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## Arrangement of Molecules in a Single Layer and in Multiple Layers

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Electron diffraction studies have been made upon layers of molecules of barium stearate and of stearic acid built upon surfaces by the Langmuir-Blodgett method. Upon clean metal surfaces odd numbers of layers have been built, and investigated by the reflection method; upon thin organic supporting foils even numbers of layers have been built, and investigated by the transmission method. On foils of Resoglaz the molecules are regularly arranged. The hydrocarbon chains of barium stearate molecules form hexagonal arrays with their axes normal to the supporting surface and separated by distances of 4.85Å. Stearic acid molecules form crystals of monoclinic form with  $a=8.27\text{\AA}$ ,  $b=4.96\text{\AA}$ ,  $\beta=70^\circ$ , the  $a$  and  $b$  axes lying in the plane of the supporting surface. In built-up films we previously observed a different polymorphic form of stearic acid; a correction to the data on this earlier structure is given here. On a clean metal surface molecules of the first layer stand with the axes of the hydrocarbon chains normal to the surface and the chains closely packed together laterally but irregularly arranged. The precision of alignment of the

axes normal to the surface is greater for barium stearate than for stearic acid. In layers on top of the first, molecules of barium stearate and of stearic acid are regularly arranged in the way the same molecules are arranged on organic foils. In the case of barium stearate, the arrangement is random about the surface normal, although large single arrays are often formed; in the case of stearic acid, crystals are built with the axes of the hydrocarbon chains approximately in the plane defined by the surface normal and the dipping direction and pointing *upward* from the surface. Two applications or continuations of these experiments are suggested. 1. The methods of the experiments can probably be applied to fundamental studies of boundary lubrication. 2. Interpretable diffraction patterns can be obtained from single layers of molecules which are considerably shorter than stearic acid, and comparable in scattering power with films of adsorbed gas; thus studies of films of adsorbed gas can be carried out as soon as adequate vacuum technique is available.

THE first investigation of a surface film by means of electron diffraction was described in the first comprehensive paper on electron diffraction by Davisson and Germer.<sup>1</sup> In this investigation they determined the arrangement of a single layer of gas atoms (or gas molecules) upon a crystal surface. Since these early experiments the use of low speed electrons in the study of surface structure has been entirely superseded by the use of fast electrons. The technique of experimentation with high speed electrons is vastly easier, and there seems now no likelihood of return to the use of slow electrons as a tool for studying surfaces. There is, however, an unfortunate consequence of this change; it is accompanied by greatly decreased sensitivity to small quantities of superficial material. It seems that with fast electrons one cannot detect the diffraction pattern of a single layer of adsorbed atoms. We are limited to the study of somewhat thicker layers.

It is one of the purposes of this paper to

point out that this decrease of sensitivity, serious as it really is, is not quite so bad as it may have seemed. Although we are still unable, with electrons of wave-length in the neighborhood of 0.07Å, to study the arrangement of a single layer of atoms adsorbed on a metal surface, we can get interpretable patterns from a single layer of long chain organic molecules.

In a recent paper<sup>2</sup> we described the structure of films built from many layers of stearic acid molecules by the Langmuir-Blodgett technique.<sup>3</sup> The methods used in studying these films have now been applied to a single layer of stearic acid molecules, and to a single layer and to multiple layers of barium stearate.<sup>4</sup>

It has been discovered that the structure of the films sometimes varies with  $pH$  of the water,

<sup>2</sup> Germer and Storks, *Proc. Nat. Acad.* **23**, 390-397 (1937).

<sup>3</sup> Blodgett, *J. Am. Chem. Soc.* **57**, 1007-1022 (1935).

<sup>4</sup> We have no intention of implying that the experiments described here constitute the first studies, by means of fast electrons, of arrangements of single layers of organic molecules upon surfaces. Havinga and de Wael [*Rec. Trav. Chim.* **56**, 375-381 (1937)] have carried out such investigations successfully. Finch and Wilman [*Trans. Faraday Soc.* **33**, 337-339 (1937)] also have reported a diffraction pattern which they believe to be that of a single layer of molecules.

<sup>1</sup> Davisson and Germer, *Phys. Rev.* **30**, 705-740 (1927). A more extended account of the surface film studies appeared somewhat later, Germer, *Zeits. f. Physik* **54**, 408-421 (1929).

and with other experimental conditions. That an alteration of structure of *barium stearate* films with *pH* would be observed could have been predicted from the fact that the barium content of these films changes<sup>5</sup> with *pH*. In regard to stearic acid films, we suggested at the conclusion of an earlier paper<sup>2</sup> the possibility of obtaining different polymorphic forms under different conditions; this has now been accomplished.

A detailed investigation over a wide range of experimental conditions seems to be called for, but this has not yet been made. The experiments described here are concerned chiefly with the extension of the experimental method from the study of films made up of many layers of molecules to films composed of one layer only. Justification for publishing our experiments at this time rests upon the interesting nature of some of the conclusions, upon a possible application of the methods to the study of lubrication, and upon the probability that considerable time will elapse before comprehensive results are available.

#### PREPARATION OF FILMS

A monomolecular film of stearic acid is spread upon commercial distilled water, and compressed in the usual fashion. Layers of molecules are transferred to the surface of a block by dipping the block one or more times through the film on the water surface. Built-up films of stearic acid are formed from water which has been made acid by the addition of HCl. Barium stearate built-up films are obtained from water to which  $\text{Ba Cl}_2$  has been added to make a  $7 \times 10^{-5}$  molar solution, and which has been adjusted to suitable *pH* by the addition of  $\text{KHCO}_3$ .

The block upon which the layers of molecules are deposited has a highly polished chromium plated surface, about 5 mm wide. Immediately before dipping this block is cleaned by polishing on levigated alumina to remove the last layer of greasy organic compounds, according to a technique very similar to that described by Hardy and Nottage.<sup>6</sup> The block is always wetted by water on its first immersion, and the first layer of molecules is deposited upon it as it is withdrawn from the water.<sup>3</sup> Upon each subsequent dip two layers of molecules are deposited. Thus any

odd number of layers of molecules can be built upon the chromium surface, and all of the reflection experiments reported here have been made upon odd numbers of layers.

The reflection experiments have been supplemented by transmission experiments. For these, layers of molecules are prepared upon thin foils of Resoglaz by dipping through monomolecular layers upon water surfaces.<sup>7</sup> The Resoglaz foil is not wetted as it first passes into the water, and two layers of molecules are deposited upon its front surface on each dip, including the first. Thus any even number of layers of molecules can be built upon the Resoglaz, and the transmission experiments reported here have been made upon even numbers of layers.

One must consider whether or not layers of molecules are built upon the rear surface of a Resoglaz foil at the same time they are being built upon the front. The knife edges, across which the foil lies, support a large drop of water at the rear. Thus successive dips do not add successive layers on this side of the foil, although a single layer may be built upon the rear on the first dip. After the last removal of the knife edge from the water the adhering drop is always removed by blotting paper. It seems highly doubtful that a second layer can be deposited upon the rear surface at this time. A foil dipped once through a barium stearate layer on water, or once through a stearic acid layer, sometimes shows a diffraction pattern characteristic of a single array of molecules (Figs. 2 and 10, respectively); this would be a rare occurrence if two layers had been deposited upon the rear as well as upon the front. None of the conclusions reached in this paper would be altered, however, if each diffraction pattern made by the transmission method were due to one or two layers of molecules on the rear of the foil as well as to the layers upon the front.

#### BARIUM STEARATE MOLECULES IN A SINGLE LAYER AND IN MULTIPLE LAYERS

##### One layer of molecules

The diffraction pattern at the left of Fig. 1 was produced by a single layer of barium stearate

<sup>5</sup> Langmuir and Schaefer, *J. Am. Chem. Soc.* **58**, 284 (1936).

<sup>6</sup> Hardy and Nottage, Lubrication Research Technical Paper No. 1, H. M. Stationery Office.

<sup>7</sup> A photograph of the foil support used in these experiments appears as Fig. 4 in reference 2, and also as Fig. 1 in a paper by Germer, *J. App. Phys.*, **9**, 143 (1938). Resoglaz is the trade name of a polystyrene resin.

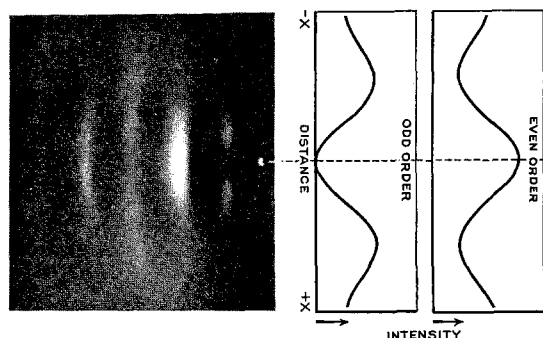


FIG. 1. Electron diffraction pattern from a single layer of barium stearate molecules on a chromium surface. ( $\lambda=0.070\text{\AA}$ .) The curves represent intensities along the diffuse vertical bands, calculated on the basis of some simplifying assumptions.

molecules upon a block of chromium. Separations of the diffuse vertical bands of this figure correspond to a spacing of  $2.50\text{\AA}$  normal to the supporting block. Observation of this spacing seems conclusive proof that the bands are due to planar hydrocarbon chains standing approximately normal to the support.<sup>8</sup>

There are no well-defined diffraction features upon the diffuse bands of Fig. 1. Their absence suggests that the molecules are not built into well-defined crystals. Diffraction spots from crystals might, however, be smeared out beyond recognition if, for the various crystals, the axes which are approximately normal to the surface are not strictly so but are distributed over small angles about the direction of the normal. That the axes of the hydrocarbon chains, and of the hypothetical crystals into which they might be built, do really deviate appreciably from parallelism with the surface normal is proved by the slight curvature of the bands of Fig. 1; if the axes were strictly parallel and normal to the support the diffuse bands would be sensibly straight. From the shapes of the bands we have estimated rather crudely that the axes of most of the hydrocarbon chains deviate from paral-

lelism with the surface normal by less than about five degrees. Distribution of the axes of various crystals over such angles would result in broadening diffraction spots by about 2 mm on the first-order band, 4 mm on the second-order band, etc. This would probably cause all diffraction spots to escape observation.

Although from the pattern of Fig. 1 we cannot determine whether or not the barium stearate molecules in a single layer are formed into well defined crystals, evidence will be presented later which suggests strongly that regular arrangements are not formed. It is thus worth while to calculate the diffraction pattern to be expected from unrelated planar hydrocarbon chains, each standing with its axis normal to the surface but with the planes of the chains lying in randomly distributed azimuths about the surface normal, and to compare this calculated pattern with Fig. 1.

To describe the diffraction pattern we adopt Cartesian coordinates on the photographic plate, with the origin at the primary beam position and the  $x$  axis parallel to the specimen surface. Other quantities are defined as follows:

- $\lambda$ =electron wave-length,
- $L$ =distance from specimen to photographic plate,
- $s$ =separation between alternate carbon atoms in the zigzag hydrocarbon chain,
- $\varphi$ =angle between the line joining two adjacent carbon atoms and the axis of the chain,
- $\theta$ =inclination of the plane of a hydrocarbon chain to a plane normal to the primary beam.

The simplifying assumption is made that each carbon atom of a chain scatters electron waves equally, that there is, in other words, no shielding of atoms near the surface of the metal by those further removed. It is then easy to show that the intensity of electron scattering from an entire chain of  $2N$  carbon atoms to any point  $(x, y)$  on the plate is greater than the scattering from a single carbon atom to that point by a factor proportional to

$$\frac{\sin^2 NBy}{\sin^2 By} \cos^2 \left\{ \frac{B}{2}(y+x \tan \varphi \cos \theta) \right\}, \quad (1)$$

where  $B = \pi s / L\lambda$ . Since it is assumed that various chains are unrelated, except in the common direction of their axes, the intensity of scattering from many chains is obtained by adding the

<sup>8</sup> The pattern of Fig. 1 resembles one which we previously obtained from the saturated glyceride, tristearin. From it we concluded [J. Chem. Phys. **5**, 131-134 (1937)] that the hydrocarbon chains of this glyceride orient themselves with their axes normal to a supporting metal surface. Finch and Fordham [Chem. and Ind. **56**, 632-639 (1937)] have recently stated that glycerides orient themselves upon metal surfaces with the axes of the chains inclined. Our experiments indicate (J. Chem. Phys., reference 8) that this may be, and probably is, true for unsaturated glycerides. It is not, however, true for tristearin, and is probably not true for other saturated glycerides.

intensities due to the separate chains. This total intensity, for hydrocarbon chains the planes of which lie randomly distributed in azimuth about the surface normal, is proportional to the quantity obtained by multiplying (1) by  $d\theta$  and integrating with respect to  $\theta$  from 0 to  $\pi$ . The total intensity<sup>9</sup> is proportional to

$$\frac{\sin^2 NBy}{\sin^2 By} \{1 + J_0(Bx \tan \varphi) \cos By\}. \quad (2)$$

The principal maxima of the factor  $\sin^2 NBy / \sin^2 By$  occur at those values of  $y$  for which  $sy/L\lambda = 1, 2, 3$ , etc.; at values of  $y$  considerably removed from these the factor is negligibly small. These values of  $y$  correspond respectively to the diffuse bands, and from the separation between adjacent bands,  $D = 11$  mm, one calculates  $s = 2.50\text{\AA}$  ( $L\lambda = 2.73 \times 10^{-6}$  mm<sup>2</sup>, as determined by calibration against a foil of metallic silver. The electron wave-length is  $0.070\text{\AA}$  in all of the experiments described in this paper).

Along a diffuse band expression (2) is proportional to

$$1 \pm J_0(Bx \tan \varphi), \quad (3)$$

the plus sign applying to bands of even order and the minus sign to bands of odd order. At the right-hand side of Fig. 1 are plotted intensity values calculated from (3), vertical distances representing positions along the bands and horizontal distances values of (3) in arbitrary units. In calculating these values  $B = \pi s / L\lambda = \pi(2.50 \times 10^{-7}) / (2.73 \times 10^{-6})$  mm<sup>-1</sup> =  $0.288$  mm<sup>-1</sup>, and  $\tan \varphi$  is assumed equal to  $1/\sqrt{2}$  which is its value in the carbon chains in the diamond lattice.

The calculated curves give intensity distributions resembling those of the diffuse bands, but the most intense parts of the bands of odd order are definitely nearer to the horizontal center line than are the maxima of the corresponding curve. In the calculated curves a number of factors have been neglected, including variation with direction of intensity of scattering from each atom and effects produced by waviness of the polished metal surface; but it seems to us that these cannot

account for the discrepancies between theory and observation. Although fair agreement would be obtained if we assumed  $\tan \varphi$  to be about 1.3 instead of  $1/\sqrt{2}$ , such an assumption is entirely untenable. We believe that the discrepancies must be attributed to the fact that the lateral spacings between hydrocarbon chains are not entirely random as assumed in the calculation. Packing of the chains closely together would result in diffuse spots located on the bands. Mean lateral spacing of the hydrocarbon chains of 5A would correspond to diffuse spots at a distance of  $L\lambda/5 \times 10^{-7} = 5.5$  mm from the center line. Such spots are clearly observable on the first-order band; on the third-order band they can account for the fact that the intensity maxima are nearer the center line than the simple theory indicates.

Considerations are presented below (at the end of the section "Three layers of molecules"), which indicate that molecules of a single layer have no regularity of lateral arrangement. On the basis of this evidence and the above calculation, we conclude that the hydrocarbon chains of a single layer of barium stearate molecules on a chromium surface are closely packed together but irregularly arranged, with the axes of the chains normal to the surface within a tolerance angle of a few degrees.

### Two layers of molecules

In Fig. 2 is reproduced a diffraction pattern from *two layers of molecules*, obtained by the transmission method. The regular spacing of the hydrocarbon chains of both layers of molecules, which one deduces from this pattern, is in striking contrast to the closely packed but irregular arrangement which accounts for the pattern of a single layer upon chromium. One naturally wonders whether the molecules of the first layer were arranged immediately upon deposition or whether they acquired their arrangement only when the second layer was added. The former seems much more likely, although our experiments offer no direct proof. Such proof is, however, apparently supplied by the experiments of Havinga and de Wael<sup>4</sup> who have obtained an electron diffraction pattern from a single layer of barium stearate molecules deposited upon nitrocellulose by a modification of the Blodgett

<sup>9</sup> The evaluation of the integral was given to us by Dr. S. A. Schelkunoff. A calculation similar to that just carried out here has been published by Murison, Phil. Mag. 17, 201-225 (1934). It is easy to show that the elaborate expression which he obtains is equivalent to (2).

method. The pattern which they obtain from a single layer resembles that of Fig. 2, and suggests strongly that the first layer of molecules on Resoglaz is arranged before the second is added.

The pattern of Fig. 2 seems to indicate the arrangement of barium stearate molecules in simple crystals having hexagonal symmetry. The smallest separation between diffraction spots of this figure is  $R_0 = 6.50 \pm 0.10$  mm, which corresponds to a unit cell in hexagonal coordinates with  $a = b = 2L\lambda/R_0(3)^{1/2} = 4.85\text{\AA}$ . The cross-sectional area of this cell normal to the  $c$  axis is  $a^2(3)^{1/2}/2 = 20.4\text{\AA}^2$ . Since this value is in good agreement with the known cross section of a single hydrocarbon chain,<sup>10</sup> one is tempted to conclude that the barium stearate molecules form a hexagonal crystal with its  $c$  axis parallel to the axes of the chains and with the cross-sectional area of each unit cell containing one chain only. In a true hexagonal crystal such an arrangement is, however, impossible; the arrangement of *planar* chains to give a diffraction pattern with hexagonal symmetry cannot be accomplished in a structure in which the cross section of the unit cell contains one chain only. We infer that although the axes of the chains intersect the corner points of an extended two-dimensional hexagonal net, the planes of the individual chains are randomly distributed in azimuth about the direction of the normal to the supporting foil. If the distribution is not entirely random, at least the regularities are so slight that the molecules do not build up unit cells which give rise to diffraction spots sufficiently clear to be observed. The diffuseness of the spots of Fig. 2 suggests that each of them may, perhaps, be made up of a number of unresolved spots occurring close together.

The pattern of Fig. 2 was selected for reproduction here because most of it arises from a single hexagonal array of molecules. Some of the patterns which we have obtained from two layers of molecules are obviously composite patterns arising from two or more hexagonal array rotated with respect to each other about the normal to the film. These are less well adapted to exhibit clearly the symmetry of the arrangement.

### Three layers of molecules

The pattern of Fig. 3 was produced by *three layers* of barium stearate molecules. This pattern shows diffuse vertical bands like those of Fig. 1, but in addition there are well-defined features which are not produced by a single layer. It is evident that, in three layers as in two, there occur marked regularities in lateral spacings between molecules.

There is also another difference between Fig. 1 and Fig. 3; the diffuse bands obtained from three layers of molecules are sensibly straight, whereas those from a single layer are slightly curved. One concludes that in the second and third layers the axes of the hydrocarbon chains are strictly normal to the supporting surface.

The horizontal features of Fig. 3 are so diffuse that precise measurements of distances from the center line cannot be obtained. The best estimates of these distances which we have been able to make are given in the first two columns of Table I. One naturally postulates hexagonal arrays of hydrocarbon chains like that which accounts for the pattern of Fig. 2, with, however, many different arrays randomly oriented with respect to the surface normal. Such an arrangement would produce lines at distances from the center line given by  $R = 6.5(H)^{1/2}\text{mm}$  where  $H = m^2 + mn + n^2 = 1, 3, 4, 7, 9, 12, 13, \dots$ ,  $m$  and  $n$  representing any whole numbers. (6.5 mm represents here the smallest spacing between diffraction spots in Fig. 2). Calculated values of  $R$  in the fourth column of Table I are in fairly good agreement with observed values, with the single exception of the extra observed spacing of 5.3 mm.

One might guess that the diffuse spots occurring at 5.3 mm have the same origin as those observed in Fig. 1 at about the same locations, that they are due to the first layer of molecules which are closely packed but irregularly arranged. The spots in Fig. 3 are, however, much better defined than those in Fig. 1. Furthermore, in a diffraction pattern which we have obtained from five layers of barium stearate molecules, all of the features are sharper and clearer than in Fig. 3; the "extra" spots are also stronger, and are as clear and sharp as any of the others. These observations have led us to the belief that the extra spots from three and from five layers of molecules may have a

<sup>10</sup> See, for example, Adam, *The Physics and Chemistry of Surfaces*, p. 50.

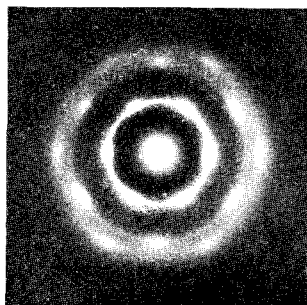


FIG. 2. Diffraction pattern from two layers of barium stearate molecules on a Resoglaz supporting foil.

different origin; they may be due to the breaking up of each of the spots at 6.5 mm into two components. This phenomenon has been observed in transmission patterns, for example in Fig. 4. If this interpretation is correct it proves that in three layers of molecules the planes of the chains have some regularity of arrangement, so that ill-defined true crystals are formed which have hexagonal symmetry.

It seems to us probable that the regularities which account for the features of Table I are confined to the two top layers of molecules, the layer next to the metal having the closely packed but irregular arrangement characteristic of a single layer by itself. Although there is no experimental evidence for this in the case of layers of barium stearate, tests on stearic acid layers described below do indicate rather clearly that this is the situation in layers of the acid.

The thus far unverified conclusion that barium stearate molecules in a *single* layer on chromium have no regularity of lateral arrangement can be reviewed at this time. The differences between Figs. 1 and 3 seem to us to offer convincing evidence in favor of this conclusion. If, in the first layer, the molecules were arranged in some regular fashion, we would expect that two additional layers would continue the regularity of the first; the pattern from three layers would then exhibit curved diffraction bands. That the bands from three layers are sensibly straight proves that any possible regularity which might have existed in the first layer is not continued in the second and third, and suggests very strongly that there was no regularity in the first.

#### Four layers of molecules

Four layers of barium stearate molecules

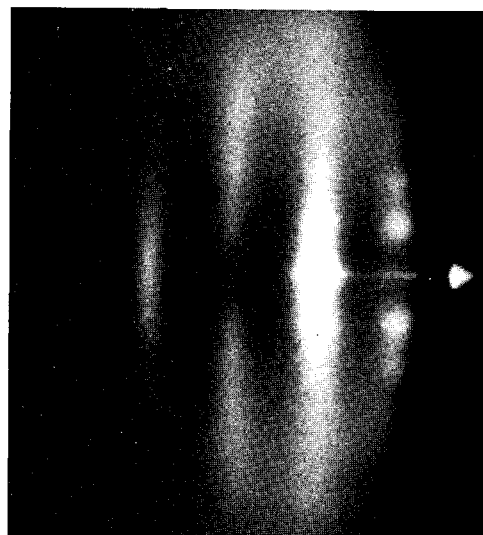


FIG. 3. Pattern from three layers of barium stearate molecules on a metal surface.

sometimes give a diffraction pattern like that of Fig. 2, but often a much more complex pattern is produced. An example of such a pattern appears as Fig. 4.

Most of the features of Fig. 4 belong to a single array which has hexagonal symmetry; the main part of the pattern appears to be that of a single crystal. (This pattern was chosen for reproduction from a number of others each of which was obviously due to two or more crystals). The strongest features correspond to the hexagonal array of diffuse spots of Fig. 2, and determine the same arrangement of molecular axes. The elaborate details of Fig. 4 appear to prove that the planes of the chains of the various molecules are related to each other in such a fashion that a true crystal is built up having a large unit cell. We have, as yet, been unable to determine the

TABLE I.

DISTANCES OF STREAKS FROM CENTER LINE IN FIG. 3		<i>H</i>	CALCULATED DISTANCES $6.5(H)^{\frac{1}{2}}$
FIRST-ORDER BAND	SECOND-ORDER BAND		
5.3 mm			
6.7		1	6.5 mm
11.8	6.5 mm	3	11.3
13.2	11.4	4	13.0
17.5		7	17.2
		9	19.5

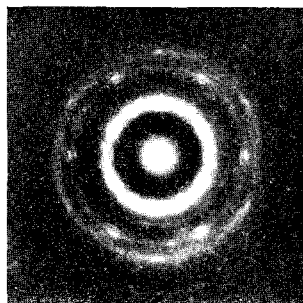


FIG. 4. Pattern from four layers of barium stearate molecules on a Resoglaz foil.

arrangement of the planes of the carbon chains or even the size of the cell. The complexity of the pattern of Fig. 4 makes it obvious that any attempt to draw significant conclusions from "extra" features in the pattern from three layers of molecules (Fig. 3), or from five layers, was doomed to failure.

One notes that the diffraction pattern of Fig. 4 appears to be rotated with respect to that of Fig. 2 through an angle of about  $30^\circ$ . This is fortuitous and is consistent with the observation that the orientations of hexagonal patterns from built-up films of barium stearate molecules are unrelated to direction of dipping when the films were formed. This fact has already been implied in the statement that a transmission pattern is often obviously due to two or more hexagonal arrays of molecules rotated with respect to each other about the surface normal.

#### Multiple layers of molecules

All diffraction patterns which we have obtained by the reflection method have been examined for reflections from crystal planes parallel to the specimen surface. In no case are the horizontal diffraction lines resolved into sharp spots which are prominent. On different plates a total of 34 spots can, however, be seen more or less clearly. As one cannot assign indices to any of these unambiguously a reliable value of the  $c$  spacing cannot be obtained. We are able to show that this spacing is of the order of  $50\text{\AA}$ , but the precision of this value is very low. The reason for this uncertainty becomes quite clear when we consider the very slight penetrating power of the electron waves; in the following section of this paper we have shown that in the

diffraction pattern from three layers of stearic acid molecules the scattering is predominantly from the two top layers. Thus most of the scattering is always from a surface layer which is only one unit cell thick, and good resolution of different orders of this spacing is never obtained.

Although the variation of structure with  $pH$  which was mentioned earlier has not been investigated extensively, some simple observations have been made. All of the barium stearate patterns reproduced here were made at  $pH$  in the neighborhood of 7. At high  $pH$ , around 10, large single arrays of molecules have not been observed; transmission patterns consist of continuous rings, instead of spots as in the patterns of Figs. 2 and 4. The radii of the rings seem to be the same as radii of spots in Fig. 4, but relative intensities are greatly altered.

#### STEARIC ACID MOLECULES IN A SINGLE LAYER AND IN MULTIPLE LAYERS

##### Reflection experiments

*One layer of molecules.*—The pattern of Fig. 5 was produced by a single layer of stearic acid molecules on a chromium surface. Adjacent diffuse bands of this figure have a separation of 11 mm, as do the bands of Fig. 1. The two patterns have other similarities also; bands of odd order are weak along the center line and bands of even order strong; there are diffuse spots on the first order band which correspond to mean lateral spacings of about  $5\text{\AA}$ . The diffuse bands of Fig. 5 are, however, markedly more curved than those of Fig. 1. We have obtained many diffraction patterns from single layers of barium stearate and from single layers of stearic acid, and have established the fact that these similarities and this difference are characteristic of the molecules of the layer. In both cases, barium stearate and stearic acid, the diffraction pattern from a single layer is the same for different directions of the primary beam relative to the dipping direction.

After the consideration which has already been given to Fig. 1 we are able to interpret the pattern of Fig. 5 readily. We conclude that stearic acid molecules are arranged in a single layer upon chromium with the axes of the hydrocarbon chains approximately normal to the



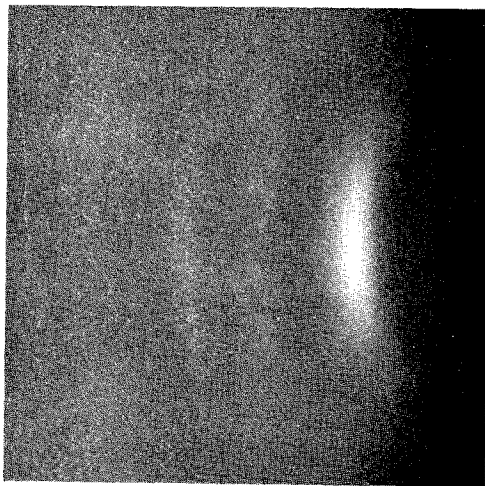


FIG. 5. Pattern from a single layer of stearic acid molecules on a metal surface.

surface. The precision of this alignment is considerably less for stearic acid than for barium stearate; we estimate from the curvatures of the bands of Fig. 5 that the axes of many of the molecules of stearic acid deviate from parallelism with the surface normal by as much as  $10^\circ$ . The molecules of stearic acid are closely packed together laterally but irregularly arranged. In this connection it is interesting to compare the approximate value of  $5\text{\AA}$  for the mean separation of hydrocarbon chains in one layer of stearic acid, and in one layer of barium stearate, with  $4.85\text{\AA}$  which was discovered to be the distance between chains in the regular arrangement of barium stearate molecules in two layers on Resoglaz.

*Three layers of molecules.*—The diffraction pattern of Fig. 6 was obtained from three layers of stearic acid molecules on a chromium block, with the primary electron beam normal to the dipping direction and the block mounted in the camera just as it was held during dipping. The dipping direction is thus downward as Fig. 6 is reproduced here.

Adjacent diffuse bands of this figure are separated by  $11\text{ mm}$  and correspond to a repeated spacing of  $2.50\text{\AA}$  along a direction normal to the bands. We conclude that the hydrocarbon chains of the stearic acid molecules of the second and third layers stand with their axes normal to the bands and thus inclined *upward* from the



FIG. 6. Pattern from three layers of stearic acid molecules on a metal surface. Primary beam normal to direction of dipping, and dipping direction *downward* as the pattern is reproduced here.

metal surface. The sharp features upon the bands prove that the molecules are arranged in some regular fashion.

One can see very weakly traces of diffuse *vertical* bands of the second and fourth orders, produced probably by the first layer of molecules standing directly on the metal surface. The relative weakness of these vertical bands proves that the electrons are scattered chiefly from the two top layers of molecules, indicating that the penetrating power of the electrons is very slight at a small glancing angle. The vertical bands are not present in diffraction patterns obtained from many layers of molecules; for example, the pattern of Fig. 7 from fifteen layers of stearic acid molecules shows no trace of vertical bands.

*Five layers of molecules.*—A diffraction pattern from five layers of stearic acid molecules is somewhat sharper and clearer than that from three layers, and better measurements can be made upon it. Measurements upon this pattern, which is not reproduced here, are contained in Table II. In the second and fourth columns are given distances of the sharp horizontal diffraction lines from the center line, those above the center line in the second column and those below in the fourth. Estimated intensities of the lines are written down also. In the first column are indicated the orders of the inclined diffuse bands upon which the diffraction lines appear.



FIG. 7. Pattern from many layers of stearic acid molecules. Dipping direction downward and normal to the primary beam, as in Fig. 6.

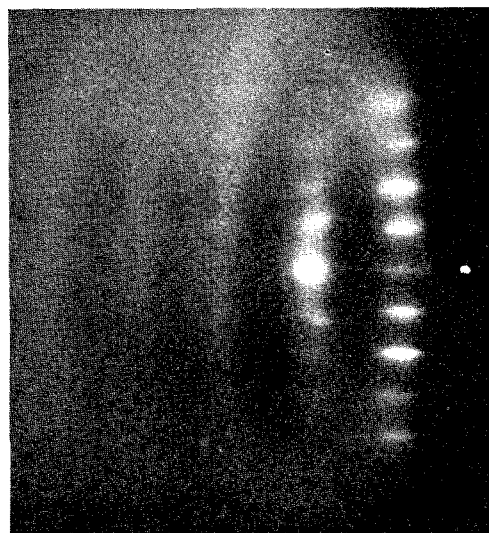


FIG. 8. Pattern from many layers of stearic acid molecules. Primary beam *parallel* to direction of dipping.

In Table II are tabulated distances from the center line of 23 diffraction features. Of these, 15 appear clearly to represent different measurements of the first six orders of a single spacing; these orders are tabulated in the last column. To obtain the best possible value of the fundamental spacing, of which the measured distances represent various orders, we have plotted these spacings against their respective orders. The

TABLE II. *Five layers of stearic acid molecules. Specimen in camera with dipping direction downward, and normal to primary electron beam.*

DIFFUSE BANDS	HORIZONTAL DIFFRACTION LINES				h
	ABOVE CENTER LINE		BELOW CENTER LINE		
	DISTANCES FROM CENTER LINE	ESTIMATED INTENSITIES	DISTANCES FROM CENTER LINE	ESTIMATED INTENSITIES	
Zero Order			13.0 mm 19.7	2 1	4 6
First Order	3.4 mm	5	3.4	10	1
	6.3	4	6.3	3	
	9.9	7	9.9	8	3
	11.3	2			
	14.3	3	14.3	1	
	16.5	2	16.5	4	5
Second Order	6.5	9	6.5	2	2
	11.0	1			
	13.5	4	13.5	1	4
	17.3	1			
	20.2	2			
Third Order	3.5	2	3.5	1	1
	16.8	2			5

line drawn through the origin which fits the experimental points as well as possible has a slope corresponding to a fundamental spacing of 3.30 mm. The fit would be slightly poorer if we chose 3.29 mm or 3.32 mm, although we do not imply precision of such a high order for the experimental data.

*Electron beam parallel to dipping direction. Seven layers of molecules.*—In order to proceed with analysis of the stearic acid structure it is convenient to measure also a diffraction pattern obtained with the primary electron beam parallel to the dipping direction. Such a pattern, from seven layers of molecules, is reproduced in Fig. 8.

Distances of the horizontal features of this pattern from the center line are written down in the second column of Table III, and estimated intensities in the third column. Most of the distances are approximately multiples of 5.5 mm. The best value of this fundamental distance has been obtained from a plot of the measured values of the second column against the integers of the fourth. The data are best fitted by a line corresponding to 5.50 mm, which is in better agreement with the available measurements than 5.45 mm or than 5.55 mm.

*Deductions from the reflection experiments.*—The diffuse bands of Fig. 8 are vertical, parallel to the specimen surface. This observation, to-

gether with the fact that the bands obtained with the primary beam normal to the dipping direction are inclined to the surface normal, proves that the stearic acid molecules stand with the axes of the hydrocarbon chains inclined to the supporting surface and approximately parallel to the dipping plane, which is defined by the dipping direction and the surface normal. The diffuse bands of Fig. 8 have separations of about 11 mm.

The data of Tables II and III suggest that the molecules are built into crystals of monoclinic form with

$$a = (L\lambda/3.30) \text{ mm} = 8.27\text{\AA},$$

$$b = (L\lambda/5.50) \text{ mm} = 4.96\text{\AA},$$

the crystals being oriented precisely with their  $a$  and  $b$  axes parallel to the supporting surface and the  $b$  axes showing strong preference for the direction normal to the dipping plane. The logical procedure by which these ideas are reached is described in detail in an earlier paper.<sup>2</sup> Reference to this is also necessary to justify other deductions which are made below.

In order to test the suggested values of  $a$  and  $b$ , as well as the preferred crystal orientation, we have written down measured distances of Tables II and III in the first four columns of Table IV, for the purpose of comparing them with values in the last column calculated from the relation  $R = [(3.30h)^2 + (5.50k)^2]^{1/2}$ . In this expression  $h$  and  $k$  are any integers, and all values of  $R$  are included in Table IV up to  $R = 27.5$  mm. It is found that the measured distances are in excellent agreement with the calculated values. In

TABLE III. Seven layers of stearic acid molecules (Fig. 8). Specimen in camera with primary electron beam parallel to dipping direction.

DIFFUSE BANDS	HORIZONTAL DIFFRACTION LINES ABOVE AND BELOW CENTER LINE		$k$
	DISTANCES FROM CENTER LINE	ESTIMATED INTENSITIES	
First Order	5.5 mm	6	1
	6.75	2	
	10.85	7	2
	16.6	3	3
	21.75	3	4
	22.9	2	
Second Order	27.8	1	5
	6.65	3	
	11.15	2	2
	16.5	1	3

some cases either of two, or even three, pairs of values of  $h$  and  $k$  can be assigned to a measured distance; the correct assignments are, however, obvious from the crystalline orientation which the data establish.

The reciprocal lattice of each stearic acid crystal is made up of points occurring close together along parallel lines which are normal to the supporting surface. Intersections of these lines with the surface are indicated in Fig. 9, reciprocal lattice dimensions in  $\text{mm}^{-1}$  being multiplied by  $L\lambda$  to reduce them to mm. Each point in Fig. 9 represents a section of a diffraction line which is actually observed and written down in Table IV. Points along the vertical line through the center represent reflections the Miller indices of which are of the form  $(h \ 0 \ l)$  and points along the horizontal line through the center have Miller indices  $(0 \ k \ l)$ . Points indicated by open circles are observed when the primary beam is normal

TABLE IV. Measured separations of horizontal lines from center line.

BEAM NORMAL TO DIPPING DIRECTION		BEAM PARALLEL TO DIPPING DIRECTION		$h$	$k$	CALCULATED SEPARATIONS
ODD ORDERED BANDS	EVEN ORDERED BANDS	FIRST ORDER BAND	SECOND ORDER BAND			
3.4 mm } 3.5 }				1	0	3.3 mm
		5.5 mm		0	1	5.5
6.3		6.75	6.65 mm	1	1	6.4
	6.5 mm			2	0	6.6
				2	1	8.6
9.9				3	0	9.9
		10.85	11.15	0	2	11.0
11.3	11.0			3	1	11.3
				1	2	11.5
				2	2	12.8
	13.0 } 13.5 }			4	0	13.2
14.3				4	1	14.3
				3	2	14.8
		16.6	16.5	0	3	16.5
16.5 } 16.8 }				5	0	16.5
				1	3	16.8
				4	2	17.2
	17.3			5	1	17.4
				2	3	17.8
				3	3	19.2
	19.7			6	0	19.8
				5	2	19.8
	20.2			6	1	20.5
				4	3	21.1
		21.75		0	4	22.0
				1	4	22.2
				6	2	22.7
		22.9		2	4	23.0
				7	0	23.1
				5	3	23.3
				7	1	23.7
				3	4	24.1
				7	2	25.6
				4	4	25.7
				6	3	25.8
				8	0	26.4
				8	1	27.0
				5	4	27.5
		27.8		0	5	27.5

Measurements upon this pattern give  $\beta = 70^\circ$

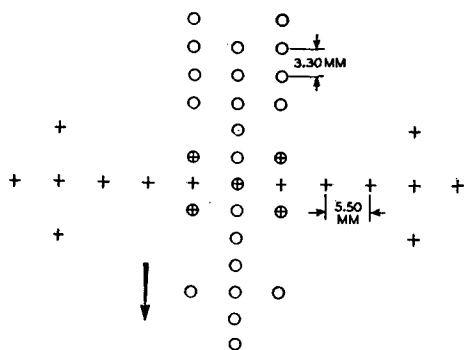


FIG. 9. Cross section of the stearic acid reciprocal lattice, showing only points corresponding to features observed in the reflection experiments. (All distances are multiplied by  $L\lambda$  to reduce to mm.)

to the dipping direction; points indicated by crosses are observed with the beam parallel to the dipping direction. The dipping direction is indicated by the heavy arrow.

The monoclinic angle,  $\beta$ , can be determined by direct measurement upon the diffraction pattern which gave the data of Table II. One measures the inclination to the surface normal of a line through the centers of diffraction streaks of the form  $(h\ 0\ l)$ . We have obtained  $\beta = 70^\circ$  in this way.

The fact that diffraction features of appreciable intensity occur approximately along the diffuse bands is equivalent to the statement that reflections occur only for values of  $l$  in the neighborhood of  $l = n(c/s)$ , where  $c$  is the length of the edge of the unit cell parallel to the  $c$  axis and  $n$  an integer representing the order of a diffuse band.<sup>2</sup> An interesting observation, which is indicated clearly in Table IV, is that of all reflections of the form  $(h\ 0\ l)$  only those with  $h$  odd occur on diffuse bands of odd order and only those with  $h$  even on diffuse bands of even order. In other words, for reflections of the form  $(h\ 0\ l)$   $h$  and  $n$  are either both odd or both even. We have not yet succeeded in interpreting this observation in terms of crystal symmetry.

**Measurement of the  $c$  spacing.**—On some diffraction patterns are observed spots corresponding to  $(0\ 0\ l)$  reflections for various orders of  $l$ . Although we have found and measured 97 such reflections, none are well defined and in no case can we determine value of  $l$  unambiguously. The spacing which we determine from these reflections is of the order of 25Å, but the pre-

cision of this value is very low. We presume that the reflections which are discovered are even orders only of the spacing  $c \sin \beta \sim 45\text{Å}$ . That even orders only appear may be due to lack of great difference between the irregularities introduced at carboxyl and at paraffin ends of the molecules. We reported a correspondingly small spacing (20Å) in our earlier observations on alpha-stearic acid.<sup>2</sup> It is interesting to note that barium stearate built-up layers yield a  $c$  spacing of the order of 50Å; in this case the irregularities introduced by the presence of barium atoms are great enough to cause odd as well as even orders to be found.

### Transmission experiments

A diffraction pattern from two layers of stearic acid molecules on a Resoglaz foil is reproduced in Fig. 10, and a pattern from six layers in Fig. 11. The diffuse rings which are prominent in the former are due to the supporting Resoglaz foil; the arrays of sharp spots are produced by the layers of stearic acid molecules. Each spot pattern is predominantly that of a single crystal.

Measurements of the separations of spots along the vertical and horizontal directions give, respectively, 3.40 mm and 5.47 mm in Fig. 10, and 3.34 mm and 5.50 mm in Fig. 11. Both sets of values agree well with 3.30 mm and 5.50 mm obtained from the reflection experiments. Thus we conclude that stearic acid molecules built upon a Resoglaz foil form crystals which have the same structure as those formed by building upon a chromium surface. From Fig. 10 we are quite certain that even molecules of the first layer upon Resoglaz fit into the structure of the crystal; Resoglaz seems to have no influence upon the arrangement of the first layer of molecules built directly upon it, as does a metal surface. A similar observation has already been recorded for barium stearate molecules upon metal and upon Resoglaz. In both cases the paraffin ends of the molecules are in contact with an organic foil, whereas the carboxyl or barium ends are in contact with a metal.

### Some general observations

**Boundary lubrication.**—The striking difference between the irregular arrangement of stearic acid molecules in the first layer upon a chromium

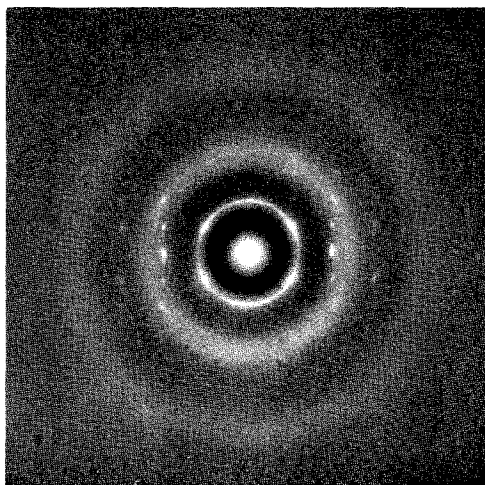


FIG. 10. Pattern from two layers of stearic acid molecules on a Resoglaz supporting foil. Dipping direction downward.

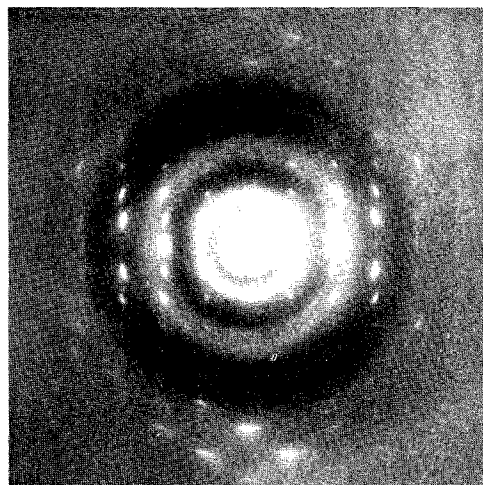


FIG. 11. Pattern from six layers of stearic acid molecules. Dipping direction downward.

surface and the regular structure in subsequent layers proves that the influence of the metal surface does not extend appreciably beyond the first layer. It seemed to us altogether probable that the same difference between the first and subsequent layers would be found if a different metal were substituted for chromium. This we have confirmed by experiments upon a highly polished steel gauge block made by Carl Zeiss; the diffraction patterns from one layer and from seven layers of stearic acid molecules upon this block are sensibly the same as those of Figs. 5 and 7, respectively. We are thus at a loss to account for the observation by Clark, Sterrett and Lincoln<sup>11</sup> that stearic acid deposited by fusion is not oriented upon iron, although it is well oriented upon copper.

The similarity of Figs. 1 and 5 suggests to us that stearic acid molecules of the first layer may react directly with a superficial layer upon a chromium surface to form stearate molecules. Layers of stearic acid molecules on top of the first layer exist in uncombined form. The effect upon its lubricating properties of the addition of stearic acid to a paraffin oil may be due to interaction of the first layer of acid molecules with a metal surface. The results of the present experiments have led us to believe that electron

diffraction methods can be successfully applied to fundamental studies of boundary lubrication. We propose to carry out tests upon various compounds which can be added to lubricating oils to increase "oiliness."

*Polymorphic forms of stearic acid.*—In the first column of numerical values of Table V are written down data regarding the stearic acid structure described above. In the second column are corresponding data from our earlier paper,<sup>2</sup> with a corrected value of the angle  $\beta$ . In the other columns are other published data regarding stearic and palmitic acids. It is evident that our values tabulated in the first two columns represent different crystalline forms, which are also differently oriented with respect to the dipping direction; in the older form (column 2) the axes of the hydrocarbon chains are inclined *downward* from the surface of the supporting block as the block is held during dipping, whereas in the present form (column 1) the axes are inclined *upward*.<sup>12</sup> We are unable to account for the occurrence of these two modifications. The newer form (column 1) has been obtained consistently for many months, although temperature of the water has been varied somewhat and pH has been changed over a considerable range; the other form (column 2) appeared with equal

<sup>11</sup> Clark, Sterrett and Lincoln, Ind. and Eng. Chem. **28**, 1318–1322 (1936).

<sup>12</sup> Clark and Leppla [J. Am. Chem. Soc. **58**, 2199–2201 (1936)] have reported that the axes of the hydrocarbon chains of stearic acid in built-up layers are inclined *downward*.

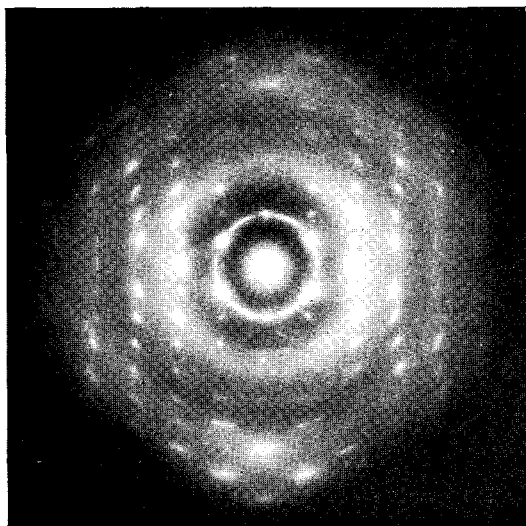


FIG. 12. Pattern from twelve layers of stearic acid molecules. Dipping direction downward.

uniformity a few months earlier. It seems that the surface of the metal block can have nothing to do with the form which appears, because at a given time identical modifications are developed upon chromium and upon Resoglaz. Dr. B. E.

Warren has suggested to us that a particular form may be determined by "seeding," the existence of tiny seed crystals about the experimental equipment.

In the second column of Table V we have given  $52^\circ$  for the monoclinic angle  $\beta$ . The earlier value of  $57^\circ$ <sup>2</sup> was incorrectly determined. The correct angle is obtained by measuring the inclination to the surface normal of a line through the centers of diffraction streaks of the form  $(h\ 0\ l)$ . In our earlier paper we measured not this inclination but the slope of the diffuse bands obtained with the primary beam normal to the dipping direction. If all crystals were precisely oriented with their  $b$  axes normal to the "dipping plane" the two measurements would yield identical values; for crystals which are not precisely oriented in this way the earlier measurement yields too high a value, by  $5^\circ$  in the case under consideration.

Values of  $c \sin \beta$  obtained by Francis, Piper and Malkin for three different modifications of stearic acid are given at the bottom of Table V. It is evident that the form which they describe as "b" is the same as that studied by Müller and

TABLE V. Comparison of present data on stearic acid with previously published quantities.

	GERMER AND STORKS		PALMITIC ACID	STEARIC ACID		
	STEARIC ACID			“α” FORM THIBAUD AND DUPRÉ LA TOUR <sup>14</sup>	“α” FORM THIESSEN AND SCHOON <sup>15</sup>	“β” FORM THIBAUD AND DUPRÉ LA TOUR <sup>14</sup>
	JOURNAL CHEMICAL PHYSICS (this paper)	PROC. N.A.S. <sup>2</sup>				
<i>a</i>	8.27 <i>A</i>	9.4 <i>A</i>	9.41 <i>A</i>	9.36 <i>A</i>	5.546 <i>A</i>	5.68 <i>A</i>
<i>b</i>	4.96 <i>A</i>	5.0 <i>A</i>	5.00 <i>A</i>	4.95 <i>A</i>	7.381 <i>A</i>	7.39 <i>A</i>
<i>c</i>	—	—	45.9 <i>A</i>	—	48.84 <i>A</i>	—
<i>β</i>	70°	52° <sup>13</sup>	50° 50′	51.2°	63° 38′	—
<i>a b sin β</i>	Upward	Downward	36.5 <i>A</i> <sup>2</sup>	36.6 <i>A</i> <sup>2</sup>	36.76 <i>A</i> <sup>2</sup>	—
<i>c sin β</i>	38.6 <i>A</i> <sup>2</sup>	37.0 <i>A</i> <sup>2</sup>	39.5 <i>A</i>	—	43.76 <i>A</i>	43.95 <i>A</i>
			after <i>c</i> has been adjusted to stearic acid value by add- ing 5.0 <i>A</i>			
( <i>h 0 l</i> ) reflections	<i>h</i> and <i>n</i> both even or both odd	<i>h</i> even				
Francis, Piper and Malkin <sup>17</sup>	Stearic Acid “ <i>a</i> ” form		Stearic Acid “ <i>c</i> ” form		Stearic Acid “ <i>b</i> ” form	
<i>c sin β</i>	46.6 <i>A</i>		39.95 <i>A</i>		44.0 <i>A</i>	

<sup>13</sup> Corrected, as described in text.

<sup>14</sup> Thibaud and Dupré la Tour, J. de Chim. Phys. 29, 153-167 (1932). Dupré la Tour, Thesis, Univ. of Paris, 1932.

<sup>15</sup> Thiessen and Schoon, Zeits. f. physik. Chemie 38, 216-231 (1937).

<sup>16</sup> Müller, Proc. Roy. Soc. A114, 542-561 (1927).

<sup>17</sup> Francis, Piper and Malkin, Proc. Roy. Soc. A128, 214-252 (1930).

by Thibaud and Dupré la Tour and designated as " $\beta$ " by the latter experimenters. Also our older form (column 2) is the same as that studied by Thiessen and Schoon, and designated by them and by us as the " $\alpha$ " modification because of its similarity with " $\alpha$ " palmitic acid. If we add 5.0Å to the  $c$  edge of alpha-palmitic acid as determined by Thibaud and Dupré la Tour, in order to make it comparable with the stearic acid edge, we obtain a value of  $c \sin \beta$  in agreement with that for the form designated as " $c$ " by Francis, Piper and Malkin; thus the " $c$ " form and the " $\alpha$ " form are identical. It may well be that our new modification of stearic acid (column 1) is that described as " $a$ " by Francis, Piper and Malkin. This cannot be tested as we do not know the length of the edge of the unit cell parallel to the  $c$  axis. One might think that this edge would be the same for the different modifications, but this apparently is not so; 5.0Å added to the  $c$  edge of alpha-palmitic acid gives a value which is definitely in disagreement with the  $c$  edge of beta-stearic acid as found by Müller.

It is interesting to observe that all values of  $ab \sin \beta$  (line five of Table V) are in rather good agreement, corresponding in every case to the cross section of two hydrocarbon chains. The high value in the first column differs from those in other columns by an amount which is probably not beyond possible experimental error in our measurements. The cross section of a single hydrocarbon chain in barium stearate,  $20.4\text{Å}^2$  as determined in the first part of this paper, is distinctly greater than the cross section in stearic acid,  $18.4\text{Å}^2$ . This may suggest that the modification of column 1 is contaminated by some metal ions. In the case of our earlier measurements (column 2) we were able to rule out such a possibility by producing relatively large crystals in which no significant contamination could occur. Although we have not done this in the case of the new crystal modification, we believe that metallic contamination is unlikely.

*Distortion of diffraction patterns.*—A curious distortion of some diffraction patterns has been observed. An example of this is exhibited in Fig. 12, a transmission pattern from twelve layers of stearic acid molecules. The spots of Fig. 12 do not fall along straight lines, as do those of Figs. 10 and 11.

A disturbance, which seems to be similar, is often found in reflection patterns from built-up layers. In both Fig. 6 and Fig. 7 horizontal diffraction features are shifted from their "correct" positions by varying amounts along the diffuse bands.

We have attempted to account for these strange phenomena by refraction, by electrostatic charging of the films or by distortion or inhomogeneity of the crystals, but without success.

#### BARIUM MYRISTATE MOLECULES IN A SINGLE LAYER

It has seemed important to find out just how thin a layer of atoms on a polished metal surface will give a diffraction pattern which can be interpreted. We have been able to build a layer of barium myristate molecules on a metal surface by the Langmuir-Blodgett technique, but we have not been able to build a layer of barium laurate molecules. A diffraction pattern was obtained from the single layer of barium myristate which resembles the pattern of Fig. 1. It seems probable that considerably shorter hydrocarbon chains than those of myristic acid (14 carbon atoms) would give interpretable diffraction patterns, if a single layer of these chains could be prepared.

These experiments have shown that a diffraction pattern can be obtained from a film whose scattering power is probably comparable with that of naturally occurring layers of adsorbed gas molecules; if the electron wave-length were increased to about 0.12Å it would seem that this could certainly be accomplished. Thus it seems to us that the study of adsorbed gas films by means of electron diffraction patterns observed photographically waits now only upon improvement in vacuum technique.

We are greatly indebted to Dr. Irving Langmuir for the stimulus to carry out these experiments, and to him and to Dr. Katharine Blodgett and to Mr. Vincent J. Schaefer for assistance with technical details. We wish also to thank Drs. C. J. Davisson and W. Shockley and Mr. W. E. Campbell for helpful suggestions and criticisms.