Acta Cryst. (1954). **7**, 135

Pressure effects on the measurement of lattice parameter.*

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(*Received* 18 *August* 1953)

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), $2·30\times10^{-12}$ dyne cm.$^{-2}$, with the assumption of a Poisson ratio of $\frac{1}{3}$, is $E = 4·4\times10^{11}$ dyne cm.$^{-2}$. For a change in lattice constant, $\Delta a/a = 0·2\%$, the stress is $E\Delta a/a = 8·8\times10^{8}$ 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.

* 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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Acta Cryst. (1954). **7**, 135

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

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(*Received* 6 *July* 1953 *and in revised form* 24 *August* 1953)

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.