Table 5. *Averaged values $c'_{ij}$ and $c'_{ijk}$ (in $10^{10}$ $\mathrm{Nm^{-2}}$) of calcium formate complying with symmetry group m3m and TOEC of cubic calcium fluoride*

| | $Ca(HCOO)_2$ | $CaF_2$ |
|---|---|---|
| $c'_{11} = (c_{11} + c_{22} + c_{33})/3$ | 3·634 | 16·357 |
| $c'_{12} = (c_{12} + c_{13} + c_{23})/3$ | 2·128 | 4·401 |
| $c'_{44} = (c_{44} + c_{55} + c_{66})/3$ | 1·695 | 3·392 |
| $c'_{111} = (c_{111} + c_{222} + c_{333})/3$ | −36·6 | −124·6 |
| $c'_{111} = (c_{112} + c_{223} + c_{133} + c_{113} + c_{122} + c_{233})/6$ | −20·4 | −40·0 |
| $c'_{123} = c_{123}$ | −27·7 | −25·4 |
| $c'_{144} = (c_{144} + c_{255} + c_{366})/3$ | −6·9 | −12·4 |
| $c'_{166} = (c_{244} + c_{355} + c_{166} + c_{344} + c_{155} + c_{266})/6$ | −4·4 | −21·4 |
| $c'_{456} = c_{456}$ | −5·4 | −7·5 |
| $c'_{111}/c'_{11}$ | −10·07 | −7·62 |
| $c'_{112}/c'_{11}$ | −5·61 | −2·45 |
| $c'_{123}/c'_{11}$ | −7·62 | −1·55 |

formate reflect the existence of general rules valid for any type of stable crystals.

### References


ALTEROVITZ, S. & GERLICH, D. (1969). *Phys. Rev.* **184**, 999–1002.

BACH, H., HAUSSÜHL, S. & WEBER, H.-J. (1977). *Z. Kristallogr.* **145**, 28–34.

BOHATÝ, L. & HAUSSÜHL, S. (1977). *Z. Kristallogr.* **145**, 172–176.

GROTH, P. (1910). *Chemische Krystallographie*, III. Leipzig: Engelmann.

GUINAN, M. W. & RITCHIE, A. D. (1970). *J. Appl. Phys.* **41**, 2256–2258.

HAUSSÜHL, S. (1963*a*). *Z. Kristallogr.* **118**, 33–50.

HAUSSÜHL, S. (1963*b*). *Phys. Status Solidi*, **3**, 1072–1076.

HAUSSÜHL, S. (1967). *Phys. Kondens. Mater.* **6**, 181–192.

HAUSSÜHL, S. & HESSE, H. (1966). *Z. Kristallogr.* **123**, 338–341.

HAUSSÜHL, S. & PREU, P. (1978). *Acta Cryst.* A**34**, 442–446.

HAUSSÜHL, S. & SCHOLZ, H. (1975). *Krist. Tech.* **10**, 1175–1179.

SEEGER, A. & BUCK, O. (1960). *Z. Naturforsch. Teil A*, **15**, 1056–1067.

SLATER, J. C. (1940). *Phys. Rev.* **57**, 744–746.

THURSTON, R. N. & BRUGGER, K. (1964). *Phys. Rev.* **133**, A1604–A1610.

WALLACE, D. C. (1970). *Solid State Phys.* **25**, 301–404.


*Acta Cryst.* (1981). A**37**, 364–368

# The Influence of In-Plane Collimation on the Precision and Accuracy of Lattice-Constant Determination by the Bond Method. I. A Mathematical Model. Statistical Errors

BY EWA URBANOWICZ

*Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Plac Katedralny* 1, 50-950 *Wrocław, Poland*

(*Received* 10 *October* 1980; *accepted* 24 *November* 1980)


## Abstract

A mathematical model based on a convolution formula has been derived which shows the effect of in-plane (horizontal) collimation on the shape of a measured profile $h(\omega)$ in the Bond method. With simplifying assumptions the profile has been presented in an analytical form. The effect of the width of collimator slits $d_1$, $d_2$ on the variance $\sigma^2\omega_0$ of the peak position $\omega_0$ was considered based on the model. From the method of analysis used by Wilson [*Br. J. Appl. Phys.* (1965), **16**, 665–674], the variance $\sigma^2\omega_0$ was estimated for the profile approximated by a least-squares parabola. It has been found that for certain collimation parameters a minimal value of $\sigma^2\omega_0$ is obtained, and the conditions of the optimal choice of collimator slit widths from the point of view of statistical errors have been given. An example of the application of such conditions has been presented.


0567-7394/81/030364-05$01.00



## 1. Introduction

A new design of Bond diffractometer constructed in this institute (Łukaszewicz, Kucharczyk, Malinowski & Pietraszko, 1978) is used more for investigations of the relative changes of lattice constants (for example as a result of changing temperature to investigate phase transitions) than for measuring their absolute values. In such measurements there are no high requirements regarding systematic errors and accuracy, $\Delta d/d$, analysed in part II (Urbanowicz, 1981), but they

concern the precision of measurements, $\sigma d/d$, determined by statistical errors, independent of the systematic ones.

The precision $\sigma d/d$ ($\sigma d$ is the standard deviation of the interplanar spacing $d$) for Bragg angle $\theta$ depends on the standard deviation $\sigma\theta$ in Bragg angle:

$$\sigma d/d = \cot\theta\,\sigma\theta. \tag{1}$$

Thus, an essential problem is to obtain the required precision of $\theta$.

In the Bond (1960) method, the angle $\theta$ is determined from the measurements of two symmetrical peak positions $\omega_0'$ and $\omega_0''$:

$$\theta = \left| |\omega_0' - \omega_0''|/2 - 90°\right|. \tag{2}$$

Thus

$$\sigma\theta = (\sigma^2\omega_0'/4 + \sigma^2\,\omega_0''/4)^{1/2}. \tag{3}$$

Assuming $\sigma\omega_0' = \sigma\omega_0'' = \sigma\omega_0$, we obtain

$$\sigma\theta = \sqrt{2}/2\;\sigma\omega_0 = 0{\cdot}7071\;\sigma\omega_0. \tag{4}$$

The variance $\sigma^2\omega_0$ depends on the shape of the measured profile, the peak definition and the method of scan. This dependence was examined by Wilson (1965) and Thomsen & Yap (1967). A prerequisite in their considerations is an assumption that

$$\sigma^2 N = N, \tag{5}$$

where $N$ is the number of counts.

According to Wilson (1965), an estimation of the variance $\sigma^2\omega_0$, when the profile $h(\omega)$ is treated with a least-squares parabola, can be written (with the symbols of the present paper) as

$$\sigma^2\omega_0 = Ch(\omega_0)/[h''(\omega_0)]^2, \tag{6}$$

where

$$C = 3/(2p\Omega^2) \tag{6a}$$

depends on the method of scan, $p$ is the number of measuring points at one side of the peak position (the total number of points is $n = 2p + 1$), $\Omega = p\delta\omega$, and $\delta\omega$ is the length of one scanning step.

A formula analogous to (6) is obtained by Wilson (1965) to estimate the variance of peak position in the case of the midpoint-of-chord procedure. The coefficient of proportionality $C$, however, is different from that given by (6*a*) and is a few times (in practice about 4·5 times) larger. An advantage of the midpoint-of-chord procedure, however, is a less-biased determination of the peak position for asymmetrical profiles.

The aim is to make $\sigma\omega_0$ as small as possible. The commonly used way to diminish $\sigma\omega_0$ is to obtain a sufficient number of counts by increasing the counting time $\Delta t$ of every scanning step or by increasing the total number of steps, $n$. Both methods are time-consuming.

For measurements of temperature dependences, however, when it is necessary to carry out several series of measurements with good temperature stabilization, the total measurement time, $T$, of one profile,

$$T = n\Delta t, \tag{7}$$

should be shortened to a minimum.

It has been found in the present work that there is a possibility of decreasing $\sigma\omega_0$ by affecting the shape and intensity of the measured profile $h(\omega)$ by collimation.

## 2. The profile measured in the Bond method as a convolution. The determination of the functions $g(\alpha)$ and $f(\omega)$

To analyse the effect of collimation conditions in the Bond method the measured profile $h(\omega)$, determined by a number of physical and apparatus factors, can be presented as a convolution of two functions: (1) $g(\alpha)$, dependent on the collimator length $L_2$ and widths $d_1$, $d_2$ of its exchangeable slits, *i.e.* the angular distribution of the primary beam intensity; and (2) $f(\omega)$, the original function, taking into account all the remaining factors. The convolution has the form

$$h(\omega) = \int_{-\infty}^{\infty} f(\omega')\,g(\omega - \omega')\,d\omega'. \tag{8}$$

The function $g(\alpha)$ describes the intensity associated with individual ray direction $\alpha$ within the primary beam. Since the form of $g(\alpha)$ cannot be found from a simple experiment (a rather sophisticated method was proposed by Blake, Barrus & Fenimore, 1976) it was determined theoretically by geometric and algebraic analysis and then verified indirectly by experiment. The procedure for determining $g(\alpha)$ is illustrated in Fig. 1. The intensity corresponding to a given angle $\alpha_p$ is assumed to be directly proportional to the number of quanta from the part of the tube focus surface (here the sector $x_B - x_A$) seen at this angle:

$$g(\alpha_p) = k_1 \int_{x_A(\alpha_p)}^{x_B(\alpha_p)} i_s(x)\,dx, \tag{9}$$

where $i_s(x)$ is the tube focus emissivity along the $X$ axis, and $k_1$ is a coefficient of proportionality.

The integration limits $x_A$ and $x_B$ depend on the angle $\alpha$, the width of slits $d_1$ and $d_2$, the width of the focal spot along the $X$ axis, and the distance of the first and the second slit from the focus ($L_1$, $L_1 + L_2$, respectively). The limits are determined by the conditions

$$x_A = \max\{-d_1/2 - L_1\alpha, -d_2/2 - (L_1 + L_2)\alpha, -s/2\} \tag{9a}$$

$$x_B = \min\{d_1/2 - L_1\alpha,\ d_2/2 - (L_1 + L_2)\alpha,\ s/2\} \quad (9b)$$

and

$$x_B - x_A > 0 \quad (9c)$$

is required for the condition that $g(\alpha) > 0$.

The shape of the $f(\omega)$ function can be obtained by measuring the profile $h(\omega)$ with very narrow collimator slits or by deconvolution of the $h(\omega)$ function when $g(\alpha)$ is known.

### 3. Assumptions

For the purpose of variance analysis a knowledge of $h(\omega)$ in an analytical form is necessary. To obtain this form the following simplifying assumptions have been made:

(1) $f(\omega)$ has the form of a Cauchy function which is a good approximation for a silicon single crystal of almost perfect structure:

$$f(\omega) = F/\{1 + [2(\omega - \omega_0)/\omega_f]^2\}, \quad (10)$$

where $\omega_f$ is the half-width;

(2) the widths of the slits $d_1$ and $d_2$ are small in comparison with the focus size $s$ and the integration limits do not depend on the focus size

$$d_1(1 + L_1/L_2) + d_2 L_1/L_2 \le s; \quad (11)$$

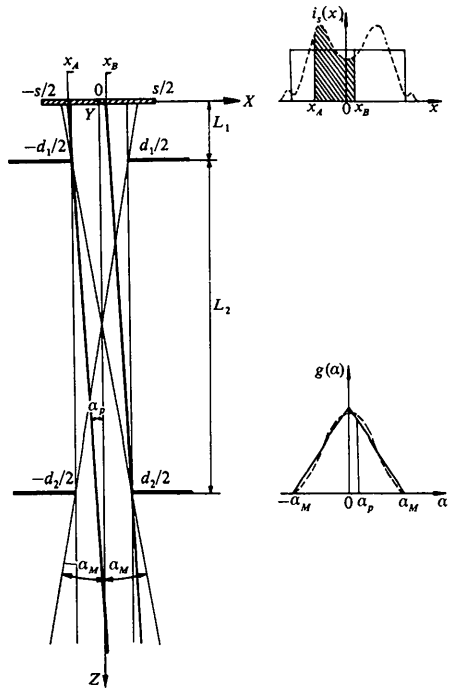


Fig. 1. Theoretical determination of the angular distribution $g(\alpha)$ of the primary beam intensity.

(3) the real distribution of $i_s(x)$ is replaced by a gate function $\hat{i}_s(x)$

$$\hat{i}_s = \begin{cases} S, & |x| \le \hat{s}/2 \\ 0, & |x| > \hat{s}/2, \end{cases} \quad (12)$$

where $S$ and $\hat{s}$ are parameters selected according to

$$\int_{-s/2}^{s/2} (i_s - \hat{i}_s)^2\, \mathrm{d}x = \text{minimum} \quad (13a)$$

and

$$\int_{-s/2}^{s/2} i_s(x)\, \mathrm{d}x = \int_{-\hat{s}/2}^{\hat{s}/2} \hat{i}_s(x)\, \mathrm{d}x. \quad (13b)$$

It has been calculated that for small slits the error of determination of the half-maximum width $\omega_h$ of $h(\omega)$, with this assumption, is $\pm 1\%$, while the error of the peak-height $H$ determination is $\pm 5\%$.

With the assumptions (2) and (3), $g(\omega)$ has the form

$$g(\omega) = \begin{cases} K(\omega_1 + \omega), & -\omega_1 < \omega < -\omega_2 \\ K(\omega_1 - \omega_2), & -\omega_2 \le \omega \le \omega_2 \\ K(\omega_1 - \omega), & \omega_2 < \omega < \omega_1, \end{cases} \quad (14)$$

where

$$K = k_1 S L_2, \quad (14a)$$

$$\omega_1 = \tfrac{1}{2}(d_1 + d_2)/L_2 \quad (14b)$$

$$\omega_2 = \tfrac{1}{2}|d_1 - d_2|/L_2. \quad (14c)$$

Combining (8), (10), (14) and, for simplification of notation, substituting

$$2(\omega - \omega_0)/\omega_f = x, \quad 2\omega_1/\omega_f = x_1, \quad 2\omega_2/\omega_f = x_2, \quad (15)$$

we finally obtain

$$\begin{aligned} h(x) = A\{&x[\tan^{-1}(x + x_1) + \tan^{-1}(x - x_1)] \\ &+ x_1[\tan^{-1}(x + x_1) - \tan^{-1}(x - x_1)] \\ &- x[\tan^{-1}(x + x_2) + \tan^{-1}(x - x_2)] \\ &- x_2[\tan^{-1}(x + x_2) - \tan^{-1}(x - x_2)] \\ &+ \tfrac{1}{2}\ln[1 + (x - x_2)^2] - \tfrac{1}{2}\ln[1 + (x - x_1)^2] \\ &+ \tfrac{1}{2}\ln[1 + (x + x_2)^2] - \tfrac{1}{2}\ln[1 + (x + x_1)^2]\}, \end{aligned} \quad (16)$$

where

$$A = 0{\cdot}5 F k_1 S L_2 \omega_f. \quad (16a)$$

The peak height of this function is

$$\begin{aligned} H = h(0) = 2A[&x_1 \tan^{-1} x_1 - x_2 \tan^{-1} x_2 \\ &+ \tfrac{1}{2}\ln(1 + x_2^2) - \tfrac{1}{2}\ln(1 + x_1^2)]. \end{aligned} \quad (16b)$$

$g(\omega)$ is often described in a still simpler manner as a gate function, $\hat{g}(\omega)$:

$$\hat{g}(\omega) = \begin{cases} K\omega_4, & |\omega| \le \omega_3 \\ 0 \quad , & |\omega| > \omega_3 \end{cases}, \qquad (17)$$

where $\omega_3$ is the mean divergence of the primary beam. In this case the result of the convolution is

$$h(x) = A\, x_4[\tan^{-1}(x + x_3) - \tan^{-1}(x - x_3)], \quad (18)$$

where

$$x_3 = 2\omega_3/\omega_f, \quad x_4 = 2\omega_4/\omega_f. \qquad (18a)$$

The peak height of $h(x)$ is

$$h(0) = H = 2Ax_4 \tan^{-1} x_3 \qquad (18b)$$

and its half-maximum width, $\omega_h$, is

$$\omega_h = \omega_f(1 + x_3^2)^{1/2}, \qquad (18c)$$

which is easy to estimate.

It is necessary, however, to relate the parameters $\omega_3$ and $\omega_4$ with the collimation parameters $d_1$, $d_2$ and $L_2$. If $\hat{g}(\omega)$ is treated as an approximation of $g(\omega)$ given by (14), satisfying a criterion similar to that given by (13$a$), (13$b$):

$$\int_{-\omega_1}^{\omega_1} [g(\omega) - \hat{g}(\omega)]^2\, d\omega = \text{minimum}, \qquad (19)$$

while

$$\int_{-\omega_1}^{\omega_1} g(\omega)\, d\omega = \int_{-\omega_3}^{\omega_3} \hat{g}(\omega)\, d\omega, \qquad (19a)$$

the following relations are obtained:

$$\omega_3 = [(\omega_1^2 + \omega_2^2)/2]^{1/2} = (d_1^2 + d_2^2)/(2L_2), \qquad (20)$$

$$\omega_4 = (\omega_1^2 - \omega_2^2)/[2(\omega_1^2 + \omega_2^2)]^{1/2} = d_1\, d_2/[(d_1^2 + d_2^2)^{1/2}\, L_2]. \qquad (20a)$$

Equations (18$b$) and (18$c$) jointly with (20) and (20$a$) give a quick and good estimate of a peak height and its half-maximum breadth for narrow slit widths $d_1$, $d_2$.

## 4. The minimum variance conditions

The second derivative in the peak position for the profile given by (16) is

$$\frac{d^2h}{d\omega^2} = \left(\frac{2}{\omega_f}\right)^2 \frac{d^2h}{dx^2} = -\left(\frac{2}{\omega_f}\right)^2 2A\, \frac{x_1^2 - x_2^2}{(1 + x_1^2)(1 + x_2^2)}. \qquad (21)$$

Substitution of (21) and (16$b$) into (6) gives the dependence between $\sigma^2\omega_0$ and collimation parameters [closed in $x_1$ and $x_2$, (15) and (14$b$), (14$c$)] in the form

$$\sigma^2\omega_0 = C_1\, V^2(x_1,x_2), \qquad (22)$$

where

$$C_1 = (C/2A)\,(\omega_f/2)^4, \qquad (22a)$$

$$V^2(x_1,x_2) = [2x_1 \tan^{-1} x_1 - 2x_2 \tan^{-1} x_2 + \ln(1 + x_2^2) - \ln(1 + x_1^2)]\,(1 + x_1^2)^2 \times (1 + x_2^2)^2/(x_1^2 - x_2^2)^2. \qquad (22b)$$

It has been calculated that for

$$x_1 = 1\cdot 13, \quad x_2 = 0, \qquad (23)$$

the factor $V^2(x_1,x_2)$ has its minimum value

$$V^2(1\cdot 13, 0) = V^2(x_1,x_2)_{\min} = 3\cdot 46, \qquad (23a)$$

so the minimum standard deviation $(\sigma\omega_0)_{\min}$ is

$$(\sigma\omega_0)_{\min} = \sqrt{C_1}\, V(x_1,x_2)_{\min} = 1\cdot 86\, \sqrt{C_1}. \qquad (23b)$$

The conditions for optimal collimation parameters, $d_1$ and $d_2$, resulting from (23), (15) and (14$b$), (14$c$) are

$$d_1 = d_2 \qquad (24a)$$

$$d_1 = 0\cdot 565 L_2\omega_f. \qquad (24b)$$

## 5. An example

The 444 reflection for a silicon single crystal has been measured with Cu $K\alpha_1$ radiation ($\theta$ = 79° 18′ 45″). Collimation parameters were $L_2 = 297$ mm, $d_1 = d_2 = 0\cdot 05$ mm; the focus size $s = 1$ mm, so assumption 2 (formula 11) was satisfied. The scanning parameters were $\Delta t = 4$ s, $n = 21$, $\delta\omega = 10''$. The measured profile has the peak height $h(\omega_0) = 1215$ counts and the half-width $\omega_h = 457''$. The following questions arise.

I. What is the standard deviation $\sigma\omega_0$?

II. What is the value of $(\sigma\omega_0)_{\min}$, when optimal $d_1$ and $d_2$ are used (all the remaining factors are constant)?

III. How to choose collimator slits (as small as possible) to obtain the precision $\sigma d/d = 10^{-6}$?

The following values, based on the formulae given in this paper, were obtained.

$\omega_1 = (0\cdot 05 + 0\cdot 05)/297 = 1\cdot 68 \times 10^{-4}$ rad $= 34\cdot 7''$ (from 14$b$)

$\omega_2 = 0$ (from 14$c$)

$\omega_3 = 24\cdot 6''$ (from 20)

$\omega_f = 456''$ (from 18$c$)

$x_1 = 0\cdot 152$ (from 15)

$x_2 = 0$

$$2x_1 \tan^{-1} x_1 - \ln(1 + x_1^2) = 0\cdot 0231,$$

so

$A = 52\,600$ (from 16*b*)

$C_1 = 0{\cdot}193$ (from 22*a*, 6*a*)

$\sigma^2\omega_0 = 0{\cdot}193\ V^2(x_1, x_2)$ (from 22)

$\sigma\omega_0 = 0{\cdot}439\ V(x_1,x_2)\ ['']$. (25)

Since $\cot\theta = 0{\cdot}188$,

$\sigma d/d = 0{\cdot}188\ \sigma\theta = 0{\cdot}133\ \sigma\omega_0$ (from 1,4). (26)

The dependence of $\sigma\omega_0$ on the width of the collimator slits $d_1$ and $d_2$ is shown in Fig. 2. Values of $\sigma\omega_0$ for various combinations of $d_1$ and $d_2$ available in practice are marked with points.

The resulting values are as follows.

I.

$V(0{\cdot}152, 0) = 6{\cdot}705$, (from 22*b*)

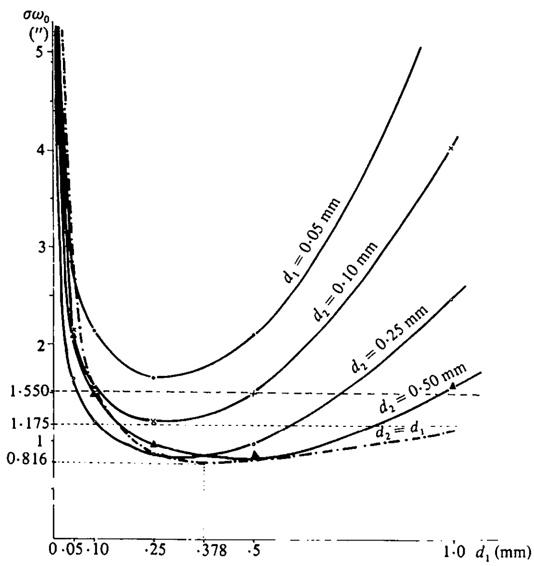


Fig. 2. The influence of the collimator slit $d_1$ on the standard deviation $\sigma\omega_0$ of the peak position $\omega_0$ as a function of $d_2$.

$\sigma\omega_0 = 2{\cdot}94'' = 14{\cdot}25 \times 10^{-6}$ rad, (from 25)

$$\frac{\sigma d}{d} = 1{\cdot}895 \times 10^{-6}, \quad \text{(from 26)}$$

when the measured profile is treated by a least-squares parabola. In the case when the midpoint-of-chord method is used, the variance would be about 4·5 times greater.

II.

$(\sigma\omega_0)_{\min} = 0{\cdot}439\ V_{\min}$

$= 0{\cdot}439 \times 1{\cdot}86 = 0{\cdot}816'' \simeq 3{\cdot}956 \times 10^{-6}$ rad,

(from 25)

$$\frac{\sigma d}{d} = 0{\cdot}526 \times 10^{-6}, \text{ for } d_1 = d_2 = 0{\cdot}378 \text{ mm.}$$

(from 26)

III.

$\sigma\omega_0 = 7{\cdot}519 \times 10^{-6}$ rad $= 1{\cdot}55''$. (from 26)

This value of $\sigma\omega_0$ can be obtained approximately from Fig. 2 for $d_1 = d_2 = 0{\cdot}10$ mm.

## References

BLAKE, R. L., BARRUS, D. M. & FENIMORE, E. (1976). *Rev. Sci. Instrum.* **47**, 899–905.

BOND, W. L. (1960). *Acta Cryst.* **13**, 814–818; *erratum: Acta Cryst.* (1975), A **31**, 698.

ŁUKASZEWICZ, K., KUCHARCZYK, D., MALINOWSKI, M. & PIETRASZKO, A. (1978). *Krist. Tech.* **13**, 561–567.

THOMSEN, J. S. & YAP, F. Y. (1967). *J. Res. Natl Bur. Stand. Sect. A*, **72**, 187–205.

URBANOWICZ, E. (1981). *Acta Cryst.* A**37**, 369–373.

WILSON, A. J. C. (1965). *Br. J. Appl. Phys.* **16**, 665–674.