Accurate Lattice Parameters from Weissenberg Photographs

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A technique is described for obtaining unit-cell parameters from ordinary zero-layer Weissenberg photographs. The method is simple, and rapid to apply; it gives an accuracy which matches present-day requirements for bond lengths. Results obtained by this technique are compared with the results of well-established precision methods.

1. Introduction

Unit-cell dimensions may readily be obtained from single-crystal rotation photographs, but are usually subject to a 1% error. More often than not, bond lengths are required to a much greater accuracy than this, and a number of methods have been developed which are capable of giving unit-cell dimensions correct to 1 part in 10,000 or better — notably by Buerger (1937), Farquhar & Lipson (1946) and Weisz, Cochran & Cole (1948). Buerger's method involves the use of a special goniometer, Weisz *et al.* admit that their method is both lengthy and tedious when film techniques are employed, while the method of Farquhar & Lipson is time-consuming and presents certain difficulties when applied to monoclinic or triclinic crystals. For all these methods special photographs must be taken, but in this paper a technique is described which uses normal zero-layer Weissenberg photographs and is also rapid to apply to any of the seven crystal systems. While not matching the accuracy of some other methods, it is sufficiently accurate for all normal measurements of interatomic distances.

2. Theory

The basis of the method is the determination of $\sin \theta$ for a number of reflexions from a measure of the separation of resolved α doublets.

Bragg's Law states that

$$\sin \theta = \lambda/2d \qquad (1)$$

where the symbols have their usual meanings.

Let equation (1) apply to the $K\alpha_1$ radiation; then for the $K\alpha_2$ radiation we have

$$\sin (\theta + \Delta\theta) = (\lambda + \Delta\lambda)/2d \qquad (2)$$

where $\Delta\lambda$ is the difference in wavelength between the $K\alpha_1$ and $K\alpha_2$ radiations and $\Delta\theta$ is the resultant difference in the Bragg angle.

Subtracting (1) from (2) and using the approximations $\sin \Delta\theta/2 = \Delta\theta/2$ and $\cos \Delta\theta/2 = 1$ we find

$$(\cot \theta - \Delta\theta/2)\Delta\theta = \Delta\lambda/\lambda . \qquad (3)$$

For a zero-layer Weissenberg photograph it is clear that

$$2\Delta\theta = t/r$$

where t is the separation of the doublet on the film in a direction perpendicular to the camera axis and r is the camera radius.

Substituting for $\Delta\theta$ in (3) we obtain

$$\cot \theta = (2r/t).(\Delta\lambda/\lambda) + (t/4r) \qquad (4)$$

from which $\sin \theta$ may be found.

The relationship between $\sin \theta$, the indices of the reflexion, and the reciprocal-lattice parameters is expressed by the well-known formula

$$h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2klb^*c^* \cos \alpha^* \\ + 2lhc^*a^* \cos \beta^* + 2hka^*b^* \cos \gamma^* = 4 \sin^2 \theta/\lambda^2 . \qquad (5)$$

Putting $s = 2 \sin \theta/\lambda$ and differentiating we have

$$(h^2a^* + hlc^* \cos \beta^* + hkb^* \cos \gamma^*)da^* \\ + (k^2b^* + kha^* \cos \gamma^* + klc^* \cos \alpha^*)db^* \\ + (l^2c^* + lkb^* \cos \alpha^* + lha^* \cos \beta^*)dc^* \\ - klb^*c^* \sin \alpha^* d\alpha^* - lhc^*a^* \sin \beta^* d\beta^* \\ - hka^*b^* \sin \gamma^* d\gamma^* = s.ds . \qquad (6)$$

Approximate values of the lattice parameters will be known from oscillation and Weissenberg photographs; therefore the coefficients of the left-hand side variables can be evaluated for a particular reflexion. On the right-hand side, s has been determined from the film measurements and ds is given by

$$ds = s - s_c$$

where s_c is obtained from (5) by using the approximate lattice-parameter values.

As many equations as reflexions can be set up in this way and these may be solved, by means of a least-squares technique, to give the corrections $da^*, db^*, dc^*, d\alpha^*, d\beta^*$ and $d\gamma^*$ which are applied to the reciprocal-lattice parameters. The lattice restrictions of the various crystal classes are all observed while the equations are being set up; for example in the monoclinic case, $d\alpha^*$ and $d\gamma^*$ are automatically made equal to zero by omitting these variables from

the original equations. Using the latest values of the lattice parameters to calculate the coefficients, the equations are again set up and re-solved to obtain further corrections. This process is continued till the calculated corrections are all smaller than a pre-determined amount and the latest values of the lattice parameters are accepted.

The accuracy with which $\sin \theta$ can be found from equation (4) depends not only on the accuracy with which t is measured but also on the actual value of t. For this reason, each equation is weighted before it is used and a suitable weighting factor is found to be $\Delta t/\Delta (\sin \theta)$ where $\Delta (\sin \theta)$ is the error in $\sin \theta$ produced by an error Δt in t and is given by

$$\Delta (\sin \theta) = \sin \theta \cos \theta (\cos \theta/t - \sin \theta/2r)\Delta t . \quad (7)$$

3. Standard deviations

Standard deviations for the lattice parameters may be calculated as follows. Each lattice parameter is some function of the $\sin \theta$ values obtained from the photographs. For example, we may write

$$a = f(s_1, s_2, \ldots, s_n) .$$

On differentiation

$$da = (\partial f/\partial s_1) ds_1 + (\partial f/\partial s_2) ds_2 + \ldots + (\partial f/\partial s_n) ds_n . \quad (8)$$

Provided sufficient reflexions have been used, the distribution of da will be normal about the mean value zero. Therefore the variance of da, which is also the variance of a, will be the sum of the variances of all the separate terms in equation (8) above. That is

$$\sigma_a^2 = (\partial f/\partial s_1)^2 \sigma_1^2 + (\partial f/\partial s_2)^2 \sigma_2^2 + \ldots + (\partial f/\partial s_n) \sigma_n^2$$

where σ_a^2 is the variance of a and σ_i^2 is the variance of $2 \sin \theta_i/\lambda$.

The coefficients $\partial f/\partial s_i$ may be evaluated in turn by altering the value of s_i to $s_i + \delta$ and finding the resultant change in a. If the new value of a is $a + \varepsilon$ then equation (8) becomes

$$\varepsilon = (\partial f/\partial s_i)\delta$$
or
$$(\partial f/\partial s_i) = \varepsilon/\delta .$$

The values of σ_i^2 can be calculated from an estimate of the accuracy of the film measurements, using equation (7). Thus, it is possible to evaluate σ_a^2 and similarly the variances of the other lattice parameters.

4. Performing the calculations

A program has been written for the Manchester University Mercury computer which enables the above calculations to be carried out for all seven crystal systems. The input data for the program consist of approximate reciprocal-lattice parameters,

wavelength of the $K\alpha_1$ radiation, difference in wavelength between the $K\alpha_1$ and $K\alpha_2$ radiations, camera diameter, a code number denoting the crystal system and the estimated standard deviation of the film measurements. Then follow the indices and $\alpha_1 - \alpha_2$ separation for each of the chosen reflexions. The output gives the refined reciprocal- and real-lattice parameters, together with the standard deviations of the latter. The running time of the program depends, of course, on the number of reflexions used and the number of parameters to be refined, but should never be longer than about five minutes; three minutes would be an average.

5. Accuracy of the method

The accuracy with which the α-doublet separation can be measured is not very high because of the small distances involved, but with a travelling microscope it is possible to measure a 1 mm separation with an accuracy of about 3%. If copper $K\alpha$ radiation has been used and the camera diameter is 57·3 mm, this corresponds to a $\sin \theta$ value of $0·9888 \pm 0·0015$, which is an error of about 1 part in 670. When a sufficient number of reflexions are used, say at least three for every parameter to be determined, the finally expected error in the lattice parameters is of the order of 1 part in 1000. Systematic errors can conveniently be ignored because the errors due to film shrinkage, absorption, lack of knowledge of camera radius and eccentricity of specimen are all very small compared with the 3% error assumed above in the measurement of the α-doublet separation. It has also been found that the final values of the lattice parameters are almost completely independent of the initial approximate values, provided the error in the latter is not greater than about 10%.

6. Practical results

To compare results, this technique has been tried out on two crystals whose unit-cell dimensions have already been accurately determined, namely thallium hydrogen tartrate, which is orthorhombic (Farquhar & Lipson, 1946) and an unheated orthoclase feldspar which is monoclinic (results published by Cole, Sörum & Kennard, 1949, using the method of Weisz, Cochran & Cole, 1948). Ordinary zero-layer Weissenberg photographs of each specimen were taken about each of its three axes. These photographs were indexed and several suitable high-angle reflexions were chosen for measurement. Doublet separations were measured with a low-magnification travelling-microscope at each of the places where they appeared on the films, and an average separation was found for each of the chosen reflexions. These values, together with approximate lattice parameters obtained from oscillation photographs, were used with the computer program to give the results shown in Table 1. They

Table 1. *Comparison of unit-cell dimensions as determined by established accurate methods and the present new technique*

Lattice parameter	Thallium hydrogen tartrate		Unheated orthoclase feldspar	
	Farquhar & Lipson	Main & Woolfson	Cole, Sörum & Kennard	Main & Woolfson
a	$7{\cdot}6550 \pm 0{\cdot}0005$ Å	$7{\cdot}656 \pm 0{\cdot}006$ Å	$8{\cdot}5616 \pm 0{\cdot}0002$ Å	$8{\cdot}558 \pm 0{\cdot}016$ Å
b	$11{\cdot}0165 \pm 0{\cdot}0005$ Å	$11{\cdot}012 \pm 0{\cdot}005$ Å	$12{\cdot}9962 \pm 0{\cdot}0004$ Å	$12{\cdot}984 \pm 0{\cdot}042$ Å
c	$7{\cdot}9260 \pm 0{\cdot}0005$ Å	$7{\cdot}929 \pm 0{\cdot}004$ Å	$7{\cdot}1934 \pm 0{\cdot}0002$ Å	$7{\cdot}204 \pm 0{\cdot}023$ Å
β			$116{\cdot}015 \pm 0{\cdot}005°$	$116{\cdot}00 \pm 0{\cdot}22°$

can be seen to be quite satisfactory, especially those for thallium hydrogen tartrate where 24 reflexions were used in the calculations, and the largest deviation from the accurately measured parameters is only 1 part in 2500. The orthoclase feldspar has a centred lattice which results in many systematic absences; only 13 reflexions could be found which were suitable for the method. In addition, four parameters had to be determined as opposed to three for the orthorhombic crystal, and this resulted in a higher standard deviation for these values of the lattice parameters. Nevertheless, the largest deviation from the accurately measured lattice constant is only 1 part in 650 — for the c axis. However, there is a little uncertainty in comparing the orthoclase feldspar results since naturally occurring minerals can have differing compositions with resultant slight differences in lattice constants. To reduce this uncertainty to a minimum a crystal from the same mineral specimen (not the same crystal) as used by Cole, Sörum & Kennard was used in the present investigations.

7. Conclusions

Since the Weissenberg photographs used in this technique are those normally taken to collect intensity data, the time required to apply the method is merely that of measuring the α-doublet separation of all the suitable reflexions. For example, the time taken to obtain the thallium hydrogen tartrate results, once the photographs had been taken, was about 5 hours and an accuracy of 1 part in 2500 is ample return for so little work. Also, for monoclinic and triclinic crystals the cell angles are determined without any extra work, and these are often difficult to obtain accurately without recourse to rather time-consuming techniques. It is felt by the authors that this method adequately fills the gap between the 1 part in 100 accuracy from oscillation photographs and the 1 part in 10,000 accuracy obtainable from the longer and more accurate methods mentioned in the introduction.

References

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