FURTHER NOTES ON THE PRECISION OF THE BUERGER PRECESSION INSTRUMENT

W. H. Barnes, Maria Przybylska and Violet C. Shore
National Research Council, Ottawa, Ontario

Abstract

Tests of various factors that might affect the accuracy of unit cell constants obtained from Buerger precession films are described. The use of horizontal and vertical fiducial dots for evaluating film shrinkage is advocated.

During the summer of 1949 this laboratory commenced using fiducial dots on zero level precession films for estimating film shrinkage. Since then a number of tests of various factors that might affect the accuracy of measurement of precession films have been carried out and a summary is presented herewith. The instrument in use was supplied by Mr. Charles Supper in 1948 and has the variable F.

Film Shrinkage and Fiducial Dots

Provision is made in the Supper instrument for imprinting two dots on the x-ray negative in the zero level cassette on a horizontal line through the centre of the film, parallel to the dial axis. These fiducial marks establish a horizontal axis for purposes of crystal orientation from angular measurements carried out on the precession films (Evans, Tilden & Adams, 1949). In connection with a redetermination of the unit cell constants of sucrose in this laboratory, A. W. Hanson (1949) used the distance apart of these dots on the film as compared with the distance apart of the holes in the back plate of the zero level cassette to determine film shrinkage. These tests have now been repeated and extended to film shrinkage measurements along the vertical direction as well as the horizontal.

The distance apart of the fiducial dots on a film when the film shrinkage is zero was established as follows. The distance between the pin-holes in the back plate of the zero level cassette on the side in contact with the x-ray film was measured by means of a travelling microscope. The scale of the Buerger precession measuring device (Buerger, 1945), (Charles Supper Co.), having a vernier reading to 0.05 mm., was compared with that of the travelling microscope by measuring the distances between the fiducial dots of several exposed and processed x-ray films on both instruments. As a further check, several exposures of the pin-holes were made on Kodak Studio Proof (printing out) paper, replacing x-ray film in the cassette but requiring no wet processing, and the distances apart of the dots on the paper were measured with the precession measuring device. It probably is advisable to determine the distance apart of the dots for zero film shrinkage separately for each instrument. In the instrument employed for the present tests a new back was made to improve the light-tightness of the zero level cassette. The two holes for imprinting the dots are 11.725 cm. apart which brings them just within the illuminated square area of the measuring device. The distance apart of the holes in the cassette of a new precession instrument recently received, however, is 12.214 cm. which places the dots over the flange supporting the clear glass plate of the viewer. In this laboratory about $\frac{1}{2}$ inch has been removed from the centre of each side of the flange to illuminate the area around the horizontal and vertical pairs of dots on the films.

The following procedure is recommended for the determination of film shrinkage corrections to be applied to measurements on zero level precession photographs. Immediately after the *x*-ray exposure, the horizontal pair of pin-holes is exposed for a few seconds to ordinary light in the darkroom. (It is desirable that a standard set of conditions be set up in order that the spots on each film shall be sufficiently well defined, without halation and of the same intensity from film to film.) The square back of the cassette is then lifted out, turned through 90° and replaced. The pin-holes, now vertical, are again exposed to light and the film is removed and processed. The horizontal pair of fiducial dots on the film continues to serve its original purpose of establishing a horizontal line; the vertical pair, however, is not normally used to define a vertical line because of the possibility of slight disturbance of the position of the film in the cassette when the back is removed, turned and replaced. In actual practice, however, it has been found that the vertical dots define a line that is seldom more than 5 or 10 minutes from being strictly perpendicular to that joining the centres of the horizontal dots.

Using Kodak No-Screen *X*-ray Film, size 5 in.×7 in., cut to 5 in.×5 in. for the zero level cassette, the film shrinkage in the seven-inch direction has always differed from that in the five-inch direction regardless of which direction was vertical or horizontal during tank processing. Although exhaustive tests have not been made, a survey of some sixty films representing six boxes (75 sheet size) and four film lot numbers suggests that the direction of maximum shrinkage is associated primarily with the lot number, usually being the same for different boxes of the same lot. In two boxes of the same lot number, however, the film shrinkage was greater in the five-inch direction throughout one box and more than half-way through the second. It then changed to the seven-inch direction and this persisted to the end of the box. Presumably the reason is to be found in the manufacturing process or cutting routine at the factory.

In magnitude the film shrinkage commonly is of the order of 0.15% to 0.45% in the direction of larger shrinkage although it has been observed as high as 0.9%. In the direction of smaller shrinkage it usually amounts to 0.05% to 0.15% although values up to 0.3% have been encountered. The difference between the shrinkage in the two directions on a given film frequently is less than 0.3% but may be as high as 0.5% on occasion. To take full advantage of the precession instrument, therefore, in the measurement of unit cell constants, both horizontal and vertical fiducial dots should be printed on the film before processing and film shrinkage corrections should be evaluated separately for the two directions on the film.

No appreciable change (less than 80 microns) was found in the distances between the fiducial spots on two *x*-ray films measured on the travelling microscope at intervals over a period of two months. During times of extreme change in humidity or temperature, however, the apparent film shrinkage may change by significant amounts and even negative shrinkage corrections are possible.

Horizontal Axis, Vertical Axis and Goniometric Arcs

The line joining the horizontal fiducial dots may be tested for parallelism with the rotation axis of the goniometer head as follows. By means of a template the plane of one of the arcs is brought parallel to the plane of the film in the zero level cassette and the dial reading is noted. For convenience the set-screw in the dial may be loosened and the dial turned to a reading of 0°00′ and the set-screw tightened. A crystal, such as quartz, is mounted and, by means of precession setting photographs, orientated by means of the arc parallel to the plate so that a principal reciprocal lattice line is exactly collinear with the horizontal fiducial dots. The dial is turned through exactly 180° from this position and another precession photograph is taken. If the fiducial dots are parallel with the rotation axis the reciprocal lattice line will again be collinear with the fiducial dots. If they are not, the crystal should be moved on the arc by one-half the angle required to remove the difference. The test may be checked using the other arc and dial positions 90° and 270° with reference to the first position. The line joining the fiducial dots in the present instrument is off parallelism with the rotation axis by an angle of less than 5 minutes.

Based on this test, a most convenient method of completing the accurate setting of a crystal, already advocated by Evans, Tilden & Adams (1949), is to bring a reciprocal lattice line truly horizontal (*i.e.*, along the dial rotation axis) at dial settings 0° and 90° (alternate arcs parallel to the film) and then check it by photographs at 180° and 270°. That leaves only a dial correction necessary to make the required zero level perpendicular to the x-ray beam.

A series of tests of the effect of missetting of the dial on measurements of Fd^* was made. Two series, each of eleven c-axis zero level photographs of a crystal of childrenite with b^* vertical, were recorded over a range of 50 minutes (dial reading) at positions 180° apart and similar series with a^* vertical. A set of c-axis zero level photographs of quartz with a^* horizontal also was obtained covering a 4° range. The results showed (a) a small difference in dial readings between those photographs in which the criterion for perfect setting was the white radiation "tails" from the outermost spots to the limit of the zero level circle, and those having equal distances from the outermost diffraction spots to the center of the level, and (b) slight differences in Fd^* apparently dependent on dial missetting. The observed differences may be fortuitous but the important feature of these tests was to demonstrate that missetting of the dial by as much as 2° does not affect the accuracy of measurement of Fd^* by more than about 0.3%.

The detailed results of these tests indicated that the magnitude of Fd^* obtained for an axis set horizontally might not be identical with that observed when the same axis was vertical. As a test of this point and of the overall accuracy of the precession instrument under average conditions, a series of photographs of a quartz crystal was taken. The prismatic crystal (from a miarolitic cavity in a quartz cobble, Pitman Field Beach, Marblehead, Mass.) was clear and well formed, about 0.37 mm. long and 0.15 mm. in cross-section. It was mounted with the a^*, (orthohexagonal), b^* and c^* axes, respectively, along the horizontal (dial) axis of the instrument. Using molybdenum radiation six photographs were obtained (a^* horizontal, b^* vertical; a^* horizontal, c^* vertical; b^* horizontal, a^* vertical b^* horizontal, c^* vertical; c^* horizontal, a^* vertical; c^* horizontal, b^* vertical). This series was then repeated using copper radiation. Measurements of Fd_a^*, Fd_b^*, Fd_c^* were employed to calculate F which had been set as closely as possible at 6.00 cm. For this purpose the following data were chosen: values of a and c given by Wilson and Lipson (1941) ($a=4.90320$ kX, $c=5.39371$ kX), converted to international Ångström units by the ratio of the wavelength of copper $K\alpha_1$, 1.54050 Å to that used by Wilson and Lipson (1941), 1.537395 kX, giving $a=4.9131$ Å, $c=5.4046$ Å, $b(=\sqrt{3}a)=8.5098$ Å. In each case horizontal and vertical measurements on the films were corrected for film shrinkage determined directly for the horizontal and vertical directions from the fiducial dots on the films. Results are shown in Table 1. In this table the second, third and fourth columns give the values of F obtained from Fd^* measurements along the designated (a^*, b^*, c^*) axes when the latter were horizontal; the last three columns give the F values calculated from Fd^* measurements along the same axes when they were vertical.

TABLE 1. F (CMS.)

Radiation	Horizontal			Vertical		
($K\alpha$)	a^*	b^*	c^*	a^*	b^*	c^*
Mo	6.000	6.003	6.003	5.981	6.002	5.990
Mo	5.988	5.997	6.008	5.985	5.998	5.998
Cu	6.007	6.011	6.013	6.001	5.989	5.992
Cu	6.001	6.001	5.998	5.982	6.000	5.978

It must be emphasized that the films were of average quality only, some better than others, and no attempt was made to obtain an ideal photograph in every case. In general, those obtained with copper were not as easy to measure as those with molybdenum, partly due to greater absorption by the crystal and partly due to the smaller number of row lines on the films. The object, however, was to test the instrument under average, rather than ideal, conditions so all films were included in the results.

In each of these films, shrinkage was greater in the vertical direction. Without correction for film shrinkage all values of F calculated from Fd^* measurements made along the vertical axis were lower (5.959 cm. to 5.980 cm.) than those obtained from Fd^* measurements along the horizontal axis (5.983 cm. to 6.008 cm.). The average of all values of F after correcting for film shrinkage (Table 1) is 6.002 cm. ±0.2% based on horizontal axes and 5.992 cm. ±0.2% based on vertical axes. This confirmed the indication that experimental values for direct lattice constants might not be the same when the axis was horizontal as when it was vertical. It seems desirable, therefore, to investigate this point for each instrument[1] and, if necessary, to use two values for F depending on whether a given axis under investigation is horizontal or vertical. Alternatively, a single F value may be used and the difference in the "apparent" F's can be incorporated in the distances apart of the horizontal and vertical fiducial dots for zero film shrinkage. That the difference in the present instrument, although small, probably is real receives support from the fact that in all twelve quartz films the corrected F value from the hori-

[1] *Note added in proof.* Values of F obtained with a new precession instrument, having a fixed F, are 5.994 cm. ±0.06% for horizontal measurements and 5.997 cm. ±0.15% for vertical measurements, with a mean for all values of 5.995 cm. ±0.15%, *i.e.*, in this case there is no significant difference. The older instrument, therefore, may be slightly out of adjustment.

zontal measurements was greater than that obtained from the vertical measurements in every case except one. Some earlier photographs of quartz and of eosphorite also showed the same small difference between measurements of Fd^* when a given axis was vertical and horizontal, respectively.

The personal factor in measuring precession films was tested by having two people independently measure some of the foregoing films. Resulting values for F usually differed by less than 0.1% and never by more than 0.25% even for the poorer films.

Various methods of averaging the measurements of row line spacings were tested but resulting values of Fd^* did not differ by more than about 0.1%.

Small missettings of the goniometer arcs of 0.1° and 0.2° and miscentering of the crystal within the limits of the collimator aperture did not affect measurements of Fd^* by more than 0.1%.

CONCLUSIONS

H. T. Evans (1949) has recognised the importance of film shrinkage on the accuracy with which unit cell dimensions can be obtained with the precession camera. The use of vertical and horizontal fiducial dots allows a film shrinkage correction to be applied. Experience in this laboratory indicates that provided film shrinkage is taken into account, that the F setting is calibrated against a suitable standard such as quartz, and that reasonable care is exercised in orientating the crystal, the maximum probable error in unit cell constants determined with the precession instrument should not exceed ±0.3% and should seldom be more than ±0.2%. Previous estimates (Barnes, 1949; Evans, 1949) of about ±0.25% for the accuracy to be expected from the precession instrument under normal routine operating conditions thus appear to be fully justified.

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