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Some sources of error in measuring lattice parameters.

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The accurate determination of lattice parameters requires consideration of certain sources of error which have been neglected until now. One factor is the radiation damage produced in the specimen by the measuring beam of X-rays. Although it is generally appreciated that color centers are produced in alkali halides and metal oxides by the radiation used in diffraction experiments, the corresponding changes in lattice parameters have been measured only in KCl (Berry, 1955). With KCl, an increase of lattice parameter of about 1 part in 10^5 was observed during exposure in the diffraction apparatus after about 15 minutes when using unannealed crystals, and after an hour with annealed crystals. Thus, a given specimen can be used only for very short times when high accuracy is required. These limitations do not apply to metals where displacement of atoms can occur only by direct collision of an atom with a photoelectron having an energy in excess of about 0·5 MeV. (Glen, 1955).

The well known photo decomposition of silver halides into metallic silver and halogen vapor has stimulated many workers to search for intermediate states of decomposition, associated with latent-image formation, which might be detected by observing changes in lattice parameters of photographic emulsion grains (Hess, 1943; Burgers & Mesritz, 1947; Brentano & Spencer, 1947; Berry, 1953; Junghanss & Staude, 1953; Waidelich, 1955). The results of such experiments have been quite inconsistent, some workers reporting changes in lattice parameters by irradiation as large as 2 parts in 1000 and others reporting only much smaller changes, if any. A possible reason for some of these contradictory results may be connected with another source of error in measuring lattice parameters. It has been shown (Berry, Van Horn & Griffith, 1954) that changes in lattice dimension as large as 2 parts in 1000 may arise from changing pressures exerted by the gelatin binder when a film is subjected to bending of the type which occurred in some of the moving-specimen arrangements used in much of the work cited here. Errors of a much smaller order may occur when specimens measured in vacuum are compared with those at atmospheric pressure, but even then differences of the order of 1 part in 10^5 may result.

In measurements of lattice parameters using electron diffraction, crystals are usually in a size range from a few tens to a few hundreds of Ångström units. In such small crystals, surface forces may alter the interatomic spacings (Lennard-Jones & Dent, 1928). Although DuMond and his co-workers (DuMond & Bollman, 1936; Miller & DuMond, 1940) were unable to detect a definite parameter change in X-ray diffraction experiments with fine particles, decreases of 5 parts in 1000 were observed (Boswell, 1951) in electron diffraction from alkali-halide crystals having a size of about 30 Å. In measurements of this kind, it is necessary to consider the possibility of large deviations of the peak positions from the Bragg angle. On using the gas-scattering equation, as applied to small spherical crystals by Germer & White (1941), it was shown that the positions of the maxima may depend on the shape and size of the crystals in the specimen (Berry, 1952). Peak shifts of 2 parts in 100 may occur when the crystals are as small as about 25 Å, even in the absence of any surface forces.

References

Berry, C. R. (1952). *Phys. Rev.* **88**, 596.
Berry, C. R. (1953). *Proc. R. P. S. Centenary Conf.*, London, 1951, p. 113.
Berry, C. R. (1955). *Phys. Rev.* **98**, 934.
Berry, C. R., Van Horn, M. H. & Griffith, R. L. (1954). *Acta Cryst.* **7**, 135.
Boswell, F. W. C. (1951). *Proc. Phys. Soc.* A, **64**, 465.
Brentano, J. C. M. & Spencer, L. V. C. (1947). *Phys. Rev.* **71**, 142.
Brentano, J. C. M. & Spencer, L. V. C. (1949). *J. Chem. Phys.* **17**, 944.
Burgers, W. G. & Mesritz, F. A. (1947). *Physica*, **13**, 490.
DuMond, J. W. M. & Bollman, V. L. (1936). *Phys. Rev.* **50**, 524.
Germer, L. H. & White, A. H. (1941). *Phys. Rev.* **60**, 447.
Glen, J. W. (1955). *Advances in Phys.* **4**, 381.
Hess, B. (1943). *Phys. Z.* **44**, 245.
Junghanss, H. & Staude, H. (1953). *Z. wiss. Photogr.* **48**, 194.
Lennard-Jones, J. E. & Dent, B. M. (1928). *Proc. Roy. Soc.* A, **21**, 247.
Miller, P. H. & DuMond, J. W. M. (1940). *Phys. Rev.* **57**, 198.
Waidelich, W. (1955). *Z. Phys.* **140**, 241.

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Another graphical aid for the evaluation of absorption corrections by Albrecht's method.

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Rogers & Moffett (1956) have described a graphical aid based on Albrecht's (1939) method, for evaluating absorption corrections to observed X-ray diffraction intensities. It has become the practice in this Department to use a rather similar method, which may have advantages.

The reciprocal lattice of the crystal is plotted on a

reasonably large scale (say, $1/\lambda = 5$ in.). This chart is also used for determining counter and crystal settings in a manner similar to that of Evans (1953). Two Bernal circles (Fig. 1(*a*)) have been cut from perspex. The bottom

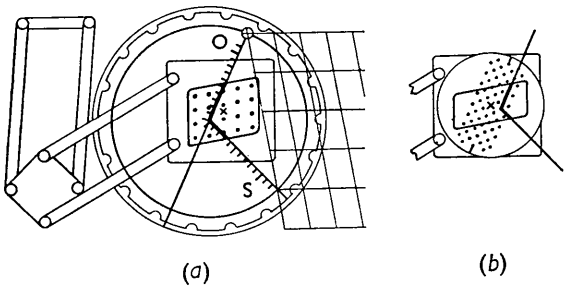

Fig. 1. (*a*) The heavy lines indicate the distances l_1 and l_2 which give μx. The medium lines show the outline of the crystal model, and the incident and reflected directions and the Bernal circle. The pantograph device is not drawn to scale. (*b*) For cases (3) and (4) the distribution of scattering elements is determined by the direction of the incident beam and is displayed by another chart which rotates about the rotation centre of the crystal.

one rotates about the origin, O, of the reciprocal lattice and its diameter defines the direction of the incident beam. The top circle carries a scribed radius to define the direction of the reflected beam and rotates about a pin through the centre of the lower Bernal circle. To define the directions of the incident and reflected rays, both circles are rotated as a whole about the origin of the reciprocal lattice until the particular lattice point S lies on the Bernal circle. The upper circle is then rotated until the scribed radius also meets the lattice point S.

Along each of the direction-defining radii is pasted a replaceable strip of paper carrying a scale calibrated in terms of μx, where μ is the linear absorption coefficient of the crystal and x is proportional to length (the proportionality is determined by the magnification of the crystal model, see below).

A scale model of the crystal is drawn on another sheet of perspex and a suitable number (N) of points representing equal volume elements are marked in. This model is then attached to a pantograph device so that it can be moved to any required position over the Bernal circles whilst maintaining its correct angular orientation with respect to the reciprocal lattice net. (A T-square may be used in lieu of the pantograph but it would normally require both hands for operation, whereas the pantograph leaves one hand free for recording results.) For the nth volume element, $\mu x = l_1 + l_2$. l_1 and l_2 are read from the scales, summed, and recorded. Then the absorption factor (A) is given by

$$A = N^{-1} \sum^{N} \exp\{-(l_1+l_2)\},$$

where N remains constant (in contrast to previous methods). Should it be desired to measure the exponentials directly, then the use of a scale and dividers, as outlined by Rogers & Moffett (1956), is perfectly feasible.

The method as outlined here is applicable to prismatic crystals of constant cross-section (i) bathed completely in a uniform incident beam, and (ii) of length in the direction of the rotation axis extending beyond the incident beam. The method could be extended in the following ways:

(1) For crystals whose cross-sections vary in the direction of the rotation axis, a suitable number of different cross-sections can be drawn on the crystal model.

(2) For crystals falling in category (ii) above, it is possible to use this graphical aid for the computation of absorption factors in cases where either or both the incident and reflected beams are not normal to the rotation axis by modifying the μx scales by the relevant cosine factors.

(3) For crystals whose cross sections extend beyond the incident beam (Fig. 1(*b*)), the centres of equal volume elements may be represented on a fourth perspex sheet, which is attached to and rotated about the rotation centre of the crystal model. For each reflexion, the orientation of this sheet is defined by the direction of the incident beam. The number, N, which will now normally be variable, will also give an indication of the effective reflecting volume of the crystal.

(4) Where the incident-beam cross-section is not uniform, and is known, the distribution of reflecting points on the fourth perspex sheet of (3) may be approximately arranged to represent the intensity distribution of the incident beam, and once again N will give an indication of the effective reflecting volume of the crystal.

References

ALBRECHT, G. (1939). *Rev. Sci. Instrum.* **10**, 221.
EVANS, H. T. (1953). *Rev. Sci. Instrum.* **24**, 156.
ROGERS, D. & MOFFETT, R. H. (1956). *Acta Cryst.* **9**, 1037.

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A preliminary investigation of some heterocyclic compounds.

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A preliminary survey has been made of the crystallographic data for the compounds listed below. The unit-cell and space-group data (Table 1) were obtained from oscillation and Weissenberg photographs; the crystal densities were determined by flotation.

2-Hydroxypyrimidine

N.C(OH).N.CH.CH.CH

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