UNIT CELL MEASUREMENTS OF Pb_3O_4, Pb_2O_3 AND Tl_2SO_4

Sir:

X-Ray measurements and space groups recently determined in these laboratories for Pb_3O_4, Pb_2O_3 and Tl_2SO_4 are listed below. The Pb_3O_4 and Pb_2O_3 represent new structure types.

1. Pb_3O_4. Tetragonal: a_0 = 8.86 Å.; c_0 = 6.66; density, 9.1; 4.2 $\simeq$ 4 Pb_3O_4 per unit cell; extinctions, *h0l* interferences present only when *h* is even; probable space group, $P\bar{4}b2$ (D_{2d}^7). These crystals were previously described in a paper from this Laboratory[1] as monoclinic. It is now desired to correct this conclusion which was the result of the high distortion of the crystals, produced under the conditions of their formation (high temperature and pressure). Goniometer X-ray patterns, similar to those shown for Pb_2O_3 in Fig. 1, establish the tetragonal nature of the material.

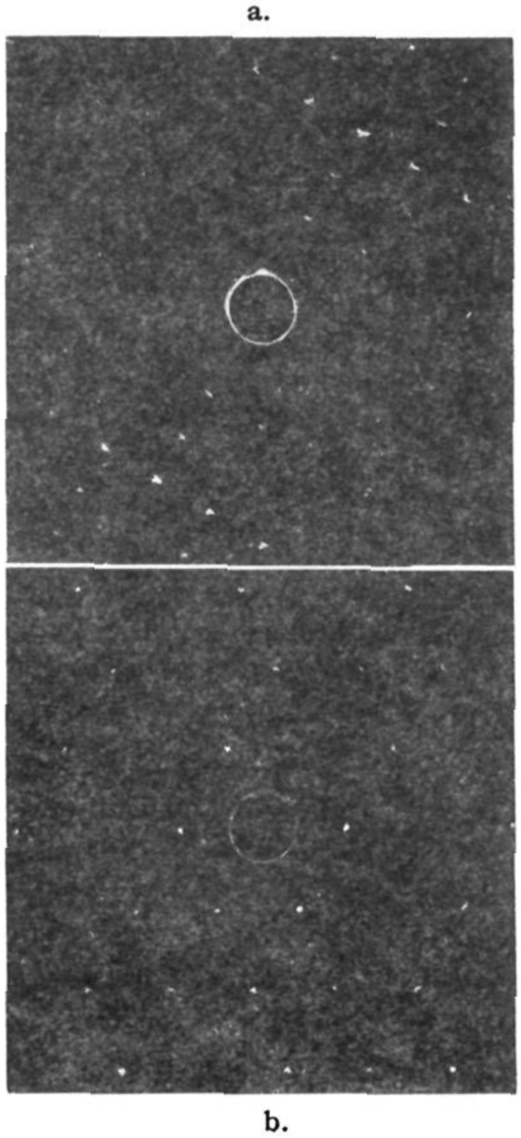

Fig. 1.—Goniometer patterns for Pb_2O_3, $\rho d = K\lambda$. a. *hk*0 interferences (K = 3.46, λ = 1.54 Å.). b. *h*3 interferences (K = 3.00, λ = 1.54 Å.).

2. Pb_2O_3. *Monoclinic:* a_0 = 7.03 Å.; b_0 = 5.62; c_0 = 3.93; β = 82°; density, 9.925; 2.00 $\simeq$ 2 Pb_2O_3 per unit cell; apparent extinctions, 0*k*0 present only when *k* is even; probable space groups, $P2_1/m$ (C_{2h}^2) or $P2_1$ (C_2^2). Patterns of various apparently untwinned crystals of this material, originally described as triclinic,[1] require a monoclinic crystal symmetry (see Fig. 1).

3. Thallous sulfate, Tl_2SO_4. Orthorhombic: a_0 = 10.68 Å.; b_0 = 6.02; c_0 = 7.81; density, 6.77; 4.08 $\simeq$ 4 Tl_2SO_4 per unit cell; extinctions, 0*kl* present only when (*k* + *l*) is even; *hk*0 present only when *h* is even; space group, *Pnma* (V_h^{16}). Patterns are similar to those of the isomorphous K_2SO_4.

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[1] G. L. Clark, N. C. Schieltz and T. T. Quirke, THIS JOURNAL, **59**, 2305 (1937)

SEPARATION OF STARCH INTO ITS TWO CONSTITUENTS

Sir:

Although numerous attempts have been made to separate the two constituents of starch (α-amylose, amylopectin, erythroamylose and β-amylose, amylose, amyloamylose) in pure form (ultrafiltration, electrodialysis, etc.), there seems to exist no method that would allow the isolation of the two amyloses in sufficiently large quantities and high purity. In searching for such a method it occurred to us that perhaps the preferential adsorption of either constituent on the surface of some suitable material would lead to complete separation. Preliminary experiments carried out on activated carbon, fuller's earth and Brockmann alumina showed that selective adsorption did occur, in that the β-amylose became firmly bound to these materials, whereas the α-amylose remained in solution. Our best results, however, were obtained by the use of cellulose as adsorbent. It is well known that the ancient peoples employed starch for sizing papyrus and paper. Further, it is a matter of common experience that starched linen, even after it has been washed several times in water, retains its ability to give blue coloration with iodine. The preferential adsorption of β-amylose by cotton in considerable amount (1.7%) was recently reported by Samec [*Ber.*, **73A,** 88 (1940)]. We have found that the cotton-β-amylose adsorbate, which is formed instantaneously when a cold 1% corn starch paste is brought in contact with cotton, can be washed free of α-amylose with cold water. The adsorbate is then easily broken up by hot water to yield a clear solution of pure β-amylose. From the solution that has been passed several times through the regenerated cotton α-amylose can be obtained by concentration of the solution and precipitation with alcohol. On the other hand, the isolation of β-amylose from its aqueous solution in dry form is not possible. It can be precipitated with alcohol, but almost all of the substance so obtained becomes insoluble in water when dried in a desiccator. Also, the originally clear solution of β-amylose rapidly develops turbidity and the β-amylose precipitates out in granules (retrograded β-amylose or starch-cellulose), which are insoluble in cold water but soluble in cold, strong alkali solution. By addition of pyridine to the original aqueous solution of β-amylose the retrogradation can be prevented. On distillation of this solution with occasional addition of pyridine finally a clear pyridine solution of β-amylose can be obtained, from which β-amylose can be precipitated with alcohol. Evaporation of this pyridine solution results in the formation of an insoluble film of β-amylose. Preliminary experiments showed that both our α- and β-amyloses possess identical specific rotation $[\alpha]^{20}\text{D}$ 145° in a 20% sodium hydroxide solution, and both of them use almost exactly one mole of periodic acid for oxidation. So far the only chemical difference we have found between the two amyloses exists in the complete absence of phosphorus in β-amylose and the presence of this element (0.020%) in α-amylose. Furthermore, the original solution of β-amylose gives a deep blue color with iodine, whereas α-amylose shows a purple color. An extensive investigation of these two materials has been initiated in this Laboratory.

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NEW BOOKS

Scattering of Light and the Raman Effect. By S. BHAGAVANTAM, M.Sc., Ramchandra Deo Professor of Physics, Andhra University. The Registrar, Andhra University, Waltair, India, 1940. x + 333 pp. 2 plates and 41 figs. 18 × 25.5 cm. Price 22s. or Rs. 15 net.

As remarked by the author in his preface, this book deals mainly with the physical aspects of the scattering of light and the Raman effect. The chapter headings are as follows:

Preface, Foreword by Sir C. V. Raman
I. Some Natural Optical Phenomena
II. Light Scattering as a Residual Effect
III. Laws of Scattering of Light
IV. Experimental Results in Gases and Comparison with Theory
V. Theory of Light Scattering by Dense Media
VI. Experimental Results in Liquids and Comparison with Theory
VII. Binary Liquid Mixtures and Liquid Boundaries
VIII. Optical Anistropy and Molecular Structure
IX. Optical Anistropy and Different Types of Birefringence
X. The Principal Experimental Results in Raman Effect
XI. Theory of Raman Scattering
XII. Symmetry, Selection Rules and Molecular Oscillations
XIII. Raman Effect and Molecular Structure
XIV. Raman Effect in Relations to Crystal Structure
XV. Experimental Technique
XVI. Raman Effect in Relation to Inorganic Chemistry
XVII. Raman Effect in Relation to Physical Chemistry
XVIII. Raman Effect in Relation to Organic Chemistry

Appendices:
I. Radiation from Moving Charges
II. Convergence Correction
III. Fluctuations
IV. Evaluation of the Various Matrix Elements of Polarizability Tensor
V. Tensor Components and their Transformation from One Coordinate System to Another
VI. Groups and Group Characters
VII. Group Theory and Normal Oscillations of Molecules

Over one-third of the book deals with Raleigh scattering. The experimental material and theory of Raleigh scattering form a natural background for the full understanding of the Raman effect. These are fully presented in an interesting manner with a mathematical formulation that can be followed easily. The chapter on birefringence will be