty$, although, of course, the macro-absorption factor $\alpha$ varies quite considerably.

If we compute the values of $\frac{\Delta r}{2R} \cot\theta$ for the cases of divergent radiation from uniform, exponential and point foci, we find they plot as near-linear functions of $\cos^2\theta$ over the limited range from 60 to 90°. The R.H.S. of equation (5) is thus a near-linear function of $\cos^2\theta$. By plotting $a$ against $\cos^2\theta$, it is possible to obtain almost straight extrapolation curves which simultaneously eliminate eccentricity and absorption errors. Provided we have sufficient spectra in the high-angle region, the $\cos^2\theta$ extrapolation would seem to be the best one to use.

The possible case of parallel radiation is worthy of mention as it may arise if a perfect crystal is used as a means of producing monochromatic radiation. The term $\frac{\Delta r}{2R} \cot\theta$ is then no longer a linear function of $\cos^2\theta$, because of the abrupt manner in which $\Delta r$ falls to zero between 85 and 90°. In such an instance the Bradley and Jay extrapolation against $\cos^2\theta$ will no longer apply, and it then becomes necessary to correct all individual values of $S$ by the amount $\Delta r$ before computing the values of $\theta$. The residual error in $a$ would then be entirely due to the eccentricity factor alone and would simply be $\frac{da}{a} = -\frac{p\cos\phi}{R}\cos^2\theta$, which plots as a straight line against $\cos^2\theta$.

For comparison purposes it is easiest to plot curves of $da/a$ rather than $a$ against $\cos^2\theta$. These are shown in figure 3 for conditions of parallel radiation and divergent radiation. The values for the eccentricity in each example are $p\cos\phi = 0$ and $\pm 0{\cdot}5$ mm.

For parallel radiation, the curves show a sudden upward inflexion below $\cos^2\theta = 0{\cdot}025$, which corresponds to the sudden change in $\Delta r$ in the range $85° < \theta < 90°$. For divergent radiation, the extrapolation curves are very slightly convex upwards and are almost straight for the case of a uniform focus. This is no longer true if the plots are made against $\theta$ or $\cot\theta$ unless $p\cos\phi = 0$.

In their original derivation of the $\cos^2\theta$ extrapolation rule, Bradley and Jay take an extreme case by assuming $\mu r = \infty$ and a point focus. The positions of the peaks are assumed to be near the high-angle outer edge of the lines at a fractional distance

$$\frac{\Delta r}{r} = \frac{\sin 2\theta}{2\theta}\left(1 + \frac{R}{\mathrm{AX}}\right) \qquad \ldots\ldots(6)$$

from the central ray. No formal proof is given for this relation, its sole justification apparently lying in the fact that when added to the eccentricity correction one arrives at the expression

$$\frac{da}{a} = \left(\frac{p\cos\phi}{R} - \frac{r}{2\theta R} - \frac{r}{2\theta\,\mathrm{AX}}\right)\cos^2\theta, \qquad \ldots\ldots\ldots(7)$$

which plots almost linearly against $\cos^2\theta$.

Equation (6) gives results for $\Delta r/r$ rather different from our own, which are obtained directly from the line-contours. In the following table we make a comparison of $\Delta r/r$ calculated from equation (6) and the line-contour method for a point focus when $R = 95$ mm., $\mathrm{AX} = 150$ mm. and $\mu r = \infty$.

Comparison of $\Delta r/r$ with $\mu r=\infty$ and point focus

| $\theta$ (°) | 0 | $22\frac{1}{2}$ | 45 | 50 | 60 | 70 | 80 | 90 |
|---|---|---|---|---|---|---|---|---|
| Bradley and Jay | 1·635 | 1·432 | 1·042 | 0·930 | 0·670 | 0·430 | 0·225 | 0·000 |
| Contour method | 1·635 | 1·510 | 1·185 | 1·115 | 0·910 | 0·665 | 0·370 | 0·000 |

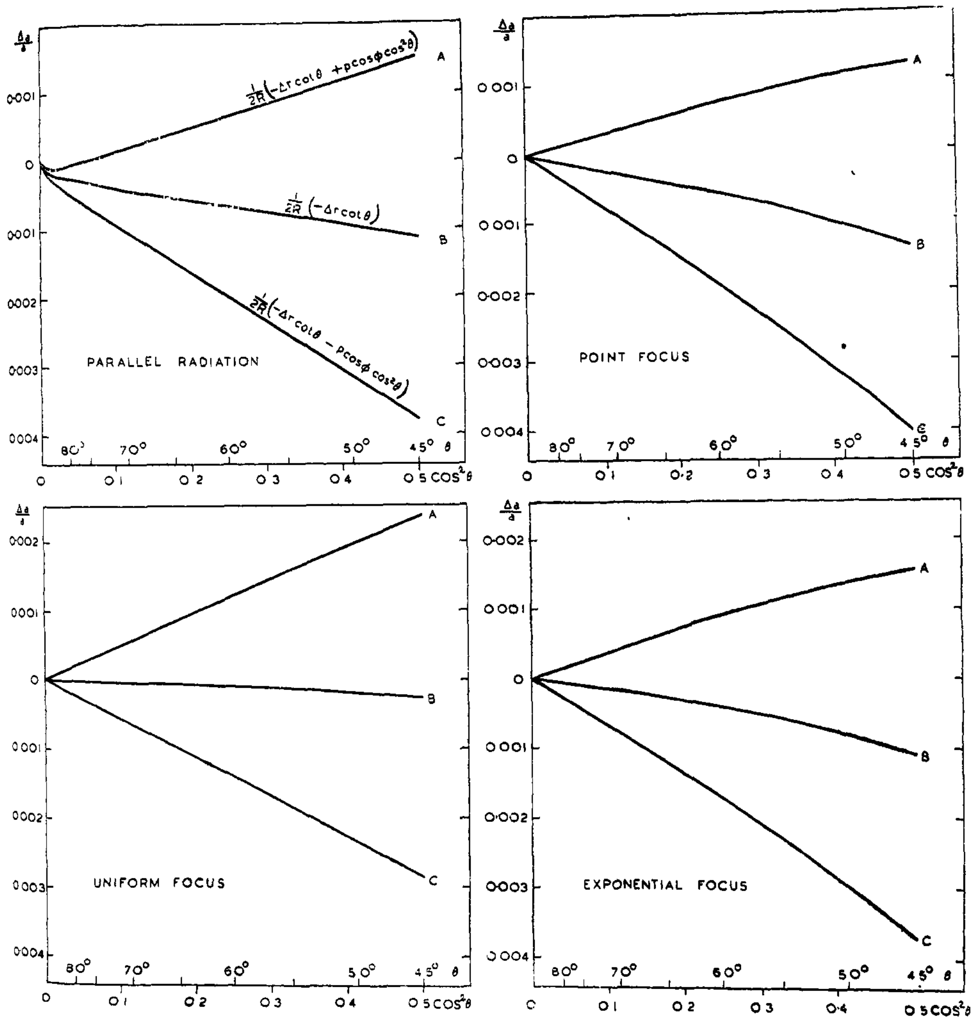



Figure 3. Plots of $da/a$ against $\cos^2\theta$.

$$\text{(A)}\quad \frac{da}{a}=\frac{1}{2R}(-\Delta r\cot\theta+p\cos\phi\cos^2\theta),$$

$$\text{(B)}\quad \frac{da}{a}=\frac{1}{2R}(-\Delta r\cot\theta),$$

$$\text{(C)}\quad \frac{da}{a}=\frac{1}{2R}(-\Delta r\cot\theta-p\cos\phi\cos^2\theta),$$

with AX=150·0 mm., $R$=95·0 mm., $r$=0·25 mm., $\mu r$=2·0, $p\cos\phi$=0 and $\pm$0·5 mm.

Although Bradley and Jay's results differ appreciably from our own, they follow substantially the same course, and it is for this reason that their approximation works. Their theory does not include the effects of a finite focal spot, which, as we have seen, has a major influence on the final positions of the peaks. Our investigation has shown that in the real case of a finite focus, the extrapolations against $\cos^2\theta$ actually plot straighter than those given by the original theory for all values of $\mu r > 1{\cdot}0$.

(b) *Other extrapolation possibilities—uniform focus, no eccentricity*

We have seen how over the limited range extending from $\theta = 60$ to $90°$, the term $\Delta r/2R \cot\theta$ of equation (5) was a near-linear function of $\cos^2\theta$. This leads us to examine the curves of $\Delta r$ against $\theta$ to see if we can express them as simple trigonometrical functions.

Consider first of all curve (*d*) in fig. 2, which refers to a uniform focus. This is a straight line, and its equation is of the form

$$\Delta r = k\,(\pi/2 - \theta). \qquad \ldots\ldots(8)$$

Thus in the absence of eccentricity, equation (5) reduces to the very simple form

$$\frac{da}{a} = -\frac{k}{2R}(\pi/2 - \theta)\cot\theta. \qquad \ldots\ldots(9)$$

If, then, the focal spot were uniform, as would most likely be the case in a gas tube, and if the camera were so accurately constructed that the specimen holder were at its geometrical centre, then the correct extrapolation procedure to use would be to plot $a$ against the function $(\pi/2 - \theta)\cot\theta$. This would be a *perfectly straight-line plot* from 0 to 90°, and two reflexions, one in the region of 80° and one in the low orders, say 10 to 20°, would be quite sufficient to yield a high enough accuracy in the parameter determination. This opens up entirely new possibilities in the accurate determination of the lattice parameters of non-cubic crystals when very few suitable reflexions are available.

*Exponential focus*

The exponential focus with an intensity distribution of the form $e^{-k^2x^2}$ is probably the most prevalent type. The nature of the $\Delta r$ curve given by such a focus is illustrated by (*b*) in figure 2. This curve can be matched *exactly* by the expression

$$\Delta r = k\left(\cos\theta + \frac{\sin 2\theta}{2\theta}\right), \qquad \ldots\ldots(10)$$

where $k = 0{\cdot}15$ for the experimental conditions considered.

In the absence of eccentricity we have

$$\frac{da}{a} = -\frac{\Delta r}{2R}\cot\theta$$

$$= -\frac{k}{2R}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right). \qquad \ldots\ldots(11)$$

In this particular case of exponential focus and no eccentricity, we obtain a perfectly linear extrapolation curve between $\theta = 0°$ and $\theta = 90°$ if we plot $a$ against corresponding values of $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$. This plot should be even more valuable than the previous example given in equation (9), since an exponential focus is much more likely to be encountered in practice.

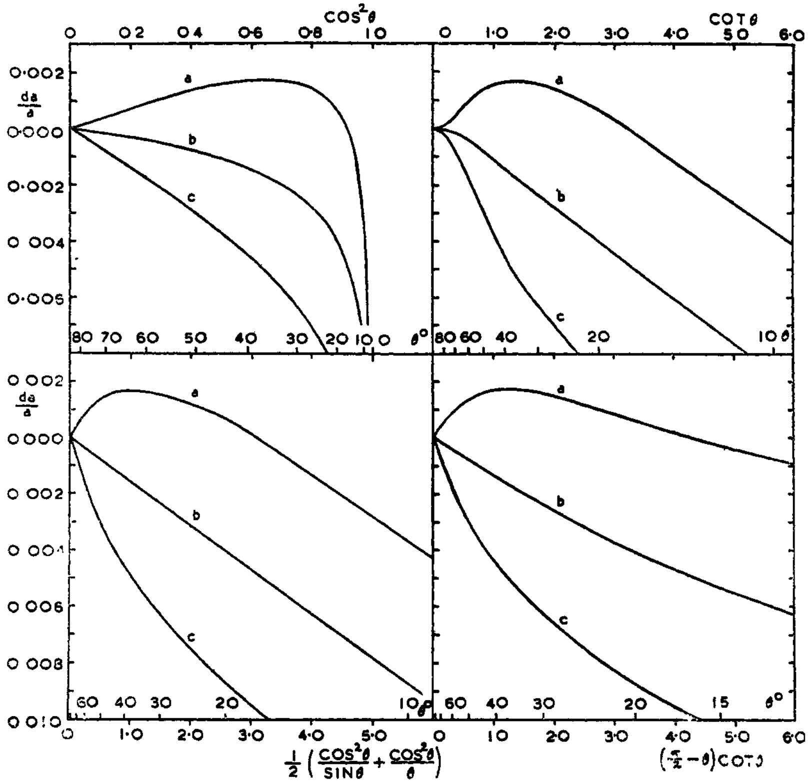



Figure 4 Typical extrapolation curves for exponential focus.
Camera radius $R = 95{\cdot}0$ mm
Specimen-focus distance AX = 150 0 mm.
Specimen radius $r = 0$ 25 mm. ; $\mu r = 2$ 0.
($a$) $p \cos\phi = 0{\cdot}50$ mm.
($b$) No eccentricity, or $p \cos\phi = 0$ mm.
($c$) $p \cos\phi = -0{\cdot}50$ mm.

When eccentricity is present, the error curve takes the form

$$\frac{da}{a} = -\frac{k}{2R}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right) + 2p\cos\phi\cos^2\theta. \qquad \ldots\ldots(12)$$

This departs quite appreciably from the curve of equation (11) if plotted against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ as shown in figure 4 (drawn for $p\cos\phi = \pm 0{\cdot}5$ mm.). The curvature is rather exaggerated by the crowding of the high-order reflexions into a region very close to the axis of ordinates.

If we increase the horizontal scale until it is comparable with that for the $\cos^2\theta$ plot, we find that in the range 30 to 90° the curves are not very different from each other. The great advantage to be gained by plotting $a$ against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ is that in the absence of eccentricity the curve becomes a perfectly straight line, and the fullest use can be made of the lowest orders.

It should not be difficult to make cameras free from eccentricity. Should eccentricity be present in an existing camera, it could be allowed for in the first stages of the $\theta$ calculations by correcting all values of $S$ by the amount $\Delta S_{ecc} = -2p\cos\phi\sin 2\theta$. The magnitude $2p\cos\phi$ is a constant of the camera. It could be obtained by direct measurement or by plotting extrapolation curves for a cubic crystal and finding by trial a value of $2p\cos\phi$, which leads to a straight-line plot of $a$ against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$.

*Point focus*

This is an idealized case. The $\Delta r$ curve illustrated by ($a$) in figure 2 can be matched over the range 60 to 90° by the expression

$$\Delta r = k\cos\theta. \qquad \ldots\ldots (13)$$

Thus, in the absence of eccentricity,

$$\begin{aligned}\frac{da}{a} &= -\frac{k\cos\theta}{2R}\cdot\cot\theta\\ &= -\frac{k}{2R}\frac{\cos^2\theta}{\sin\theta},\end{aligned} \qquad \ldots\ldots (14)$$

and a plot of parameter against $\frac{\cos^2\theta}{\sin\theta}$ is perfectly linear over the range 60 to 90°. Since $\sin\theta$ changes very slowly, from 0·8660 to 1·0000 over this range, there is only a slight curvature in a $\cos^2\theta$ plot. This is, of course, the reason why Bradley and Jay's extrapolation proves to be so good.

An attempt was made to fit an expression of the form $\Delta r = k\left(\cos\theta+\frac{\sin 2\theta}{2\theta}\right)$ to the $\Delta r$ curve for the point focus. The calculated points shown by triangles in figure 2 are rather high in the low orders and low in the high orders, with coincidences at 0°, 45° and 90°. The agreement is sufficiently close, even in this case, to justify an extrapolation of $a$ against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$.

## § 4. CONCLUSIONS

With careful camera construction there should be no eccentricity of the specimen. In that event perfectly linear extrapolation-curves can be drawn covering the range $\theta = 0°$ to $\theta = 90°$ for the real cases of uniform and exponential foci. Which type of plot should be used can easily be ascertained by taking a powder photograph of a cubic crystal, plotting extrapolation curves of $a$ against $(\pi/2-\theta)\cot\theta$ and $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ and finding which gives a straight-line plot over the whole measurable range.

These straight-line extrapolation plots require fewer reflexions to obtain the same accuracy in spacing as given by $\cos^2\theta$ curves, for the maximum use can be made of those low-order reflexions which lie in the region of 10°. Also, any "scatter" of the calculated parameters which personal errors introduce into film measurement can easily be allowed for by using the method of least squares to derive the most probable straight-line extrapolation curve.

In the past it has proved very difficult to make accurate parameter measurements on non-cubic crystals owing to the small number of reflexions with suitable indices. Instead, the complicated analytical method of M. U. Cohen (1935 and 1936) had to be employed. The straight-line plots described above should remove these difficulties.

It is felt that the new types of linear extrapolation-curve will enable lattice parameters to be measured with a much higher degree of accuracy than the one part in 50,000 which has hitherto been possible. It is quite probable that in the near future a greater precision in the determination of the X-ray wave-lengths will be required if full use is to be made of the increased accuracy in spacing determination. It will also be more necessary than ever to keep the temperature of the specimen constant while the powder photograph is being taken.

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## REFERENCES

Bradley, A. J. and Jay, A. H., 1932. *Proc. Phys. Soc.* **44**, 563 ; 1933. *Ibid.* **45**, 507.
Buerger, M. J., 1942. *X-ray Crystallography* (J. Wiley and Sons).
Cohen, M. U., 1935. *Rev. Sci. Instrum.* **6**, 68 ; 1936. *Z. Kristallogr.* (A), **94**, 288.
Compton, A. H. and Allison, S. K., 1935. *X-rays in Theory and Experiment* (London : Macmillan and Co., Ltd., 2nd edition), pp. 279 and 672.
Jette, E. R. and Foote, F., 1935. *J. Chem. Phys.* **3**, 10.
Kettmann, G., 1929. *Z. Phys.* **53**, 198.
Taylor, A. and Sinclair, H., 1945. *Proc. Phys. Soc.* **57**, 108.
Weigle, J., 1934. *Helv. phys. Acta,* **7**, 46.
Wilson, A. J. C. and Lipson, H., 1941. *Proc. Phys. Soc.* **53**, 245.