

in reflection from the surface of the bars revealed no changes during sintering.

Preliminary measurements indicated very low resistances for all samples, including PdS. Of this latter compound, only one test bar had been made, which was accidentally damaged before accurate measurements could be carried out. The preliminary experiments would put its conductivity in the same order of magnitude as that of the other palladium sulfides. For the other samples, measurements were made both with direct current and at different A. C. frequencies up to 10 kc/sec. They gave practically identical values, indicating that grain boundary resistance had no appreciable influence on the results.

The following values were recorded:

Compound	$\rho_{20^\circ\text{C}}$ * ( $\Omega\text{cm}$ )	$d\rho/dt$ ( $\Omega\text{cm}/\text{degree C}$ )
Pd <sub>4</sub> S	$3.20 \times 10^{-4}$	$+1.05 \times 10^{-6}$
Pd <sub>2,9</sub> S	$10.00 \times 10^{-4}$	$+1.80 \times 10^{-6}$
Ag <sub>2</sub> Pd <sub>3</sub> S	$1.93 \times 10^{-4}$	$+0.22 \times 10^{-6}$

The positive temperature coefficient as well as the low absolute values of the resistivities indicate that these compounds are metallic conductors. For the Pd sulfides, Grønvd and Røst had inferred, from magnetic susceptibility measurements, that they should be essentially non-ionic, *i. e.* either metallic or covalent. The present measurements show that the former is the case. As for Ag<sub>2</sub>Pd<sub>3</sub>S, its high metal content suggested that this compound should be considered as an alloy phase.

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\* Without correction for porosity, which was of the order of 10 %.

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## A New Crystalline Modification of Cellulose as Revealed by X-Ray Diffractograms of Hydrolyzed Cotton and Wood Pulp

Ø. ELLEFSEN

*The Norwegian Pulp and Paper Research Institute, Oslo;*

J. GJØNNES and N. NORMAN

*Central Institute for Industrial Research, Oslo, Norway*

In an attempt to obtain cellulose II with a high degree of crystallinity, it was discovered that surgical cotton as well as mercerized surgical cotton after 2–4 h treatment at 20°C with 40.3 % hydrochloric acid gave X-ray diffractograms which could not be explained exclusively by the hitherto known crystalline modifications of cellulose. A microphotometer curve of such an X-ray diffractogram obtained in an evacuated Guinier camera with CuK $\alpha$ -radiation is shown in Fig. 1a. Shorter or prolonged HCl treatments gave residues containing cellulose II only, as shown by the microphotometer curve in Fig. 1b. Diffractograms like the one in Fig. 1a could also be obtained from wood pulp and ground cotton at a lower acid concentration.

To investigate whether the strong reflections corresponding to the interplanar spacings 6.31 Å, 5.70 Å, 5.13 Å and 3.99 Å in Fig. 1a may be due to sodium cellulose formed during the neutralization, or to cellulose hydrates, oxycelluloses or hemi-celluloses, tests were carried out leading to the following results: Flame photometry showed only negligible (0.4 %) amounts of sodium. Drying for 18 h at 105°C gave no observable change in the diffractograms. An infrared spectrogram indicated no bonds other than those characteristic of cellulose, and a chromatogram of the sample showed glucose to be the only monosaccharide present. It should also be mentioned that viscosity measurements for the sample led to a DP-value below 100.

It must, therefore, be concluded that the sample consists of pure cellulose. The few reflections in Fig. 1a are of course insufficient for solving the structure of the unknown phase or phases, but it is reasonable to assume a unit cell and an arrangement of the glucose rings not too different from

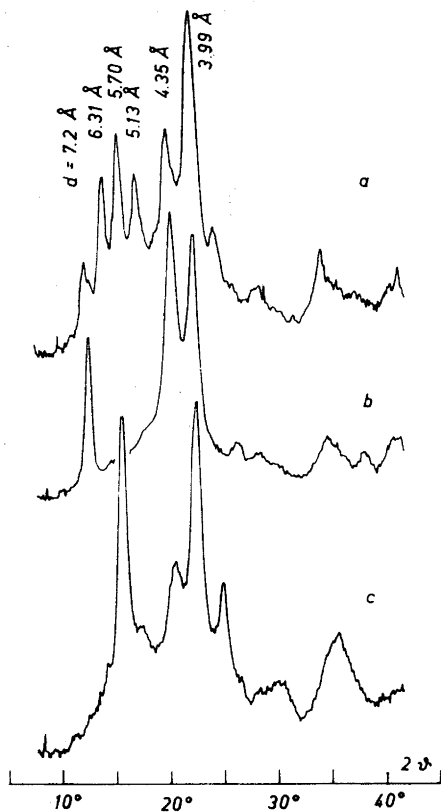


Fig. 1. Microphotometer curves: (a) surgical cotton after 3 hours treatment with HCl, (b) cellulose II, (c) cellulose IV.

cellulose I and II. Utilizing this for indexing the reflections, the three alternatives A, B and C in Table 1 may all be possible. In the three phase alternative C, the peak

$d = 5.70 \text{ \AA}$  and part of the peak  $d = 3.99 \text{ \AA}$  are ascribed to cellulose IV, a diffractogram of which is shown in Fig. 1c. Unit cell dimensions and density for this modification and for cellulose I and II based on the best crystalline samples prepared in our laboratories are also included in Table 1.

In our experiments the three lines  $d = 6.31 \text{ \AA}$ ,  $5.70 \text{ \AA}$  and  $5.13 \text{ \AA}$  always appeared in the same reciprocal intensity ratio. This makes it likely that only one phase exists besides cellulose II. Of the two-phase alternatives A and B, the first one gives a rather long  $a$ -axis and a low density and must be considered the less probable one. Alternative B has the cell dimensions of cellulose IV and may look as an ordered form of this modification. Strong (011) and (020) reflections would require a very strict ordering of the cellulose chains with respect to each other along the chain axis in the crystalline lattice, but even then it is questionable whether reflections of the observed strength can be realized.

Further it should be mentioned that the indexing under A and B in Table 1 would make the relative intensities of the lines very sensitive to preferred orientation. No difference between transmission and reflection diffractograms could be observed, however, even after severe pressing of the samples into thin sheets. Alternative C thus seems to have a preference since all the strong reflections here would originate from planes containing the axis of the cellulose chain.

There are also other facts that favour the three phase alternative. Thus the proposed new monoclinic modification has a unit cell closely resembling those of cellulose I and cellulose IV, and has the same density. One would accordingly expect an arrangement of the glucose rings similar to

Table 1. Indices and cell dimensions for possible cellulose modifications.

Modification	Indices				Cell dimensions				Density (g/cm <sup>3</sup> )
	$d=6.31 \text{ \AA}$	$d=5.70 \text{ \AA}$	$d=5.13 \text{ \AA}$	$d=3.99 \text{ \AA}$	$a \text{ (\AA)}$	$b \text{ (\AA)}$	$c \text{ (\AA)}$	$(^\circ)$	
Alternative A	101	101	020	002	9.08	10.3	8.03	95.9	1.44
• B	011	101	020	002	8.12	10.3	7.99	90	1.61
• C	101		101	002	8.10	10.3	8.16	101.7	1.615
Cellulose IV		101		002	8.12	10.3	7.99	90	1.61
• I					8.20	10.3	7.90	96.7	1.625
• II					8.02	10.3	9.03	117.2	1.62

that in the lattice of cellulose I. For alternative *C* this seems to hold true since the relative intensities of the three predominant reflections (101), (10 $\bar{1}$ ) and (002) are very near the same as for cellulose I.

Attempts have also been made to utilize the other less pronounced peaks in the X-ray diffractograms in order to discriminate between the different possibilities without this leading to any substantially new arguments. Further experimental and theoretical work are in progress. A more comprehensive description of the hydrolysis and the experimental technique will be given elsewhere.

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## Luminescence of Aqueous Solutions of Substances Irradiated with Ionizing Radiation in the Solid State

G. AHNSTROM and G. v. EHRENSTEIN

*Institute of Organic Chemistry and Biochemistry, University of Stockholm, Sweden*

If we place glucose crystals irradiated with X-rays, gamma rays or with fast neutrons over the window of a sensitive photomultiplier (EMI 9514S) we observe a luminescence. This luminescence is also exhibited by some other substances irradiated in the solid state, *e. g.* sorbitol, amylopectin, saccharose and glycine. Dry seeds of *Agrostis stolonifera* also show luminescence after irradiation with X-rays.

The luminescence disappeared completely in all substances investigated during the first hour after irradiation. However, by dissolving *e. g.* irradiated glucose in water, in air and at room temperature, a new luminescence appeared which, after the lapse of one minute from the start of

the dissolution, reached a comparatively constant level. During storage for one day at room temperature the luminescence decays to half of the value observed after one minute. Non-irradiated glucose showed no luminescence when dissolved in water.

Glucose which had been irradiated and stored in air at room temperature for some months, still showed luminescence after dissolving in water. The following experiments have been carried out with glucose which was irradiated three months ago in a reactor with a fast neutron dose of 200 Mrad and a contaminating gamma dose of 200 Mrad.

The water solution of this sugar had a pH of 3, 0.2 mole of acid ( $pK_a = 4.2$ ) had been formed from one mole of glucose. The intensity of luminescence — *i. e.* the number of pulses recorded by a scaler (Ecko N530) — was a function of the pH of the solution. After alkalization with 0.1 N NaOH the intensity of luminescence increased twentyfold. The luminescence of a solution of non-irradiated glucose was negligible on alkalization. The absorption spectrum of the acid (pH 3) and the alkaline (pH 12) solution of irradiated glucose showed an absorption peak at 265  $m\mu$ , probably due to the presence of dihydroxyacetone<sup>1</sup>. The alkaline solution exhibited a stronger light absorption, thus excluding the possibility of the increase of the luminescence intensity of the alkaline solution being due to a decrease of the light absorption.

The luminescence intensity in aqueous alkaline solutions is directly proportional to the amount of irradiated glucose dissolved and also directly proportional to the radiation dose. This experiment has been performed with <sup>60</sup>Co gamma irradiated glucose at different dose levels between 60 and 170 Mrad. It should be noted here that irradiation of crystalline glucose with fast neutrons produced five to seven times more luminescence after dissolving in alkaline solution than irradiation with the same dose of gamma rays from <sup>60</sup>Co.

The addition of hydrogen peroxide, benzoylperoxide or dioxan containing hydroperoxides to the alkaline aqueous solution of irradiated glucose increases the luminescence intensity about tenfold. The luminescence of non-irradiated glucose in this system was negligible. Burnt glucose, however, also exhibited a strong luminescence in this system. On addition of trace amounts of Fe<sup>++</sup> or Cu<sup>++</sup> to the peroxide-irradiated glucose system at pH 3, the