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Debye–Waller factors for magnesium oxide.

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The Debye–Waller factors for magnesium oxide have been calculated and compared with recent experimental results.

The Debye–Waller factors for MgO have been recently measured by Lawrence (1973) from X-ray diffraction. Earlier experimental measurements by Togawa (1965) on powder samples gave quite different values for the Debye–Waller factors. It was therefore decided at this stage to make a theoretical calculation of Debye–Waller factors in an attempt to resolve the paradox between the two sets of experimental data.

The Debye–Waller exponent, $W_\kappa(\mathbf{K})$ for all atoms κ in a cubic crystal may be written as (Buyers & Smith, 1968)

$$W_\kappa(\mathbf{K}) = B_\kappa \frac{\sin^2\theta}{\lambda^2}$$

with B_κ values independent of the magnitude of the momentum transfer **K**, which may be written as

$$B_\kappa = \frac{8\pi^2}{3}\sum_{\mathbf{q}j}\frac{\hbar}{NM_\kappa\omega_j(\mathbf{q})}[|e(\kappa|\mathbf{q}j)|^2\{n[\omega_j(\mathbf{q})]+\tfrac{1}{2}\}]\,,$$

where N is the number of unit cells in the crystal, $n[\omega_j(\mathbf{q})]$ is the population factor

$$[\exp(\hbar\omega_j(\mathbf{q})/K_\beta T)-1]^{-1}\,,$$

$e(\kappa|\mathbf{q}j)$ is the eigenvector of κth ion and $\omega_j(\mathbf{q})$ the eigen frequency for the jth branch corresponding to the wave vector **q**. 2θ is the scattering angle and λ is the wavelength of the radiation.

The eigen frequencies and corresponding eigenvectors for 8000 points in the Brillouin zone were computed using the shell-model parameters giving best fit to the neutron results. These are the parameters of Model *B* in paper of Sangster, Peckham & Saunderson, (1970). These eigen frequencies and eigenvectors were then used to calculate the B_κ values for magnesium and oxygen ions. The contribution from acoustic modes at the zone centre was taken into account by converting the summation into an integration over the volume 1/8000 of Brillouin zone along the lines of Buyers & Smith (1968) and assuming a Debye approximation over the volume of integration. This contribution was found to be less than 1% of the total value.

The calculated values at 300°K and experimental values are given in Table 1.

Table 1. *The B values for magnesium and oxygen ions*

	B(magnesium) in $\text{A}^{\circ 2}$	B(oxygen) in $\text{A}^{\circ 2}$
Theoretical values	0·30	0·33
Experimental values (Lawrence, 1973)	0·31 ± 0·01	0·34 ± 0·02
Experimental values (Togawa 1965)	0·24	0·19

Our theoretical values are in close agreement with the latest measurements of Lawrence (1973). Thus our calculations favour the recent measurements of Lawrence on a single-crystal specimen as against the measurement of Togawa on powder samples. The calculated results also show that the anharmonic contribution is negligibly small for this crystal at this temperature.

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References

Buyers, W. J. L. & Smith, J. (1968). *J. Phys. Chem. Solids*, **29**, 1051–1055.
Lawrence, J. L. (1973). *Acta Cryst.* A**29**, 94–95.
Sangster, M. J. L., Peckham, G. & Saunderson, D. H. (1970). *J. Phys. C. Solid State Phys.* **3**, 1026–1036.
Togawa, S. (1965). *J. Phys. Soc. Japan*, **20**, 742–752.

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Precession photography: an extrapolation method for more accurate cell dimensions.

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Shifts of reflexions caused by absorption of X-rays lead to systematic errors in cell dimensions. The effect is eliminated by an extrapolation procedure that affords an accuracy of about 0·1%. It can be used only if enough reciprocal rows are recorded.

One source of inaccuracy in cell dimensions is the shift of reflexions from their ideal positions caused by absorption of X-rays in the crystal. Although measurable in most photographs, the effect is best visible on reflexions with a blind spot in the centre: low-angle reflexions have a clear outline, higher-angle reflexions have a markedly stronger high-angle contour and their low-angle contour is weak or absent. The unit spacing is smaller if based on rows of reflexions near the centre of the film and larger if measured further away (Fig. 1). These shifts lower the apparent cell dimensions.

The unit spacing is obviously unaffected by absorption at zero θ, where it cannot be measured. An extrapolation to zero, similar to procedures used in high-angle techniques, is desirable. When plotted against each other, the unit spacing and its product with the crystallographic index of the row approach a linear relationship (Fig. 1). (The data available do not warrant the use of higher-order or trigonometric functions.) The scatter of the low-angle data is associated with the reading error (a division on most devices is 0·05 mm), and its effects can be minimized if weights are conferred equal to the number of unit spacings constituting the spacing measured. A weighted linear regression of these data is calculated by least squares. The precision of the extrapolated spacing is one standard error of the regression estimate.

The slope outlined by points in Fig. 1 varies from crystal to crystal leading thus to erroneous cell dimensions if the row spacings are represented by the arithmetic mean (*a*) or weighted arithmetic mean (*b*). A camera calibrated with quartz will yield wrong cell dimensions of absorbent crystals such as lead nitrate (and *vice versa*) as is seen in Fig. 2. The means of the data for quartz and lead nitrate in (*a*) and (*b*) differ from each other at the 0·01 % significance level, while the null hypothesis cannot be rejected at the 0·1 % level in (*c*). Consequently, measurement of more photographs tends to improve the extrapolated parameter, but does not remove the bias from the data obtained by (*a*) or (*b*) of Fig. 2. [Note that Patterson & Love's (1960) least-squares estimates behave like the arithmetic mean].

Parameters obtained on a calibrated precession camera relate to the true parameter much as the data points relate to the mean crystal-to-film distance in Fig. 2. The 'true' parameter lies then within the precision of five (out of ten) measurements in (*a*), of one measurement in (*b*), and of seven measurements in (*c*). Even if the precision is se tequal to a fixed value (*e.g.* 0·1 %), the result from extrapolated data remains the best. The standard error of the mean extrapolated crystal-to-film distance is 0·08 %, which is an indication of the accuracy of extrapolated cell dimensions.

Admittedly, extrapolation requires that all reciprocal rows photographed (at least three pairs) be precisely measured. Also, to use extrapolation for calibration and calculation of cell dimensions is time consuming. Considering, however, that the present precession cameras cannot attain an accuracy of 0·01 %, since a (reasonable) uncertainty of 0·01 mm in cassette setting or centring the crystal represents nearly 0·02 % alone, the presently claimed ~0·1 % accuracy in extrapolated cell dimensions brings us closer to the ultimate limits of the method.

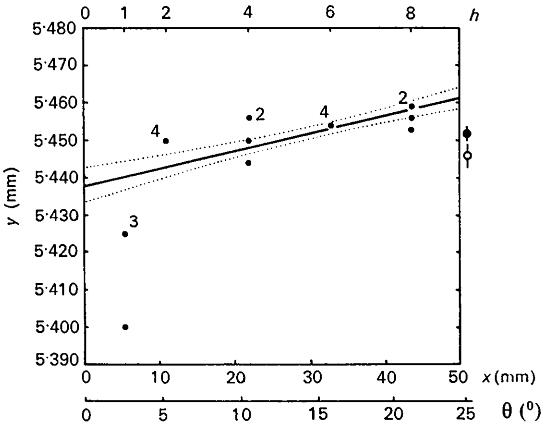

Fig. 1. Unit spacing (y) between reciprocal rows parallel to $\mathbf{c}^*$ in an $h0l$ net (Mo $K\alpha$ radiation) of lead nitrate plotted against its product with index h ($x=hy$). A weighted linear regression of y on x (weights equal to $2h$) is shown together with its standard error of estimate (dotted). Integers accompanying some points show the number of coincident values. Arithmetic mean (open circle), weighted arithmetic mean (solid circle), and their standard errors appear to the right. Data are not corrected for film shrinkage.

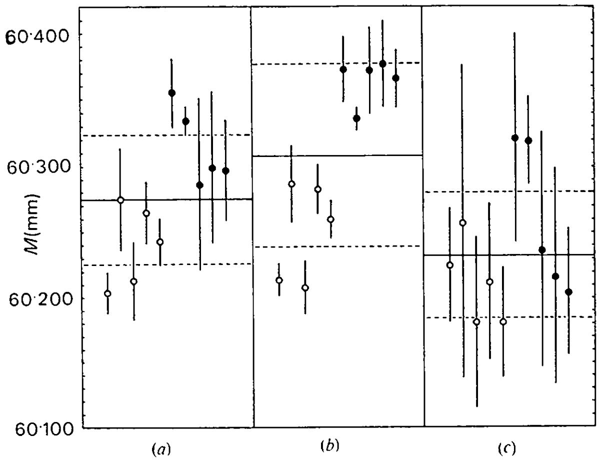

Fig. 2. Crystal-to-film distance of a precession camera (M) calculated from a and c of α-quartz (Huebner, 1967; open circles) and a of lead nitrate (*International Tables for X-ray Crystallography*, 1968; solid circles) by arithmetic mean (*a*), weighted arithmetic mean (*b*), and extrapolation to zero θ (*c*). Full horizontal lines represent the weighted mean for each method; dashed lines embrace ± one standard error. Four films were used with Mo $K\alpha$, Cu $K\alpha$, and Cu $K\beta$ radiations. No two points represent repeated measurements. Data were corrected for film shrinkage; the remaining shrinkage errors are less than ~0·01 %.

References

Huebner, J. S. (1967). Thesis, Johns Hopkins Univ., U.S.A.

International Tables for X-ray Crystallography (1968). Vol. III, p. 122. Birmingham: Kynoch Press.

Patterson, A. L. & Love, W. E. (1960). *Amer. Min.* **45**, 325–333.