Pramāṇa, Vol. 3, No. 6, 1974, pp 370–376. © Printed in India

Effect of crystal and collimator misalignments on Bragg angle measurements

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MS received 13 September 1974; after revision 20 November 1974.

Abstract. A mathematical analysis has been made of the combined effect of crystal and collimator misalignments on Bragg angles measured from zero-layer Weissenberg photographs. The results obtained here have been compared with those available for Bond's method of measuring Bragg angles with diffractometers. The comparison shows that, for a given amount of crystal and collimator misalignments, Bond's method and the 2θ-method do not give identical results for small and intermediate Bragg angles.

Keywords. Lattice parameter determination; Bragg angle measurements; crystal and collimator misalignments.

1. Introduction

For an accurate determination of lattice parameters of crystals, it is essential to account for the effect of the various systematic errors which affect the measurement of Bragg angles. For this purpose, a routine procedure followed by the author, during the course of crystal structure investigations by Weissenberg technique, is to measure the Bragg angles for a number of reflections from zero-layer photographs and then account for the effect of systematic errors like those due to film shrinkage, beam divergence, eccentrcity of specimen, and absorption through a least-squares fitting procedure, by adding correction terms to the calculated value of Bragg θ:

$$\theta\,(\text{cal}) = \theta_0 + \Sigma_i C_i f_i(\theta_0) \tag{1}$$

Here θ_0 is the nominal value of the Bragg angle. The coefficients C_i of the various correction terms, $C_i f_i(\theta_0)$, are treated as the extra independent parameters, to be determined along with the lattice parameters by the least-squares algorithm (Wadhawan 1972). This requires a knowledge of the form of the correction functions, $f_i(\theta_0)$, for the relevant systematic errors. For example, if $i = 1$ represents the correction term for radius error and linear film shrinkage, we have

$$f_1(\theta_0) = \theta_0$$

so that the correction term is $C_1\theta_0$. Similarly for any other error terms that may be important.

The form of the correction function required for accounting for the effect of incorrect crystal alignment was derived in a previous paper (Wadhawan 1973). The present paper considers the combined effect of crystal and collimator misalignments. But whereas the previous calculation was based on the reciprocal-lattice method, the present one is done in direct space. For the case when collimator misalignment is zero, the two treatments lead to the same results.

The analysis presented is also applicable to diffractometer data obtained by recording the counter position (2θ). For diffractometers, however, Bragg angles are better measured by employing Bond's method (Bond 1960), *i.e.*, by recording the *crystal* position, rather than the counter position (2θ). The method is conceptually analogous to the considerably tedious θ-method for films (Weisz *et al* 1948). The effect of crystal and collimator misalignments for Bond's method has been discussed by Burke and coworkers (Burke and Tomkeieff 1968, 1969; Walder and Burke 1971). A comparison is made here of the results obtained by them with those derived here for what may be called the " 2θ-method " of measuring Bragg angles.

2. Mathematical analysis

Figure 1 shows a stereographic projection down the rotation axis. The rotation axis has been taken as vertical, and O is its upper point of intersection with the reference sphere. When there is no misalignment present, the incident beam, I, the plane normal, N, and the reflected beam, R, will all lie in the equatorial plane. Now suppose the collimator is misaligned by an amount β from the equatorial plane. Without much loss of generality, we can assume that the collimator misalignment is in the vertical plane only. The incident beam will then project to some point I_1. In addition, suppose the reflecting planes, which should ideally be parallel to the rotation axis, are tilted away from it by an amount α. (In general, α and β can have the same or opposite signs. In figure 1 they have been shown as having the same sign.) When the Bragg condition is satisfied, the plane normal will now project to some point N_1 and the reflected beam to R_1. In such a case, the true value of Bragg angle, θ, is that given by I_1R_1 (equal to $\pi-2\theta$), whereas the corresponding (incorrectly) measured value is that given by IR′ in the equatorial plane (equal to $\pi-2\theta'$, say).

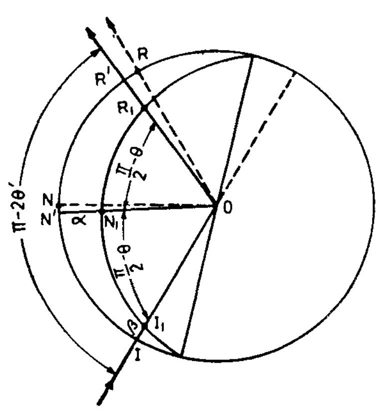

Figure 1. Stereographic projection down the rotation axis 0, depicting the Bragg reflection process in the normal-beam equatorial geometry.

We now use a theorem (Todhunter 1859) giving the length of a line drawn from a corner to the opposite side of a spherical triangle. In figure 1, ON_1 is the line drawn from the corner O to the opposite side I_1R_1 in the spherical triangle OI_1R_1 and its length is equal to $(\pi/2 - \alpha)$. The theorem then gives

$$\cos(\pi/2 - \alpha) = \cos(\pi/2 - \beta)\frac{\sin(\pi/2 - \theta)}{\sin(\pi - 2\theta)} + \cos(OR_1)\frac{\sin(\pi/2 - \theta)}{\sin(\pi - 2\theta)} \quad (2)$$

which simplifies to

$$\cos(OR_1) = 2\sin\alpha\sin\theta - \sin\beta \quad (3)$$

provided $\cos\theta \neq 0$. From the spherical triangle OI_1R_1 again,

$$\cos(\pi - 2\theta) = \cos(OR_1)\cos(\pi/2 - \beta) + \sin(OR_1)\sin(\pi/2 - \beta) \times \cos(\pi - 2\theta') \quad (4)$$

which, on using eq. (3) and simplifying, gives

$$\cos 2\theta' = \frac{\cos 2\theta + (2\sin\alpha\sin\theta - \sin\beta)\sin\beta}{[1 - (2\sin\alpha\sin\theta - \sin\beta)^2]^{\frac{1}{2}}\cos\beta} \quad (5)$$

Let us now consider some special cases of this exact and general equation.

Case I. $\beta = 0$

For this case, which corresponds to a perfectly aligned collimator but an imperfectly aligned crystal, eq. (5) reduces to

$$\cos 2\theta' = \frac{\cos 2\theta}{[1 - 4\sin^2\alpha\sin^2\theta]^{\frac{1}{2}}} \quad (6)$$

This expression is the same as that derived earlier by the author (Wadhawan 1973) by an entirely different approach through the application of the reciprocal-lattice method [Equation (6) of that paper becomes identical to eq. (6) above if we define $\alpha = \alpha_0$ for $\xi = \pi/2$ there]. Details of this case have been discussed in the earlier paper. It was also shown there that when α is small, as is generally the case, eq. (6) reduces to

$$\theta' - \theta = -(\alpha^2/2)\tan\theta\cos 2\theta \quad (7)$$

Case II. $\alpha = 0$

When the reflecting planes are parallel to the rotation axis ($\alpha = 0$) but the incident beam, though passing through the relation axis, is inclined to it by an angle $(\pi/2 - \beta)$ instead of $\pi/2$, eq. (5) reduces to

$$\sin\theta' = \sec\beta\sin\theta \quad (8)$$

When β is small, this gives

$$\theta' - \theta = (\beta^2/2)\tan\theta \quad (9)$$

Case III. α and β are small

α and β are small enough in practice to justify the neglect of all third and higher order terms in α and β in eq. (5). We then obtain the following equation for the error $\theta' - \theta$:

$$\triangle\theta = \theta' - \theta = \tan\theta\,[\alpha^2(\sin^2\theta - \tfrac{1}{2}) - \alpha\beta\sin\theta + \beta^2/2] \tag{10}$$

For a fixed wavelength, the error in *d*-spacings is related to the error in θ by the following equation:

$$\Delta d/d = -\cot\theta\,\Delta\theta \tag{11}$$

Substituting for $\Delta\theta$ from eq. (10) we get

$$\Delta d/d = \alpha^2(\tfrac{1}{2} - \sin^2\theta) + \alpha\beta\sin\theta - \beta^2/2. \tag{12}$$

3. Discussion

Equation (12) shows that Δd does not approach zero as θ approaches 90°. Thus, unlike the effects of film shrinkage, eccentricity of specimen, and absorption on *d*-spacing measurements (Buerger 1942), the effect of misalignment cannot be eliminated by extrapolating the results to $\theta = 90°$. Therefore, either the misalignment error must be brought within the precision of measurement by careful experimental procedures, or, else, corrections for it must be applied *before* employing extrapolation techniques.

As seen from eqs (6) and (8), respectively, when either crystal misalignment alone or collimator misalignment alone is present, the error $(\theta' - \theta)$ in the measured Bragg angle is independent of the sign of α or β. But when both α and β are non-zero, eq. (5) shows that the error remains the same only when the signs of both α and β are reversed. In other words, the error is not the same for the ratios α/β and $-(\alpha/\beta)$.

Figure 2 shows the variation of $(\theta' - \theta)$ with θ for some fixed values of α and β [eq. (5)]. Except when $\alpha/\beta \sim 1$, the error is positive for large θ and increases sharply with it. The case $\alpha/\beta = 1$ is particularly interesting. For this case the error is always negative (or zero) and much smaller than that for other cases shown. This can also be seen from table 1, which gives the value of $(\theta' - \theta) \times 10^5$ in degrees for a fixed θ (75°) and various values of α and β. Some interesting facts emerge from this table.

Table 1. Values of $(\theta' - \theta) \times 10^5$ in degrees for $\theta = 75°$ and various values of α and β in degrees

β \ α	0·0	0·05	0·1	0·5	1·0
0·0 ..	0	7	28	705	2825
0·05 ..	8	− 1			
−0·05 ..		31			
0·1 ..	33	− 2			
−0·1 ..			124		
0·5 ..	814			−54	
−0·5 ..				3096	
1·0 ..	3261				−214
−1·0 ..					12436

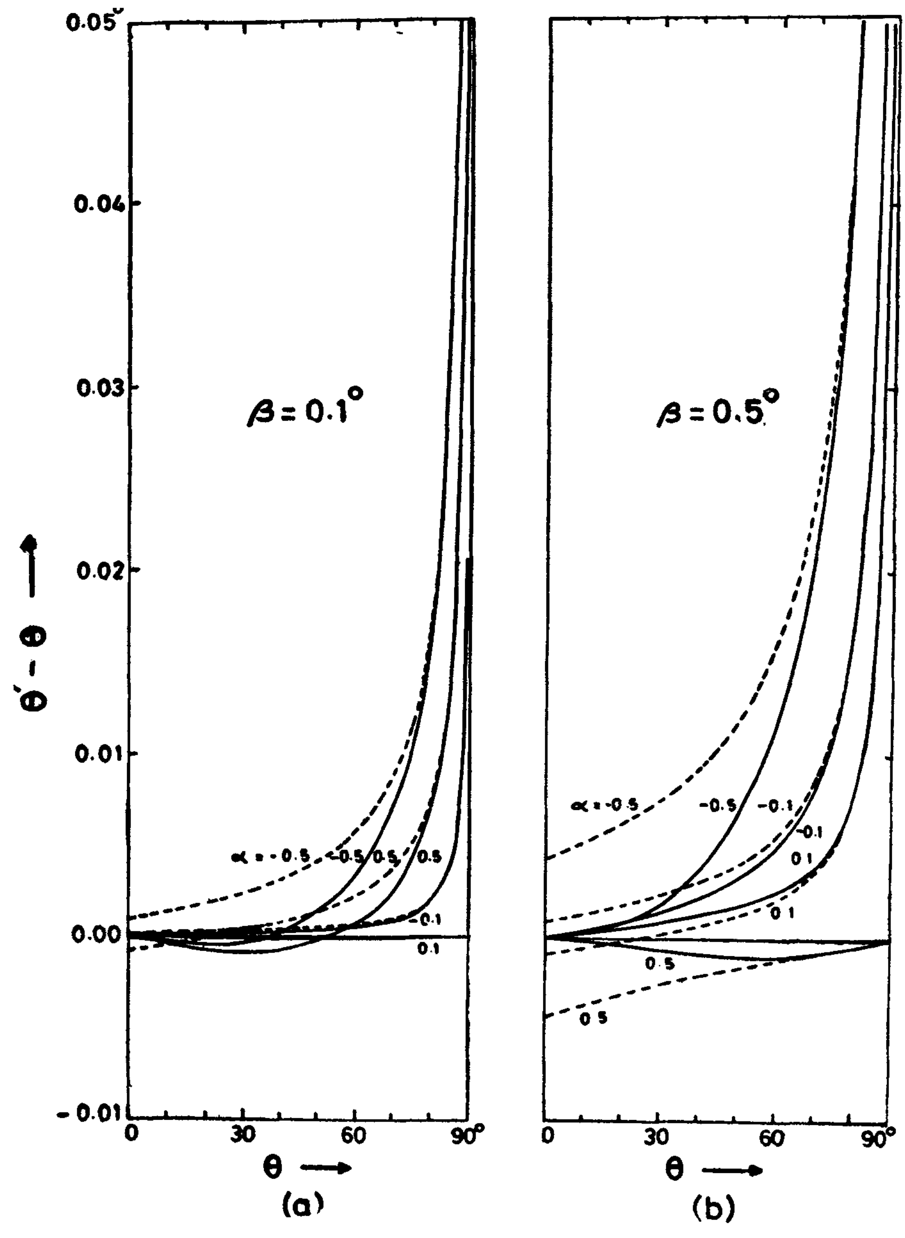

Figure 2. Plots showing the error in θ as a function of θ for various fixed values of collimator misalignment, β, and crystal misalignment, α. The solid lines are for the 2θ-method and dashed lines for Bond's method of measuring Bragg angles. For large θ, the corresponding curves for the two methods coincide. In figure (a) the two curves for $\alpha = 0{\cdot}1°$ are practically coincident with the abscissa axis.

Firstly, when $\alpha/\beta = 1$, the error in θ is much smaller than that due to α alone or β alone, and is always negative (or zero).

Secondly, when $\alpha/\beta = -1$, the error is more than twice the sum of errors due to α alone and β alone. These results show that the errors due to collimator and crystal misalignments are not additive and should not be treated independently in a least-squares fitting procedure.

Lastly, the error due to crystal misalignment alone is somewhat less than that due to collimator misalignment alone. This, of course, is due to the $\cos 2\theta$ factor in eq. (7).

Some remarks about the magnitude of the effect of misalignment may be in order here. Crystal structure investigations do not generally require an accuracy better than about 1 part in 10^4 in lattice parameters. At $\theta = 75°$, this requires a precision of about $0{\cdot}02°$ in θ measurement. Table 1 shows that at $\theta = 75°$, the error corresponding to $\alpha = 0{\cdot}5°$ and $\beta = -0{\cdot}5°$ is about $0{\cdot}03°$. It may therefore be concluded that, so far as crystal structure analysis is concerned, if the crystal and the collimator are aligned to better than about a quarter of a degree, the effect of any residual misalignment on lattice parameters will not be significant and no corrections need be applied for it.

However, the situation is different for very high accuracy lattice parameter work, for which θ measurements with a precision exceeding $0{\cdot}002°$ are quite common with both photographic and diffractometric methods (Beu 1967). Buerger (1942) developed a Weissenberg type of back-reflection precision camera, with which he measured d-spacings correct to six significant figures. An accuracy of 1 part in 10^6 in d-spacings requires Bragg angle measurements correct to about $0{\cdot}002°$ even at as high an angle as $87°\ \theta$. Misalignment error then becomes one of the principal ones (*see* table 1), the more so because it increases sharply with increasing θ (figure 2).

Comparison with results for Bond's method

In Bond's method (Bond 1960), a wide-window counter is employed and the Bragg angle for a reflection is obtained by measuring the angle through which the crystal has to be rotated between the two symmetrical diffracting positions on either side of the incident beam. For perfect crystals, errors due to eccentricity of specimen and absorption get eliminated by this procedure. However, the method, by its very nature, necessitates observing a reflection on both sides of the incident beam. This is sometimes not possible, particularly with neutron diffractometers; because of space limitations around reactor beam-holes, the movement of the counter is restricted to mainly one side of the monochromatised beam.

Burke and Tomkeiff (1968) derived for Bond's method the following equation connecting the observed Bragg angle, θ', with its true value, θ, when the crystal is misaligned by an amount α and the collimator by an amount β:

$$\sin\theta = \sin\alpha\sin\beta + \cos\alpha\cos\beta\sin\theta' \tag{13}$$

The corresponding equation for the 2θ-method is eq. (5). The dependence of $(\theta' - \theta)$ on θ, as given by eq. (13), has also been shown in figure 2 (the dashed curves). Comparison with the corresponding curves for the 2θ-method shows that the errors are not identical, except for large Bragg angles. This means that for a given amount of crystal and collimator misalignment, even when errors due to eccentricity of specimen and absorption are completely absent, Bond's method and the 2θ-method do not give identical values for Bragg angles in the small and intermediate range. The reason for this diffeıence lies in the fact that what is measured is really the projection of the angles on to the equatorial plane; and when misalignment is present, the projection of the angle between the incident and the reflected beam does not turn out to be exactly double the value of the projection of the angle between the incident beam and the plane normal. The amounts of correction required for the two cases are therefore different.

Acknowledgement

It is a pleasure to thank Dr R Chidambaram for his valuable suggestions.

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