X-Ray and Optical Properties of Barium-Copper-Stearate Films

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Barium-copper-stearate films, built by the successive deposition of layers one molecule thick, were used as diffraction crystals to obtain x-ray spectra. The measurements show that for these films the x-ray spacing has a constant value of approximately 50.47A for films with the same composition, with thicknesses varying from 301 to 3000 layers, but varies with the percent of copper in the film; thin films produce as good spectra as do thick ones; the reflecting planes are regular and definite; the spacing is the same whether the molecules in adjacent layers are oriented in the same or in opposite directions; and the unit decrement of the index of refraction is 5.1×10^{-6}. From the total thickness of a film, as measured by a Michelson interferometer, the spacing of the molecular layers was found to be 24.23A. For the films in which the molecules in adjacent layers were oriented in opposite directions it was expected that the grating space would be twice the layer spacing, or 48.46A. The marked difference between this value and the x-ray spacing of 50.47A indicates that the x-ray spacing is not determined by the method of building the film.

A METHOD of building a multiple-layer film of the salt of a fatty acid on the surface of glass or metal by the successive deposition of layers one molecule thick has been reported by Blodgett.[1] By direct count during the building process the total number of layers in the film is known. The successful use of a film of 301 layers of barium stearate in diffracting x-rays in such manner as to produce fairly sharp lines[2] suggested the possibility of an independent and direct method of measuring the grating space of a crystal. Accordingly the grating space of such a film, used as a diffraction grating, was determined from the angle of reflection of a known x-ray line, and this spacing compared with that obtained by optical means with a film of a relatively large number of layers. The results of these experiments show, contrary to our expectations, that these surface films as they are now being made cannot be used thus to obtain reliable values of the absolute crystalline grating space.

For the work of this experiment Dr. Blodgett provided several films of barium-copper-stearate with thicknesses varying from 301 layers to 3000 layers. All the films except the one of 301 layers were built on optically flat surfaces of glass with an index of refraction nearly the same as that of the film. These films were built with the alternate layers of molecules oriented in opposite directions, i.e., the films were of the "*y*" type as described by Dr. Blodgett.[1] Earlier work with a 301-layer film of this type had indicated that the grating space was approximately 47.5A.[3] In order to obtain appreciable angles of diffraction and sufficient resolving power with so large a grating space it was necessary to use long wave-length x-rays, or a high diffraction order of the shorter wave-length x-rays, and a spectrometer with high dispersive power. For the longer wave-lengths of x-rays it was necessary to use a vacuum spectrograph in order to reduce absorption.

The x-ray apparatus is shown in Fig. 1. A Dershem type of metal x-ray tube *T* with tungsten target is placed approximately 60 cm from the crystal *X*, which in turn is the same distance from the photographic plate *P*. This provides Bragg focusing in a spectrometer with high dispersive power. The camera *C*, the copper tubes *A* and *B*, and the crystal chamber *D* form a gas tight compartment. *A* is connected to the x-ray tube, and *B* to the crystal chamber by sylphons. This permits limited freedom of motion. *D* is a removable steel cylinder with several open-

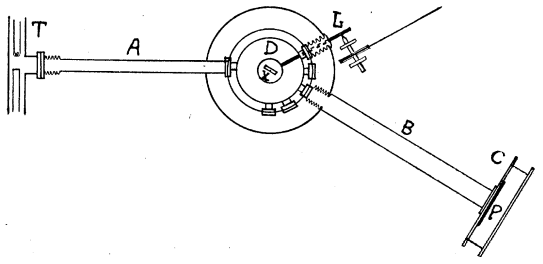


FIG. 1. Dershem vacuum x-ray spectrograph.

[1] Katharine B. Blodgett, J. Am. Chem. Soc. **57**, 1007 (1935).
[2] Clifford Holley and Seymour Bernstein, Phys. Rev. **49**, 403 (1936).
[3] Seymour Bernstein, unpublished master's thesis, University of Chicago, 1936.

ings in the side to provide for different positions of the camera. The crystal mounting, attached to a divided circle, can be moved by the lever L, which is attached through a sylphon. The cover of D can be removed to permit adjusting the crystal. All openings are closed by brass plugs seated with rubber gaskets. The bending of the sylphon permits the camera to be rotated through about 15°. When further motion is necessary, a different opening in D is used. With three cylinders in which the openings are at different positions, the entire angular position up to 90° can be covered. The lever L is oscillated by means of a pulley driven by an electric motor, and automatically reverses its direction at regular intervals. In practice the crystal oscillated through about 0.5°. The purpose of this oscillation was to eliminate the effect of crystal irregularities.

The constancy of the grating space among the different films was checked by matching x-ray reflections from the film against those from gypsum. With the film used as a crystal a photograph was taken of the fifth order tungsten $L\alpha_1$ line (1.47336A, crystal standard). The film was then replaced by a gypsum crystal and a photograph taken of the tungsten $L\gamma_1$ line (1.09630A, crystal standard). The photographic plate remained in the same position during the two exposures. Fig. 2 shows typical photographs obtained from films of 301, 1100, and 3000 layers, respectively, with an exposure time of 4.5 hours for the film, and 40 minutes for the gypsum. Tube current and voltage were approximately 25 ma and 25 kv, respectively. Photographs were taken from films with 301, 1100, 1100, 1130, 1900, 2990, 3000, and 3000 layers. The 2990-layer film and one of the 3000-layer films failed to give definite lines, but the remaining six films produced good lines. From

TABLE I. *Apparent grating spaces of films with different numbers of layers.*

NUMBER OF LAYERS IN FILM	DISTANCE BETWEEN THE TUNGSTEN $L\gamma_1$ AND FIFTH ORDER $L\alpha_1$ LINES	ANGLE OF REFLECTION OF THE FIFTH ORDER TUNGSTEN $L\alpha_1$ LINE	APPARENT GRATING SPACE OF FILM
301	1.21 mm	4° 12′ 17.7″	50.236A
1100	1.18	4 12 12.6	50.252
1100	1.13	4 12 4.0	50.280
1130	1.22	4 12 19.4	50.230
1900	1.12	4 12 2.3	50.285
3000	1.16	4 12 9.1	50.263

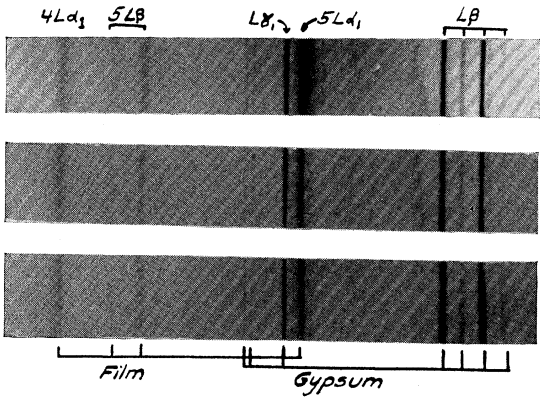


FIG. 2. Tungsten L series spectra from gypsum and films of 301 (upper), 1100 (middle), and 3000 (lower) layers.

the color of the films it was evident that those films failing to produce good spectra had a higher copper content than did the others. To check the effect of the copper, more films were used, some with no copper content and some with as much copper as they would take. A comparison of the spectra showed that the only apparent effect was a change in the spacing in the films.

The distance between the $L\alpha_1$ line from the molecular film and the $L\gamma_1$ line from the crystal on a given photographic plate was measured by a Dershem photoelectric photometer.[4] A graph of the intensity of blackening as a function of the distance along the plate located accurately the position of each line. Since the angle of reflection for the $L\gamma_1$ line was known, the angle of reflection of the $L\alpha_1$ line was thus determined without the use of spectrometer angle readings. The grating space of the film was then computed from Bragg's equation $n\lambda = 2d \sin\theta$ without correction for the index of refraction. Table I shows the distance between the two lines, the corresponding angle of reflection of the fifth order tungsten $L\alpha_1$, line and the apparent grating space of each film.

The results indicate that the spacing is the same for the different films, since there is a maximum difference of but 0.056 percent between the mean apparent value of d and its value for any one film. This difference may be due to the method of building, since, as indicated above, the spacing changes with the amount of copper present in the film.

Photometer curves of the fifth-order tungsten

[4] Elmer Dershem, Rev. Sci. Inst. **3**, 43 (1932).

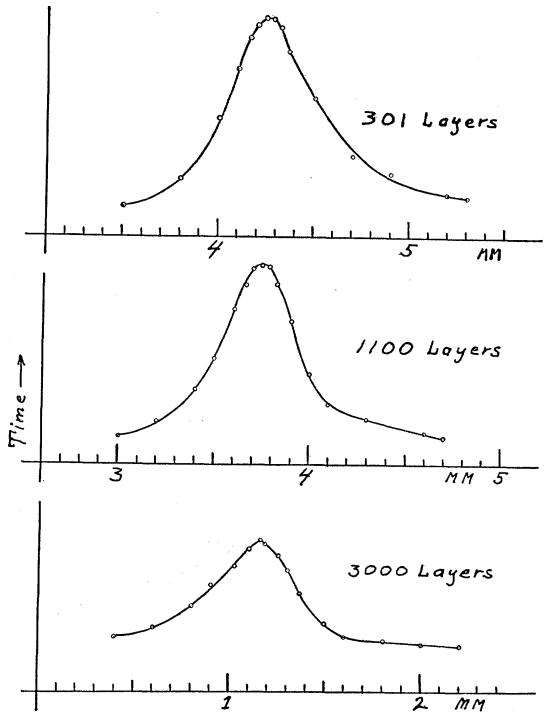


FIG. 3. Photometer curves of the fifth-order $L\alpha_1$ line of tungsten from barium-copper-stearate films.

$L\alpha_1$ line from the 301, 1100, and 3000-layer films are shown in Fig. 3 in which the distance along the photographic plate is plotted as abscissa and the time for a given electrometer deflection as ordinate. These curves show the line to be asymmetrical as diffracted by the films, but their sharpness indicates that the reflecting planes are quite regular and definite. However, curves from the second 1100-layer film and from the 1900-layer film showed small irregularities. With approximately the same exposure conditions the intensities of the lines from the different films were found to be roughly the same. This indicates that the upper layers only are effective in reflecting the x-rays.

The films were built on the optically flat surfaces of glass with a thick portion on the outer parts of each plate and 100 layers in the center. The distance from the surface of the thick part of the film to the surface of the 100-layer part was measured by means of a Michelson interferometer with the 5460.7A line of mercury as the source of light. This method of building the film was to prevent a difference in phase change in the light reflected from the two surfaces of the film. The fringes were very clear and quite straight across each part of the film except at the outer edges, where they were irregular. The thickness of each film was measured several hundred times. Thus it was possible to obtain the apparent thickness to the nearest hundredth of a fringe. With the 3000-layer film there were 25.73 fringes. The accuracy was then approximately 1/26 percent. Such measurements of the 1100-, 1900-, and 3000-layer films gave the spacing of the molecular layers as 24.26A, 24.27A, and 24.23A, respectively. From earlier work[2] it was expected that the heads of the molecules in alternate planes would act as the reflecting planes. Therefore the grating spaces would be twice the above values. In the case of the 3000-layer film, on which the measurements were most reliable because its thickness was greatest, the value of the grating space would be 48.46A. This value is 1.8A, or 3.6 percent less than the spacing found from x-ray measurements given in Table I.

To check some possible sources of error, which might cause the wide discrepancy between the spacing measurements as determined by optical and x-ray methods, the following experiments were tried: (1) X-ray photographs were taken with the film in air and in a vacuum. The spacing was the same for the two conditions. (2) Onto one of the films Mr. Bernstein evaporated a layer of aluminum to eliminate any possible phase-change difference in the reflection of the light from the thick and thin portions of the film in the interferometer measurements. The aluminum film caused no change in the relative positions of the fringes across the boundary lines. (3) The possibility of a phase change error was also eliminated

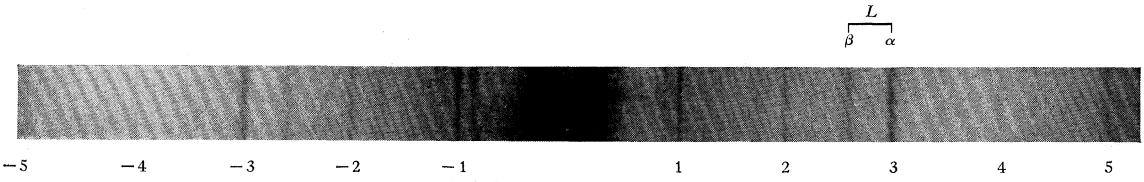


FIG. 4. Five orders of tungsten L-spectra from 1100-layer film (Bernstein).

by computing the spacing for 1900 layers from the difference in the number of fringes for the 1100-layer and the 3000-layer films. This measurement yielded the grating space as 48.36A, a value in fairly good agreement with the direct measurement of the 3000-layer film. (4) Photographs were taken with two films in which all the molecules were oriented in the same direction, i.e., the films were of the "*x*" type as described by Dr. Blodgett.[1] If the molecular layers were deposited one on another in discrete sheets, an x-ray grating space of about 24A, corresponding to the length of a single molecule, would be expected. Actually a grating space of about twice this magnitude was found, just as for the other type of film.

Thus it becomes evident that the optical measurement of the spacing of the molecular layers of these films does not yield the x-ray grating space. In a preliminary report of these measurements[5] an error in identification of a spectral line led to the opposite conclusion, that the optical and x-ray spacings were consistent. The fact that the x-ray spacing has a fixed value, which differs from the increment in thickness of each added double layer would seem to imply that this spacing is due to a crystalline arrangement of the molecules within the film.

In the x-ray determination of the grating space given above it was assumed that the index of refraction of the film was unity. Fig. 4 shows a photograph by Mr. Bernstein of five orders of the L spectrum of tungsten from a 1100-layer film, on each side of the primary beam. From this photograph he has determined the apparent values of the grating space and the index of refraction. The apparent values of d for the first, second, third, fourth, and fifth orders are 49.11A, 50.07A, 50.19A, 50.23A, and 50.30A, respectively. The unit decrement of the index of refraction is 5.1×10^{-6}. The agreement between this more directly measured value of 50.30A for the fifth order and the more precise mean value of 50.26A obtained above by comparison with the position of the $L\gamma_1$ line from gypsum confirms the validity of the method we have used. When the correction of 0.05A for the index of refraction is made, the x-ray measurements yield 50.35A for the true grating space as based on the crystal wavelength standard, or 50.47A as based on the ruled grating standard.[6] The latter value was computed by using Bearden's weighted average of 1.00248 as the ratio between the ruled grating and crystal wave-length values.[7]

It may be noted that the theoretical calculation of the unit decrement from dispersion theory[8] yields but 3.4×10^{-6} for the tungsten L spectrum, a value some 33 percent less than the experimental value. The correction for refraction in the film is in any case a minor one and does not alter the conclusions drawn above.

A final point of interest in the study of the films is that the spacing increases with age. The optical measurements show that in five months the spacing in the 1100-layer film increased by 0.22 percent, and that in the 3000-layer film increased by 0.45 percent. This suggests that the molecules probably reorient and adjust themselves in a more nearly crystalline arrangement. The use of such a film as a crystal for x-ray work thus necessitates completing the experiment within a relatively short time, or aging the film for a time sufficient to permit final orientation of the molecules.

The results of this investigation indicate that (1) most films prepared by this method show definite crystalline arrangement of the molecules with the spacing of the layers the same for all films of the same composition, but some films fail to show any such definite arrangement of the molecules; (2) thin films are as effective as thick ones in diffracting x-rays; (3) the thickness of the film increases with age; (4) the reflecting planes are not provided by the method of building, but are probably due to crystalline arrangement of the molecules in the film.

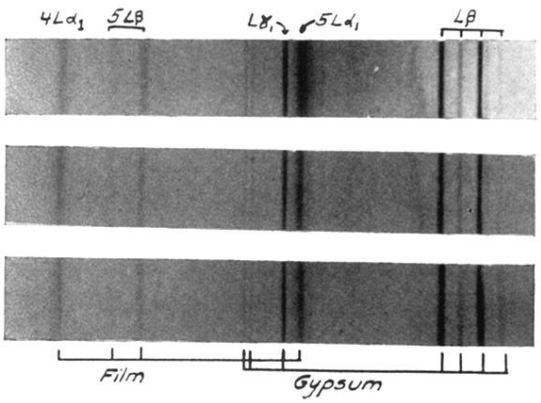
The writer wishes to express his thanks to the following people for their help in completing this experiment: To Professor A. H. Compton for suggesting the problem and guiding the work; to Dr. Katharine B. Blodgett for much time and labor spent in building the films; to Dr. Elmer Dershem and Professor G. S. Monk for valuable help in the mechanical aspects of the problem; and to Mr. Seymour Bernstein for his helpful collaboration.

[5] Clifford Holley, Phys. Rev. **51**, 1000 (1937).

[6] In a preliminary report (Clifford Holley and Seymour Bernstein, Phys. Rev. **52**, 525 (1937)) these values were given as 50.31A and 50.43A, respectively.

[7] J. A. Bearden, Phys. Rev. **48**, 385 (1935).

[8] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment*, p. 496.



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