

of the lattice along the crystal axes found in the Laue examination. Because of the high absorption coefficients of the alloys, only a limited amount of data in the high angle region could be recorded. The formation of layer lines was clear in all photographs and provided information about the size of the unit cell. Three significant axes were examined in each case; the triad, or  $c$  axis, and the two principal axes perpendicular to the  $c$  axis, the  $a$  axis and that  $30^\circ$  to the  $a$  axis, for convenience referred to here as the  $b$  axis. Values of  $8.100 \text{ \AA}$  and  $7.020 \text{ \AA}$  were obtained for  $a$  and  $b$  which are mutually consistent, and in agreement with the  $a$  parameter calculated from the cubic lattice. The  $c$  parameter obtained from the single-crystal photograph was  $8.698 \text{ \AA}$ , which is almost exactly three times the  $c$  parameter calculated previously.

These new  $a$  and  $c$  parameters were used as the trial constants in the indexing routine, the results of which are shown in Table 1. The lattice parameters of the  $\beta''$  structure are finally given as  $a = 8.1031 \pm 0.0005 \text{ \AA}$ , and  $c = 8.7033 \pm 0.0005 \text{ \AA}$  at  $20^\circ\text{C}$ . The structure implied by these constants is likely to be closely related to the  $\zeta$  phase of the AgZn and the AgGa systems save that the  $\beta''$  AuCd lattice extends over three cell lengths of the conventional  $\zeta$  phase structure and thus contains 27 unit cell atoms. A more detailed examination of the  $\beta''$  structure is in progress.

The evidence shows that the  $\beta''$  structure is thus not tetragonal and suggests either a trigonal or hexagonal unit cell. Although the Laue photographs clearly showed the symmetry elements of the structure, the reflexions were diffuse, indicating polygonization or the presence of multi-crystallites of almost identical orientation. This is significant, if the structure is similar to the  $\zeta$ -AgZn structure. True single crystals of the  $\zeta$ -AgZn structure have never been isolated, the transformation from the parent cubic  $\beta$  phase occurring

by formation of many minute crystallites of  $\zeta$  phase, having their  $c$  axes along the cube diagonals of the parent cubic grains.

The X-ray patterns obtained from quenched filings of any alloy containing 47.5 at.% Cd illustrate the change in type of transformation induced by quenching. Following sufficiently severe quenching the transformation product is the  $\beta''$  structure. The change in mode of transformation is gradual, showing first signs of deviation in the  $300^\circ\text{C}$  quench, and complete change with the  $500^\circ\text{C}$  quench. It is concluded that the previously described  $\beta_1 \rightarrow \beta'''$  transformation is really  $\beta_1 \rightarrow \beta''$ . There are indications however, in the powder photographs, that the change is not a simple switch from one transformation product to another ( $\beta' \rightarrow \beta''$ ), but that it occurs by way of an intermediate structural type since the X-ray photographs of alloys quenched from  $350^\circ\text{C}$  and  $400^\circ\text{C}$  show strong reflexions which are not characteristic of either  $\beta'$  or  $\beta''$  products.

#### References

- BIRNBAUM, K. H. (1959). *Trans. A.I.M.E.* **215**, 786.  
 CHANG, L. C. (1951). *Acta Cryst.* **4**, 320.  
 CHEN, C. W. (1954). Pub. no. 8628, University Microfilms, Ann Arbor, Michigan.  
 CLASS, W. & LIEBERMAN, D. S. (1961). *J. Aust. Met.* **6**, 11.  
 EDMUNDS, I. G. & QURASHI, M. M. (1951). *Acta Cryst.* **4**, 417.  
 HOFF, W. D., WALLACE, W. & KITCHINGMAN, W. J. (1965). *J. Sci. Instrum.* **42**, 171.  
 KÖSTER, W. & SCHNEIDER, A. (1940). *Z. Metallk.* **32**, 156.  
 ÖLANDER, A. (1932a). *Z. Kristallogr.* **A83**, 145.  
 ÖLANDER, A. (1932b). *J. Amer. Chem. Soc.* **54**, 3819.  
 SUBRAMANYA, B. S., BAKER, G. B., LIEBERMAN, D. S. & READ, T. A. (1961). *J. Aust. Met.* **6**, 11.  
 WECHSLER, M. S. (1957). *Acta Metallurg.* **5**, 150.  
 ZIRINSKY, S. (1956). *Acta Metallurg.* **4**, 164.

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## Specimen and Beam Tilt Errors in Bond's Method of Lattice Parameter Determination

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An analysis of the specimen and beam tilt errors in the Bond method of precision lattice parameter determination is presented. The assumption that the two are independent and thus additive is incorrect. Numerical values of the errors for some special cases are given.

A method of determining the lattice parameters of good-quality single crystals was described by Bond (1960). It is capable of (relative) accuracies of a few parts per million and it has been used when extreme precision is desirable (e.g. D'Heurle, Feder & Nowick, 1963). The arrangement is shown schematically in Fig.

1. Ideally the crystal is orientated with a suitable crystallographic plane parallel to the rotation axis of a divided circle and a well collimated beam of monochromatic X-rays normal to the rotation axis is diffracted into the detector  $A$ , when the crystal is in position  $a$ , and into the detector  $B$  when it is rotated to

position  $b$ . Bond showed that by computing  $\theta$  from the angle of rotation of the crystal between the two positions, the zero, specimen eccentricity and absorption errors are eliminated. The major sources of error are thus due to (i) tilt of the diffracting planes relative to the rotation axis (we refer to this as specimen tilt), and (ii) departure of the incident beam from exact normality to the rotation axis (we refer to this as beam tilt).

In evaluating the errors due to these two sources Bond assumed explicitly that they are additive. We show here that this is not so and, moreover, that the combined error may be either much less than either one alone or much greater than that predicted by simple addition, depending upon the conditions.

### Analysis

A stereographic projection of the arrangement is shown in Fig. 2 with the divided circle as the plane of projection. Ideally, the normal to the diffracting planes,  $N$ , the incident beam,  $I$ , and the diffracted beam (not shown) lie on the basic circle.  $O$  is the rotation axis. When beam and specimen tilts are present the plane normal projects to some point  $N_1$ ,  $\alpha$  being the angle by which the planes are tilted relative to the rotation axis; the incident beam projects to  $I_1$ ,  $\beta$  being the angle of beam tilt.  $\alpha$  and  $\beta$  may be in the same or opposite senses. Fig. 2 is drawn for  $\alpha$  and  $\beta$  in the same sense.

Thus in the real case the angle  $\angle N_1 O I_1$  is equal to  $(\pi/2 - \theta)$ ;  $\theta_M$ , the (incorrectly) measured Bragg angle, is given by  $\angle N O I = (\pi/2 - \theta_M)$ . Using the spherical triangle  $ON_1I_1$  gives

$$\cos(\pi/2 - \theta) = \cos(\pi/2 - \alpha) \cos(\pi/2 - \beta) + \sin(\pi/2 - \alpha) \sin(\pi/2 - \beta) \cos(\pi/2 - \theta_M). \quad (1)$$

The error in  $\theta$ ,  $\delta\theta$ , associated with the two tilts may be computed from equation (1) for particular values of  $\alpha$ ,  $\beta$  and  $\theta$  and then used with the Bragg equation to give the error in the interplanar spacing,  $\delta d$ . A number of special cases permit analytical solutions and are useful to illustrate the effects.

*Case A. Specimen tilt but no beam tilt, i.e.  $\beta=0$*

$$\text{From (1) } \sin \theta = \cos \alpha \sin \theta_M. \quad (2)$$

From the Bragg equation

$$\frac{\delta d}{d} = \frac{d_M - d}{d} = \frac{\sin \theta}{\sin \theta_M} - 1, \quad (3)$$

where  $d_M$  is the interplanar spacing corresponding to  $\theta_M$ . Combining equations (3) and (2),

$$\frac{\delta d}{d} = (\cos \alpha - 1),$$

and since  $\alpha$  is very small in practice

$$\frac{\delta d}{d} = -\alpha^2/2. \quad (4)$$

This is the result obtained by Bond.  $|\delta d/d|$  is to be added to  $d_M$  to give  $d$ .

*Case B. Beam tilt but no specimen tilt, i.e.  $\alpha=0$*   
This is equivalent to case A.

$$\frac{\delta d}{d} = -\beta^2/2. \quad (5)$$

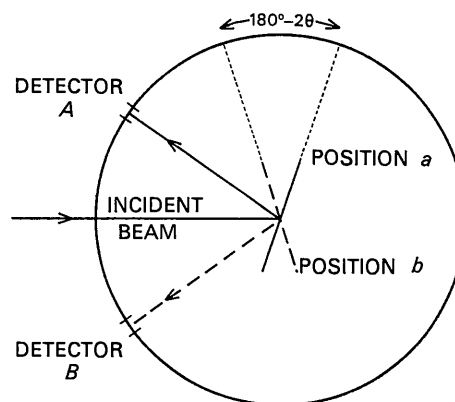


Fig. 1. Schematic arrangement of the Bond technique of lattice parameter measurement. Positions  $a$  and  $b$  define positions of the diffracting planes of the crystal to diffract into the corresponding X-ray detectors. The detectors have wide windows and only the crystal is rotated.

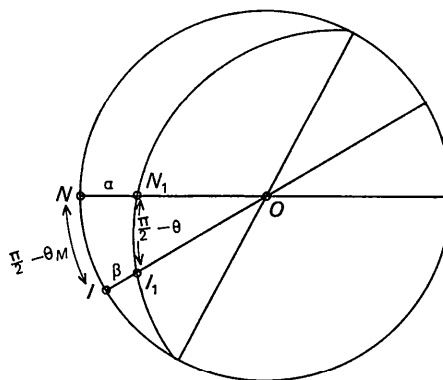


Fig. 2. Stereographic projection of the Bond arrangement.  $\alpha$  and  $\beta$  are the angles of specimen tilt and beam tilt respectively.

Table 1. Values of  $|\delta d/d|$  for some values of  $\theta$ ,  $\alpha$  and  $\beta$

$\alpha$ (rad)	$\beta$ (rad)	$\theta=45^\circ$	$\theta=60^\circ$	$\theta=75^\circ$	$\theta=85^\circ$
0.001	0	$5 \times 10^{-7}$	$5 \times 10^{-7}$	$5 \times 10^{-7}$	$5 \times 10^{-7}$
0.001	0.001	$4.14 \times 10^{-7}$	$1.54 \times 10^{-7}$	$3.52 \times 10^{-8}$	$3.82 \times 10^{-9}$
0.001	-0.001	$2.41 \times 10^{-6}$	$2.15 \times 10^{-6}$	$2.04 \times 10^{-6}$	$2.00 \times 10^{-6}$

Case C. Two tilts of equal magnitude in the same sense, *i.e.*  $\alpha = \beta$   
From (1)

$$\sin \theta = \sin^2 \alpha + \cos^2 \alpha \sin \theta_M, \quad (6)$$

and combining with equation (3),

$$\frac{\delta d}{d} = \sin^2 \alpha \left( \frac{1 - \sin \theta_M}{\sin \theta_M} \right). \quad (7)$$

Using the approximation for small  $\alpha$  gives

$$\frac{\delta d}{d} = \alpha^2 \left( \frac{1 - \sin \theta_M}{\sin \theta_M} \right). \quad (8)$$

$|\delta d/d|$  is to be subtracted from  $d_M$  in this case.

Case D. Two tilts of equal magnitude in opposite sense, *i.e.*  $\alpha = -\beta$   
Proceeding as before gives

$$\frac{\delta d}{d} = -\alpha^2 \left( \frac{1 + \sin \theta_M}{\sin \theta_M} \right). \quad (9)$$

$|\delta d/d|$  is to be added to  $d_M$ .

such an error cannot be detected by making measurements of different orders of reflexion from the same plane. Equations (8) and (9) clearly show that Bond's assumption that the two errors are additive and thus also independent of  $\theta$  is not correct. In terms of absolute errors such an assumption is also incorrect as the values of  $\delta d/d$  for some particular values of  $\alpha$ ,  $\beta$  and  $\theta$  show. These are given in Table 1.

When  $\alpha$  and  $\beta$  are in the same sense the combined error is opposite in sign and smaller in magnitude than that due to either  $\alpha$  or  $\beta$  alone, *i.e.* the errors due to specimen and beam tilt are partially compensating. At  $\theta = 90^\circ$  compensation is perfect.

For opposite tilts the combined error is of the same sign but larger in magnitude than that computed by simple addition of the two errors considered to be independent. At  $\theta = 85^\circ$ , if the errors were independent, the total error for  $\alpha = \beta = 0.001$  rad would be  $10^{-6}$  compared with an actual error of  $2 \times 10^{-6}$ . Clearly when using this technique it is desirable to make  $\alpha$  and  $\beta$  as small as possible, and as far as is possible to ensure that any residual tilts of beam and specimen are in the same direction.

### Discussion

When only one tilt is involved the error in the value of  $d$  is independent of  $\theta$  and, as Bond pointed out,

### References

- BOND, W. L. (1960). *Acta Cryst.* **13**, 814.  
D'HEURLE, F. M., FEDER, R. & NOWICK, A. S. (1963).  
*J. Phys. Soc. Japan*, **18**, Sup. II, 184.

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## Thermal Etching of (100) Surfaces in Sodium Chloride Single Crystals

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Freshly cleaved sodium chloride single crystals thermally etched both in air and in vacuum ( $10^{-5}$  torr) show three types of evaporation pit: concentric square pits and concentric circular pits in air etched crystals, and pyramidal pits in vacuum etched crystals. The pyramidal pits may be of three kinds: those with symmetric diagonals, those with one symmetric and one non-symmetric diagonal, and finally those with two non-symmetric diagonals. These pyramidal pits are of the same nature as those associated with dislocations, found on chemical etching of LiF crystals. The differences between pits produced in air and pits produced in vacuum are discussed in terms of surface fusion.

### Introduction

When freshly-cleaved faces of sodium chloride single crystals are thermally etched (by heating them up to a

temperature near the melting point), pits and other corrosion figures are produced due to the evaporation of the crystal. Grinberg (1963) reported that no relationship was found between the development of the pits and the structural crystal defects in sodium chloride single crystals, but that the pits are produced when the surface is changing to higher equilibrium states; however, a relationship between evaporation pits and crystal defects was shown by Patel, Bahl & Vagh (1965) for the case of sodium chloride.

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