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Pressure effects on the measurement of lattice parameter.*

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A difference has been found by Harker (private communication) between the lattice parameter of silver bromide measured here (Berry, 1951) and the lattice parameter of crystals dispersed in gelatin and coated on glass. Harker suggested that this difference might be attributed to pressure exerted on the grains by the gelatin as it dried. A detailed investigation has proved this explanation to be quite correct.

When silver bromide in gelatin is coated and dried on glass or film base, its diffraction pattern has broader lines and gives a smaller lattice parameter than that of the pure powdered material. If the gelatin is swollen with water, the silver bromide recovers its normal parameter and the breadth of the diffraction lines is reduced. Many coatings containing a variety of grain sizes and shapes, differing concentrations of gelatin, and various amounts of chloride or iodide in solid solution have been investigated. It has been found that contractions of the lattice parameter on changing the relative humidity from 100 % to 40 % are in the range 0·1–0·3 %, with a reproducibility of about ± 0·02 % for any one photographic emulsion.

Since the gelatin shrinkage is almost entirely in the direction perpendicular to the plane of the emulsion, the stress which it exerts is also in this direction. The experimental arrangement was such that the Bragg spacings of the crystal planes parallel to the plane of the emulsion were measured.

It is interesting to compute the stresses involved. Young's modulus for silver bromide, obtained from the compressibility (Bridgman, 1940), $2\cdot30 \times 10^{-12}$ dyne cm.$^{-2}$, with the assumption of a Poisson ratio of $\frac{1}{3}$, is $E = 4\cdot4 \times 10^{11}$ dyne cm.$^{-2}$. For a change in lattice constant, $\Delta a/a = 0\cdot2\%$, the stress is $E\Delta a/a = 8\cdot8 \times 10^{8}$ dyne cm.$^{-2}$, or 880 atmospheres. Although Young's modulus for a typical gelatin at 50 % relative humidity is about 20 times smaller than that of silver bromide,† the change in its thickness,‡ $\Delta l/l$, on changing the relative humidity from 75 % to 25 %, may be about 200 times larger than the change in silver bromide lattice parameter. Thus, it is reasonable to expect the observed change in silver bromide lattice parameter to be produced by the contracting gelatin, provided that there is not too much plastic flow in the gelatin surrounding the grains.

The lattice parameters of silver halide grains in photographic films were observed to be changed by mechanically distorting the film. Measurements were made of films held flat in the diffraction apparatus after bending at 40 % relative humidity on rods of various curvatures. Emulsions coated on both sides of the support were examined. The bending process caused the emulsions to retain a residual curvature, owing to plastic flow of the gelatin, so that by making the film flat for measurement, the emulsion which was stretched during the bending process was actually in a state of compression during measurement. It was found that increases of lattice parameter occurred in the emulsion which was stretched during bending and decreases in lattice parameter occurred in the emulsion which was compressed during bending. Limiting values of strain, $\Delta a/a$, of about 0·2 % were found, using rods of about $\frac{1}{4}$ in. in diameter or less. This limiting strain is in reasonable agreement with the expected value for the yield point of silver bromide. Bending a film at 100 % relative humidity causes no residual strains in the grains and conditioning a strained film at 100 % relative humidity releases the strains.

These results are thought to be of interest to crystallographers, particularly because of the demonstration that binding materials in sample preparation may in some cases alter the lattice parameters of specimens.

In precision measurements made here with silver halide specimens not containing binding materials, it has been found that compacting the powder in a specimen holder may alter the lattice constant and line breadth.

The authors wish to thank Messrs C. M. Berntson and S. J. Marino for their assistance in making these measurements.

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* Communication No. 1601 from the Kodak Research Laboratories.

† Measurements obtained by James Olson, of these Laboratories.

‡ Measurements obtained by R. C. Houck, of these Laboratories.

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X-ray studies of 2,4,6-trinitrotoluene.

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Crystals of 2,4,6-trinitrotoluene have been reported by some investigators (Artini, 1915; Hertel & Römer, 1930) to be monoclinic and by others (Friedlander, 1879; Hultgren, 1936; McCrone, 1949) to be orthorhombic. Ito (1950) states that TNT exists in an orthorhombic and two monoclinic forms. In the course of these studies, both monoclinic and orthorhombic forms of TNT, together with variants of these forms, have been found.

The monoclinic form (m.p. 80·9° C.) was prepared by vacuum sublimation on a surface maintained at 78° C.

Rotation, zero-level Weissenberg photographs about the needle (b) axis, and precession photographs indicate the space group C^5_{2h}–$P2_1/c$ with unit cell dimensions*

$$a = 21{\cdot}35\pm0{\cdot}05,\ b = 6{\cdot}05\pm0{\cdot}03,\ c = 14{\cdot}96\pm0{\cdot}05\ \text{Å};\quad \beta = 111°\ 15'\pm15'\ .$$

Assumption of eight molecules in this unit cell gives a calculated density of 1·673 g.cm.$^{-3}$ in agreement with the observed value of 1·654 g.cm.$^{-3}$.

The Patterson projection on (010) shows a large peak at $u = 0{\cdot}223$ and $w = 0{\cdot}362$ in the quarter-cell $0 \leq u \leq \frac{1}{2}$ and $0 < w \leq \frac{1}{2}$. It is possible that the projection of the two molecules in the asymmetric unit on (010) are mutually parallel, so that this large peak is the sum of interatomic vectors between corresponding atoms. This peak lies on the line from $(0, \frac{1}{4})$ to $(\frac{1}{2}, \frac{1}{2})$, which together with the line from (0, 0) to $(\frac{1}{2}, \frac{1}{4})$ determine the pseudo-orthorhombic cell in this projection. Further analysis of this structure is being undertaken.

The orthorhombic form, with some orthorhombic variants, was obtained by dropping an acetone solution of TNT into ether or alcohol held in a dry-ice–acetone bath. From rotation and zero-level Weissenberg photographs about the needle axis of a needle-like lath the unit-cell dimensions

$$a = 20{\cdot}07\pm0{\cdot}08,\ b = 6{\cdot}09\pm0{\cdot}04\ \text{ and }\ c = 15{\cdot}03\pm0{\cdot}07\ \text{Å}$$

were obtained. Extinction of $\{h0l\}$ with l odd and $\{hk0\}$ with h odd indicate that C^5_{2v}–$P2_1ca$ or D^{11}_{2h}–$Pmca$ are probable space groups. Assumption of eight molecules in this unit gives a calculated density of 1·642 g.cm.$^{-3}$.

When TNT crystals are grown, either from solution in various solvents or by sublimation, at temperatures between 0° C. and 70° C., the simple monoclinic form is very rarely found and the simple orthorhombic form never has been found in the course of this study. Instead of the simple monoclinic form, several variants of this form appear. These variant forms appear simultaneously and are recognized by the appearance of additional reflections in the pseudo-orthorhombic reciprocal lattice rows for which l is odd of the first- and higher-layer-line Weissenberg photographs. The appearance of these added reflections doubles (42·70 Å) or quadruples (85·40 Å) the length along the a axis without changing the lengths along the other two axes. In many cases, a streak appears along the pseudo-orthorhombic reciprocal-lattice rows for which l is odd, in the first- or higher-layer-line photographs, with or without additional spots, indicating some form of disorder along the a axis. A similar situation occurs in the case of orthorhombic crystals grown at low temperature (−70° C.). Here, along with the simple orthorhombic form, crystals have been obtained which show additional reflections on the first- and higher-layer-line photographs which indicate a doubling of the a-axis length (40·14 Å). Other crystals show a streak along the reciprocal lattice rows for which l is odd, with or without additional reflections, on the first- and higher-layer-line photographs. Some crystals obtained from acetone solution at 0° C. have given photographs which appear to be identical to those obtained from low-temperature orthorhombic crystals with the doubled a axis. Ito (1950), whose studies were based solely on photographs containing the additional reflections, reports a monoclinic variant with a tripling of the a axial length. This has not been observed in these studies.

In examining photographs of the variant forms, considerable variation is noted in the shape and intensity of equivalent reflections from crystal to crystal. These variations appear best explained by considering the crystals to be composed of twinned fragments of the simple or variant forms which are nearly aligned with respect to their pseudo-orthorhombic axes.

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* A pseudo-orthorhombic cell with these same b and c values and with $a = 39{\cdot}81\pm0{\cdot}05$ Å and $\beta = 90°\ 30'\pm5'$ can be chosen. Ito (1950) chose this cell, but concluded that the space group is C^4_{2h}–$B2/c$. However, his crystals did not consist solely of the monoclinic form.

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Unit-cell data for maltose hydrate and some acyl saccharide derivatives.*

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The unit cell data presented in Table 1 were obtained by the author and by previous investigators from oscillation and goniometer patterns of single crystals using Cu $K\alpha$ radiation. The compounds were selected in hopes of obtaining packing information which could be applied to the problem of the starch crystal structure.

Astbury & Marwick (1931) have pointed out that the spatial requirements of a glucopyranose unit are c. 4·5 Å (thickness), 5·5 Å (length along a line joining C_1 and C_4) and 7·5 Å (breadth). From space-filling models it appears that 4·5 Å is practically an irreducible packing thickness and that any other overall packing dimension is considerably larger than this. It is likely then that the 5 Å dimensions of glucose, cellobiose and maltose are closely related to the thickness of the glucopyranose unit.

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