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STRUCTURE, MOLECULAR ORIENTATION AND MECHANICALLY INDUCED REORIENTATION OF MOLECULES IN MULTIMOLECULAR FILMS OF LONG-CHAIN N-HYDROCARBON DERIVATIVES

by

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Dean of Graduate College

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I. INTRODUCTION

One of the most remarkable properties of many films and interfaces is the frequent appearance of a preferred orientation in the arrangement of the molecules. Surface and interfacial properties are often critically dependent upon molecular orientation. This fact has attracted much attention and numerous examples correlating a variety of surface properties with molecular orientation have been recorded. Properties, such as interfacial energy, adhesion, surface viscosity of films, boundary lubrication, wetting, activity of antibiotics, and many others have been found to exhibit a marked dependence upon the orientation of the molecules at an interface.

Of all the techniques available for studying molecular orientation at a surface, certainly the most direct is electron diffraction, where it is applicable. The use of electron diffraction for this purpose was quickly recognized and a study of the lubricating properties of thin films of various oils, formed on metal surfaces, as a function of molecular orientation (1) was reported only a few years after the discovery of the wave properties of the electron. Subsequently, a number of studies have appeared dealing with molecular orientation in films of various organic compounds with especial emphasis on films of hydrocarbon derivatives which have been formed on metal surfaces. However, not all films have been of well-characterized chemical composition and the variety of compounds used to form the films has been small. Moreover, data relating molecular orientation with quantitative measurements of the thickness of the film have seldom been obtained and very little is known concerning the relation of the orientation of the molecules to their molecular structure.

This investigation is concerned with a systematic electron diffraction study of films of a variety of long-chain, n-hydrocarbon derivatives. These compounds were chosen for several reasons. First, the long-chain, n-aliphatic derivatives are an important class of surface active substances. Second, many compounds containing an n-aliphatic chain exist in several polymorphic forms. The structure assumed in multimolecular films is of interest and requires further elucidation. Third, some hydrocarbon derivatives have been shown to reorient in one of several ways when their films were subjected to a mechanical shearing force. This very striking property is not well understood and invites further investigation of the mechanism involved.

II. REVIEW OF THE LITERATURE

A. The Structure of Multilayer Films

Early investigations (2, 3, 1) of films of "fatty-like" substances, formed on polished metal surfaces, clearly established a preferred orientation for the molecules in the film. These "fatty-like" substances were various oils, greases and natural products containing large amounts of long-chain hydrocarbon derivatives. Generally, the films appeared to be non-crystalline and the molecules were arranged randomly in the plane of the metal surface subject to the constraint that their long-chain molecular axis was approximately perpendicular to the metal surface.

In sharp contrast to the results of the earlier investigations more recent work on compounds of higher purity contains some examples of oriented, polycrystalline films. For instance, Germer and Storks (4) found that pure samples of methyl stearate and stearic acid gave such films. The crystallites were so arranged in the films that the long molecular axis was found to be inclined to the metal surface making an angle of 25° for methyl stearate and 33° for stearic acid. The diffraction patterns for a particular compound were essentially identical even though the multilayer films were formed by different methods, as, evaporation from benzene solution, flowing fused material over the surface or spreading the solid material on the metal.

Later detailed work by Germer and Storks (5, 6) dealt with the structure of Langmuir-Blodgett films of stearic acid and barium stearate deposited on polished chromium surfaces and upon a resoglass film mounted across a slit in a metal support. Multilayer films of stearic acid were found to be polycrystalline, polymorphic form A and form C of stearic acid being observed during different periods of the work. On the resoglass surface or upon a metal surface containing a monolayer of stearic acid or barium stearate, each two successive layers of stearic acid or barium stearate were found to have the same structure as the bulk material. The molecules from one layer formed dimers with the molecules from another layer so that the polar groups were adjacent to each other. The molecular axis of stearic acid dimers was inclined to the surface normal in both of the polymorphic forms observed whereas the molecular axis of barium stearate was parallel to the surface normal.

C. L. Sutula and L. S. Bartell (7) have recently found films of a large variety of long-chain, hydrocarbon derivatives formed on a polished, metal surface to be oriented and polycrystalline. The films were prepared by evaporation of benzene solutions or by cooling the fused compounds after spreading them over the metal surface. For films of thickness greater than a monolayer, no change in structure was observed with increasing thickness of the films. Oriented crystallites were shown to be present for an entire range of average thickness of the films from slightly more than a monolayer to a thickness much greater than 1000 A. The structure of the crystallites, whenever determinable, was that of one of the polymorphic forms adopted by the compound in the macro state.

B. The Structure of Monolayer Films

The structure and molecular orientation of monolayers appears to be quite different than that of multilayer films. Germer and Storks (5, 6) demonstrated that on a clean metal surface the first deposited layer of stearic acid or barium stearate of a Langmuir-Blodgett film contained molecules having their molecular axis approximately perpendicular to the supporting surface. Although molecules of a monolayer on such a surface were close packed laterally, no evidence of a regular arrangement in the plane of the metal surface was obtained[1].

L. O. Brockway and J. Karle (8) have determined the orientation of films of n-octadecyl amine, stearic acid and cerotic acid on carefully prepared iron, copper and platinum surfaces. The films which were prepared by adsorption of the polar compounds from cetane solutions were monomolecular

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[1] See also Appendix II.

in thickness. In all cases no regular arrangement was found but the molecular axis was approximately perpendicular to the metal surface. W. C. Bigelow and L. O. Brockway (9) obtained similar results in a detailed study of monolayers of the n-aliphatic acids. They related the wetting properties of the films to the orientation and closeness of packing of the molecules.

J. A. Chapman and D. Tabor (10) have recently published evidence showing that at least a short range order exists in monolayers of adsorbed fatty acids and other polar, long-chain compounds. The monolayers were prepared by adsorption by retraction on to freshly evaporated surfaces of metal. The study adds further support to the belief that monolayers of adsorbed polar compounds have no crystalline structure but that the molecules are not necessarily arranged at random. They proposed a short range order of about 200 A in length with a packing much like that of polymorphic form B of the even numbered fatty acids but with the molecular axis approximately perpendicular to the substrate as a model for the films.

C. Reorientation of Molecules by Mechanical Means

In 1938, G. I. Finch (11) reported the occurrence of a reorientation of molecules of stearic acid by rubbing the surface of the film with filter paper. Before rubbing, the molecules appeared to be unoriented in the sense that although the molecular axis was inclined by 53° to the metal surface they were otherwise distributed at random. After rubbing, the molecules had their molecular axis inclined at about 5° and pointed against the rubbing direction. Finch (12) also showed that "bronzed" and "non-bronzed" samples of Prussian blue could be partially oriented by rubbing. Although he considered reorientation by mechanical means important in boundary lubrication he did not publish a detailed investigation.

Following Finch's rather brief remarks about the reorientation of stearic acid Germer and Storks (13) performed a study of the effect of rubbing on Langmuir-Blodgett multilayers of stearic acid and barium stearate. The molecular orientation in multilayers and monolayers of barium stearate became only disarranged by the rubbing with soft tissue. Rubbed multilayers of stearic acid, however, gave diffraction patterns characteristic of reoriented molecules. However, the results were different from those reported by Finch. The unrubbed multilayers were composed of oriented crystallites of form A of stearic acid, the molecules of which were inclined by 70° to the metal surface and all pointing approximately against the direction of dipping during deposition of the film. The rubbed films contained crystallites of form C of stearic acid so oriented that the molecular axes were inclined by 8° to the metal surface and pointing against the rubbing direction. Crystallites in the reoriented film were found to be fairly resistant to further rubbing in the same direction but were easily removable by a few light rubs in the reverse direction. Germer and Storks were also able to demonstrate that for rubbed multilayers of stearic acid the diffraction patterns obtained were unrelated to the original direction of inclination of the molecular chains. Identical patterns were obtained for oriented, ordered Langmuir-Blodgett multilayers, which were rubbed in various directions with respect to the direction of inclination of the molecular chains, as well as for films prepared by evaporation of benzene solutions in which the crystallites, though oriented, had their basal axes arranged randomly.

K. Brummage (14) examined the effect of rubbing on films of three normal paraffins, tetracosane ($C_{24}H_{50}$), triacontane ($C_{30}H_{62}$) and tetratriacontane ($C_{34}H_{70}$) formed on stainless steel and copper surfaces. Thin (multilayer), unrubbed films of the paraffins contained oriented crystallites, so arranged, that the molecular chains were parallel to the surface normal with the basal axes of the crystallites arranged in a random fashion. The crystallites were apparently orthorhombic with basal parameters a = 7.45 A, b = 4.97 A. Rubbed multilayers gave diffraction patterns containing arcs of small radius superimposed on a pattern very similar to that of the unrubbed films.

Brummage suggested that the arcs were caused by scattering from reoriented crystallites effectively lying on 201 planes. The crystallites were so arranged that the molecular chains were inclined by 3° to the metal surface and pointing against the rubbing direction. Brummage further proposed that a 201 orientation of the crystallites could be expected for crystallographic reasons along with the often observed 001 orientation. He suggested that rubbing melted the film which then recrystallized under sliding shear of the departing rubbing surface. Since the adhesional energy of crystallites in the 001 orientation was greater than in the 201 orientation, the shearing force was likely to remove many crystals in the 201 orientation leaving most of the crystallites with an 001 orientation. Those crystallites pointing against the direction of rubbing would more effectively resist removal by the sliding shear because the presence of a component of the shearing force in that direction would tend to hold them to the surface.

Sutula and Bartell (7) have shown that a similar reorientation can be produced by a mechanical shearing force in films of palmitic, n-heptadecanoic, and isopalmitic acids as is produced for films of stearic acid. The diffraction patterns for rubbed multilayers of dotriacontane ($C_{32}H_{66}$) were similar to those reported by Brummage. Multilayer films of octadecyl and hexadecyl stearates were also demonstrated to reorient, the molecular chains being aligned parallel to the rubbing direction and parallel to the plane of the metal surface.

J. M. Cowley (15) has investigated the effect of mechanical action and heating upon the molecular orientation of films of palmitic acid formed on metal surfaces. His observations appear to be unrelated to the effect being discussed.

III. OBJECTIVES

During a preliminary study of films of a variety of long-chain n-hydrocarbon derivatives by electron diffraction, highly oriented and polycrystalline films were often observed. A shearing force applied to such films often induced unusual molecular orientations in these films. Not all of the results of this study agreed with those reported in the previous literature. Some of the electron diffraction patterns obtained with these films had not been interpreted in detail and a few compounds studied were not too pure.

In order to extend this work a detailed, systematic investigation was initiated of several homologous series of hydrocarbon derivatives. The following aspects were especially considered:

1. The variation of the structure and molecular orientation with the nature of the material used to prepare the film.
2. The variation of the structure and molecular orientation with the thickness of the film.
3. The variation of the structure and molecular orientation with the method of preparing the film.
4. The effect of impurities on the structure and molecular orientation in the film.
5. The effect of a shearing force on the structure and molecular orientation in the film.

6. A determination of several characteristic properties of reoriented films.

IV. EXPERIMENTAL

A. Apparatus

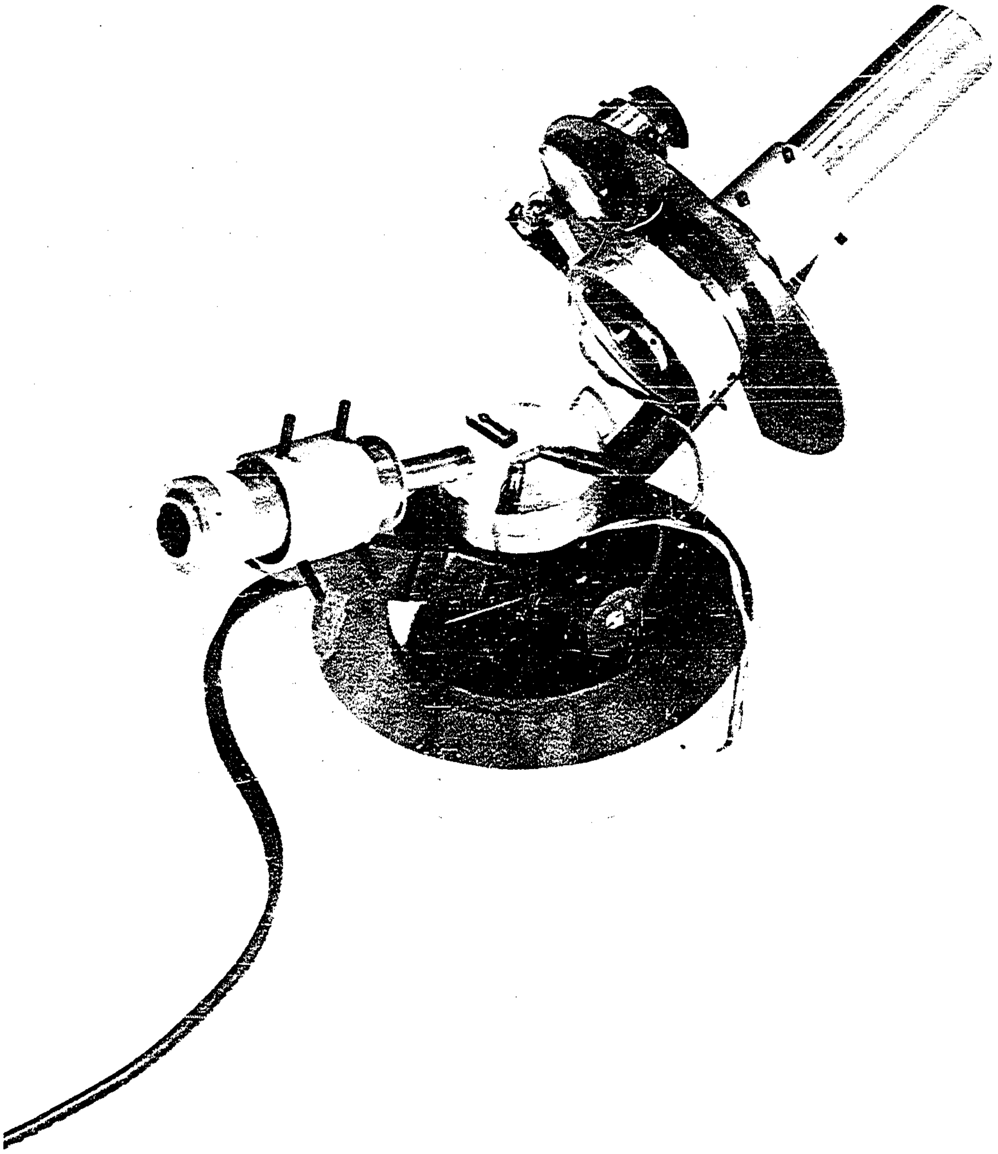
1. The electron diffraction unit

Diffraction patterns were obtained with a commercial electron diffraction unit, General Electric number 6933984G-2. The high potential used to accelerate the beam of electrons was stabilized and ripple-free to approximately 0.1 per cent in the range from 25 to 50 kilovolts. An accelerating voltage of 35 kilovolts was used in all the experiments. The de Broglie wavelength at this voltage is 0.064 A. Whenever a precise determination of the wavelength was necessary, a powder of zinc oxide smoke supported by a fine mesh screen was used as a standard.

2. The ellipsometer

An optical phase shift device, shown in Figure 1 was constructed for use in measurements of the thickness of the films. The instrument, hereinafter referred to as an ellipsometer (16), has an estimated accuracy of approximately ± 1 A in the range 0 - 100 A. Films of neutral stearic acid and films of barium stearate deposited on various metal surfaces by the method of Langmuir and Blodgett (17) were used to calibrate the instrument.

Figure 1. A photograph of the ellipsometer used in measuring the thickness of the films in this investigation



B. Materials

1. The substrate surface

Polished, platinum and "chrome" plated steel slides were used as substrates for the films. The "chrome" plated slides were used in the early part of the investigation and the platinum surfaces throughout the latter part. A particularly successful method for polishing the platinum surface is described.

Solid pieces of pure platinum (about 99% Pt) were obtained in the form of small bars approximately 5/64 in. x 3/16 in. x 3/4 in. These crude slides of the metal were firmly mounted with Duco cement onto the flat surface of a threaded, solid brass cylinder, which is shown in Figure 2. The brass cylinder was carefully machined to fit a case-hardened steel ring threaded on the inside wall. After mounting the platinum slide on the brass surface, the brass cylinder was advanced through the steel ring until "high spots" on the upper surface of the metal slide were coplanar with the upper, flat surface of the steel ring. A mounted, unpolished slide placed in this position is shown in Figure 3.

The flat surface of the ring and the surface of the slide were then made to contact various grades of abrasive paper using a copious supply of water as lubricant and a

Figure 2. The inner cylinder of the polishing device

Figure 3. The polishing device with a slide mounted on the inner cylinder

wetting agent, in the manner customary to metallurgical polishing procedure. After the platinum slide was rubbed with 600 grit abrasive paper the slide was removed from the brass cylinder by immersion in acetone for a few minutes and remounted in order that the reverse side could be similarly polished. The use of the polishing device, in this manner, gave a "wafer-like" slide of metal having two surfaces very nearly parallel to each other. Slides of this type simplified the operation of measuring the thickness of the films.

After polishing with 600 grit abrasive paper, the platinum slides were either held by hand or remounted with cement onto small discs of metal and repolished with finer abrasives on a rotating wheel covered with a polishing cloth. For platinum surfaces, polishing with Linde A followed by polishing with Linde B was satisfactory.

"Chrome" plated slides were generally given a mild abrasive treatment with levigated alumina to remove gross contamination. Slides sufficiently flat for use in the experiments were cut from very large plates.

Positive removal of abrasive particles from a metal surface was accomplished by vigorous rubbing of all the surfaces of the slide with a small piece of polishing cloth in a jet of water followed by rubbing with a cotton applicator in a stream of distilled water. The last traces of grease-like material remaining on the slide after the above operation were removed in the following way. Platinum slides were dried with soft tissue after rinsing and then were flamed for about one minute at a dull red color in the oxidizing portion of a flame of a Meker burner. "Chrome" plated slides were first wiped with benzene after rinsing and then were flamed in the oxidizing portion of a flame of a Meker burner for a total of five to seven seconds in one second steps.

Electron diffraction photographs taken of a metal surface cleaned by the above procedure did not indicate the presence of abrasive or of oriented, grease-like substances. Small drops of water placed on the metal surface would spread well and gave approximately zero contact angles. The surfaces also gave "black" breath figures and readily formed films of n-octadecyl amine by the drop retraction technique from solutions of n-octadecyl amine in highly purified cetane (concentration less than 0.1% by weight).

Figures 4 and 5 show, respectively, typical diffraction photographs of a flamed platinum surface and a flamed "chrome" plated surface. Figure 6 is a diffraction photograph of a surface covered with the abrasive Linde B.

2. The compounds studied

In Table 1 are listed the data for the source and the estimated purity of the compounds used to form the films in this investigation. Benzene, toluene, n-tetradecane, ace-

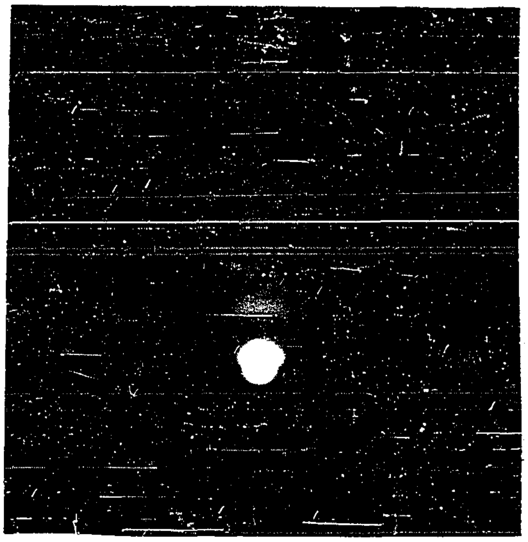


Figure 4. Diffraction pattern from a flamed platinum surface

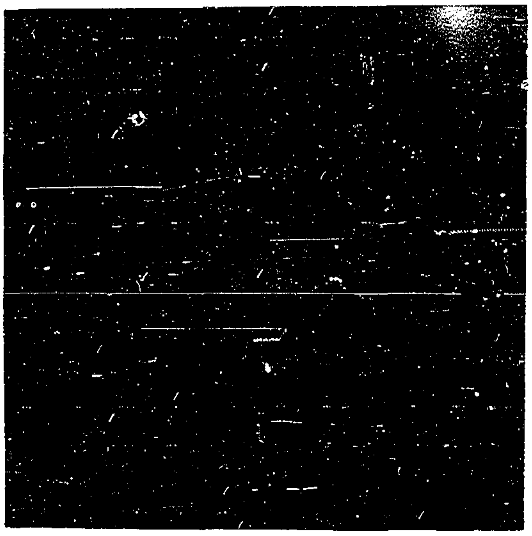


Figure 5. Diffraction pattern from a flamed "chrome" plated surface

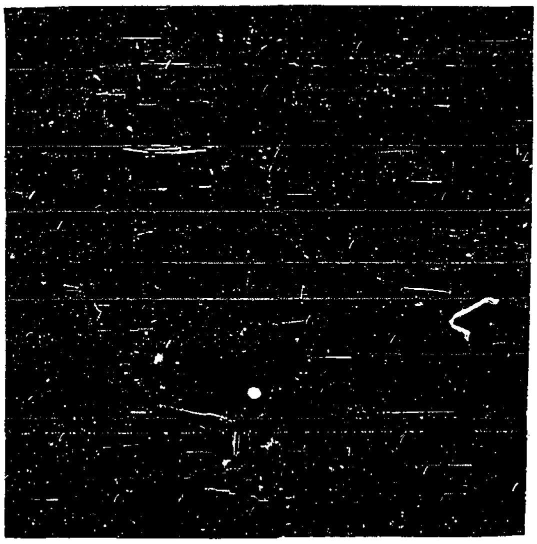


Figure 6. Diffraction pattern of a metal surface containing Linde B

Table 1. Purity and source data of the n-hydrocarbon derivatives used in the investigation

Material	Observed melting point	Estimated purity (in per cent)
Acids		
arachidic acid[a]	76-77	97
stearic acid[b]	70.0°C	>99
isostearic acid[c]	69.5 - 70.2	95
n-heptadecanoic acid[c]	60.5 - 61.3	97
palmitic acid[d]	62.7 - 63.0	>99
isopalmitic acid[c]	62.4 - .8	97
dodecanoic acid[e]	47.5 - 47.9	98
azelaic acid[a]	106 - 107	95-96
sebacic acid[a]	133.8 - 135.0	95-96
Saturated n-hydrocarbons		
n-octadecane[a]	27-28	95-96
n-eicosane[a]	36.0 - 36.7	95-96
n-docosane[f]	———	>99
n-tricosane[f]	———	>99
n-hexacosane[f]	———	>99
n-heptacosane[f]	———	>99
n-octacosane[f]	———	>99
n-nonacosane[f]	———	>99
n-triacontane[f]	———	>99
n-hentriacontane[g]	70.2°C	97-98
n-dotriacontane[a]	70-1	95

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[a] Eastman Organic Chemicals.

[b] The Hormel Foundation.

[c] Courtesy of J. Foster.

[d] Eastern Utilization Research Branch. U.S. Department of Agriculture.

[e] Armour and Co.

[f] Courtesy of A. E. Smith, Shell Development Co. Purity estimated by mass spectrometric analysis.

[g] Courtesy of M. Senkus, R. J. Reynolds Tobacco Co.

Table 1. (Continued)

Material	Observed melting point	Estimated purity (in per cent)
Esters		
n-dodecyl laurate[h]	23 - 24.5	97-98
n-octadecyl stearate[h]	60.2 - 60.4	98
n-hexadecyl stearate[h]	57.2 - 57.5	98
Miscellaneous compounds		
n-octadecyl alcohol[e]	58.4 - 58.6	98-99
n-stearamide[a]	105 - 105.5	95-96

[h] Prepared in this laboratory.

tone, and n-octane were used as solvents for the hydrocarbon derivatives when the films were formed by evaporation from a solution. All of the above solvents were carefully redistilled. Benzene, toluene, and acetone left no permanent film on a freshly prepared metal surface after the above treatment and were used without further purification. n-octane and n-tetradecane were percolated through a column of silica gel and aluminum oxide to remove polar impurities.

C. Methods

1. Methods of preparing the films

Two methods were used in preparing films in this investigation. One involved spreading a fused compound over a warm slide and allowing the material to solidify. This technique was applicable only for a few compounds which did not form oleophobic monolayers. Generally, this method also gave films too thick for convenient use in electron diffraction experiments. The alternative method was to spread a small quantity of a solution of a particular compound in a solvent over the metal slide. A film of the compound would form as the solvent evaporated.

Films prepared by the evaporation of a solution on a metal slide could be prepared in a very large range of thicknesses. An attempt was made to use films approximately 1000A thick when studying the structure of multilayer films. The films were generally heterogeneous in thickness when prepared by evaporation of a solution, although, sometimes large uniform areas were observed when the films were viewed with an ellipsometer.

Two thermal methods were found for forming multilayer films in which the crystallites were not only oriented but were also arranged so that the molecular chains were all inclined in a certain direction over large areas of the film. The techniques appear to be applicable for compounds that form oriented, polycrystalline films in which the molecular chains are inclined to the metal surface. Both methods were very useful for studying certain aspects of the mechanism of reorientation of molecules by mechanical means. They are described in detail in Appendix I.

2. Method of rubbing the films

The films were subjected to a mechanical shearing force with the aid of the device shown in Figure 7. The device consists of a movable aluminum spindle with an attached slider and a stationary, rectangular brass plate. The aluminum spindle has a circular disc on one end of a thin shaft and a rectangular plate on the other end of the shaft. A highly polished, steel slider, curved on both ends is attached to the rectangular plate. The brass plate holds the film supported by the metal surface during rubbing. The upper surface of the brass plate is smooth and flat and contains a groove, parallel to the short side of the plate, machined so that the upper surface of the metal slide can be coplanar with the brass surface when the slide is placed in the groove.

With the slide inserted in the groove, a piece of soft tissue is tightly drawn over the steel slider and the spindle is brought down on the brass surface so that the tissue contacts the brass surface some distance above the groove. A weight is placed on the circular aluminum disc and the entire assembly is slowly and smoothly pulled over the surface of the platinum slide. The process is repeated as many times as is necessary, using a new piece of soft tissue for each rub. Figure 8 shows the position of all components before a rub.

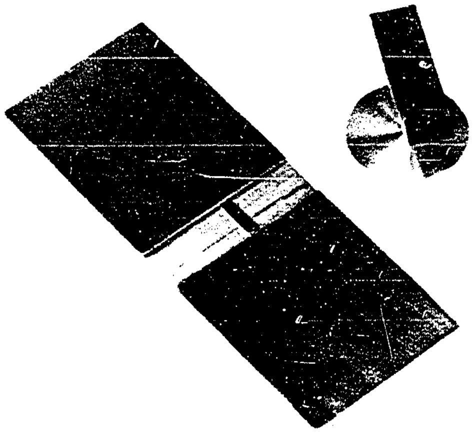

Figure 7. The separate components of the device used to apply a mechanical shearing force to the films

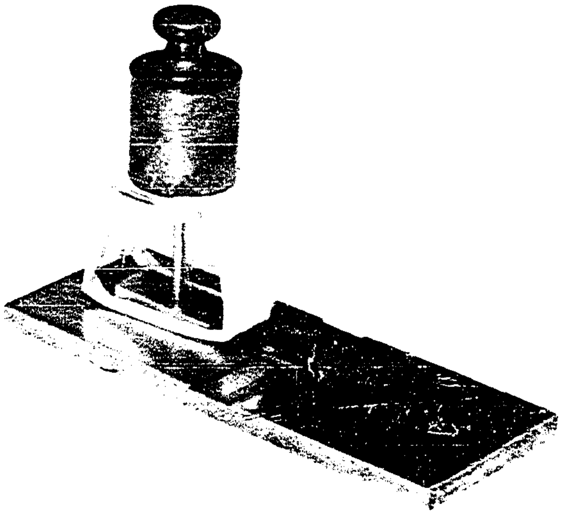

Figure 8. Position of the components immediately before applying mechanical shear to the film

3. Method of procedure

The ellipsometer was used as a differential instrument throughout this investigation, the change in reading between a fresh surface and a surface containing a film was used as an indication of the thickness of the film. The substrate surface was carefully prepared for every experiment according to the method previously described and its base ellipsometer reading was determined shortly after preparation. Immediately afterwards, a film was formed on the metal surface and its thickness was estimated. For unrubbed films, the film was then examined by electron diffraction. For rubbed films, the film was first subjected to a mechanical shearing force, its thickness was estimated and then it was examined by electron diffraction.

Lens or facial tissue performed best as contacting materials during rubbing. A number of materials were tried but were not usable because they marred or seriously contaminated the surface.

Vigorous rubbing or rubbing a few times with a heavy applied pressure would contaminate a freshly prepared surface when soft tissue was used as a contacting material. The thickness of this contaminating film as determined by ellipsometer measurements approached a limiting value of about 20 A with continued rubbing. Metal surfaces that were less active, i.e., metal surfaces that were exposed to the laboratory atmosphere for several hours after their preparation, were not additionally contaminated by rubbing with tissue. To minimize contamination from this procedure, rubbing was performed with tissue impregnated with the compound used as the material in the film.

V. INTERPRETATION OF DIFFRACTION PATTERNS

The electron diffraction patterns obtained with films of long-chain, hydrocarbon derivatives using the reflection method can often be separated into two distinct groups. In group I can be placed diffraction patterns originating from films in which the molecular chains form a certain angle with the perpendicular to the plane of the metal surface but are otherwise arranged quite irregularly in the plane of the metal surface. Patterns that contain diffraction effects caused by crystallites in the films can be placed in group II. Several typical patterns of group I are shown in Figures 9 and 10. Some patterns typical of group II are shown in Figures 11, 12 and 13.

The formation of diffraction patterns from films by the reflection technique often involves many factors and a complete analysis of the patterns is an extremely difficult problem. However, a significant amount of progress has been made toward the explanation and understanding of many of the important features of such diffraction patterns and this advance has given us a correspondingly greater insight into the detailed arrangement of molecules in hydrocarbon films.

A. Patterns of Group I

Patterns of group I have been observed by many investigators. Murison (2), Germer and Storks (6), Pinsker (18),

Figure 9. Typical diffraction pattern of group I -- arced layer line pattern

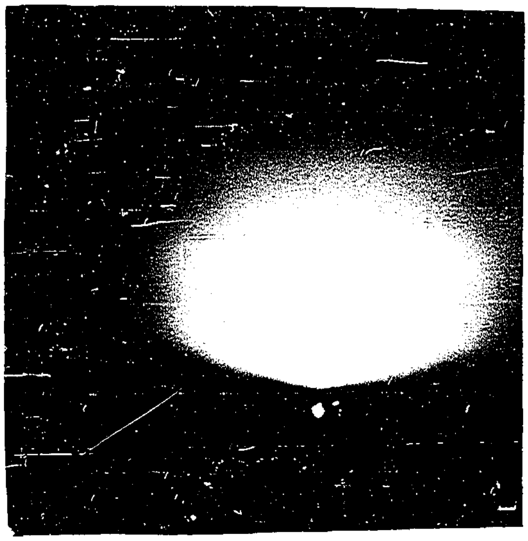

Figure 10. Typical diffraction pattern of group I -- straight layer line pattern

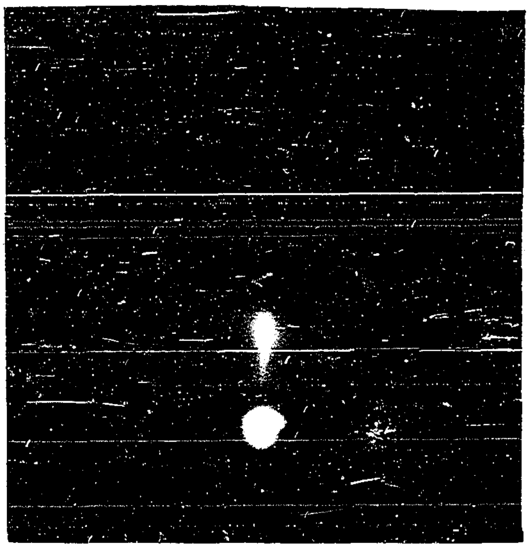

Figure 11. Typical diffraction pattern from group II

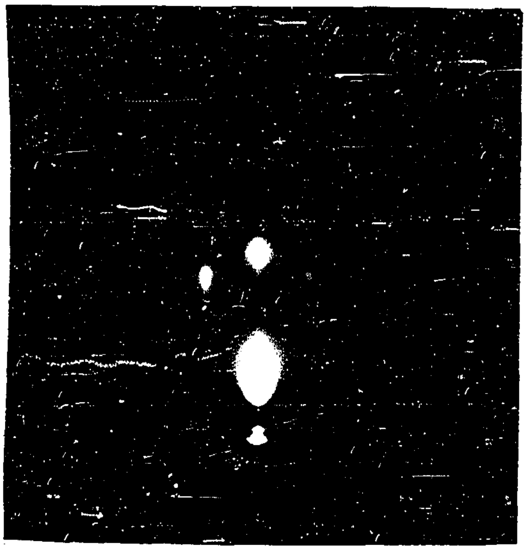

Figure 12. Typical diffraction pattern from group II

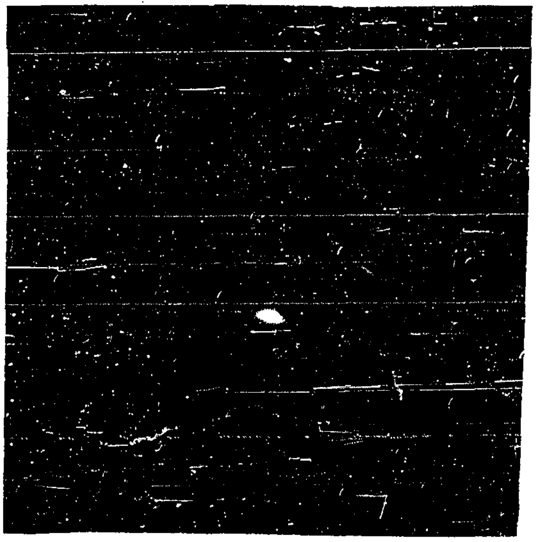

Figure 13. Typical diffraction pattern from group II

and especially Karle (19) and Karle and Brockway (20) have derived equations that describe approximately the intensity distribution of scattered electrons from films as a function of the molecular orientation[1]. The treatment of Karle and Brockway is the most extensive and will be briefly repeated here, with emphasis being placed on the practical aspect of determining the molecular orientation from diffraction photographs.

Reflection patterns from films of long-chain hydrocarbons characteristically show either arced diffuse bands, as Figure 9, or straight diffuse bands parallel to each other and either parallel or inclined at some angle to the sharp line separating the exposed portion of the photographs from the unexposed part. This sharp line is the shadow edge of the substrate surface on the photographic emulsion. These diffuse bands, sometimes called layer lines, are successive orders of diffraction from the regular intramolecular spac-

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[1] Independent, rigidly extended n-hydrocarbon molecules having specified orientations on a substrate have been used as models for the derivation of these equations. Hydrocarbon chains are insufficiently rigid by themselves, however, to maintain the extended configuration which is required to account for the characteristic patterns described below. Whenever these patterns are encountered it can be inferred, therefore, that the molecules involved are not independent as the model implies, but are cooperatively aligning each other. If the lateral ordering is very irregular, the resultant patterns will still have the aspect of patterns resulting from (hypothetical) independent extended molecules.

ings of CH_2 units in the molecules of the film. The spacing and position of the orders of diffraction is largely a function of the orientation of the molecules in the film with respect to the direction of the incident radiation and the carbon-carbon distance along one row of atoms in a molecule.

It is convenient to employ some frame of reference when discussing molecular orientation. Let a long-chain, n-aliphatic compound be represented by a "zig-zag" chain of carbon atoms all in the same plane, the hydrogen atoms being neglected. Consider this chain placed in a frame of reference such that a terminal carbon atom is coincident with the origin, as shown in Figure 14. Using the notation of J. Karle (19), let $\underline{r}_a$ be a vector at the origin, directed along a row of carbon atoms in the staggered chain. Let $\underline{r}_t$ be the vector distance between alternate carbon atoms along $\underline{r}_a$. Let $\underline{z}$ be a vector normal to a plane surface at the origin and $\underline{r}_p$ a vector in the plane of the carbon chain placed perpendicular to $\underline{r}_a$ at the origin. Let $\underline{r}_z$ be a vector in the $\underline{r_a z}$ plane placed perpendicular to $\underline{r}_a$ at the origin. Let Ψ_a be the angle between $\underline{z}$ and the molecular axis, $\underline{r}_a$. Let δ be the angle between the vectors $\underline{r}_z$ and $\underline{r}_p$, and ϕ_a, the angle between the $\underline{r_a z}$ plane and the plane defined by $\underline{z}$ and the incident beam direction, $\underline{n}_o$ (ϕ_a is measured in a clockwise sense when looking down on the surface).

Using the above frame of reference it is possible to

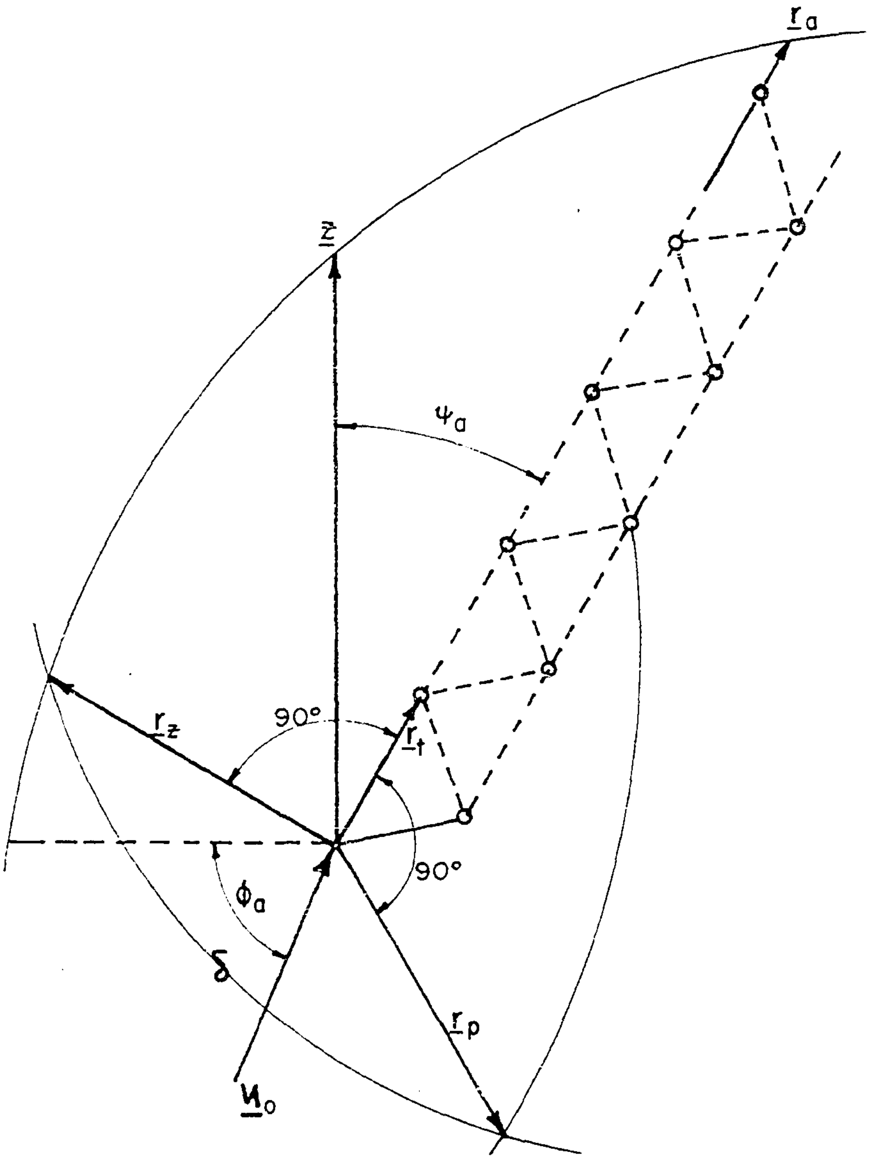

Figure 14. The frame of reference used to describe the orientation of a molecule on a surface

designate the orientation of a molecule in a film on a substrate by specifying three angular parameters, ψ_a, ϕ_a, and δ.

The formulas derived by Karle for expressing the intensity of scattered electrons were used to construct intensity contour maps for a variety of molecular orientations in hydrocarbon films. From the derived formulas and the contour maps Karle and Brockway (20) were able to show that, to an extent, the three angular parameters produced independent effects in the diffraction pattern and could be estimated separately.

Two of the contour maps constructed by Karle and Brockway are reproduced here. Figure 15 is the contour map obtained when $\psi_a = 20°$, $\phi_a = 45°$ and $\delta = 180°$. Figure 16 shows the contour map when $\psi_a = 20°$, $\phi_a = 45°$ and δ assumes all values from 0 to 2π. The maps appear to be fairly good approximations to the observed diffraction patterns. At this stage of the development of the theory the position of the layer lines in the pattern is well correlated with the orientation of the molecular chains in the film. However, the agreement in the intensity distribution along a layer line is only qualitative. Further development and refinement of the theory will require the use of a more complicated model for the film in which intermolecular scattering is considered and the contribution from the hydrogen atoms is

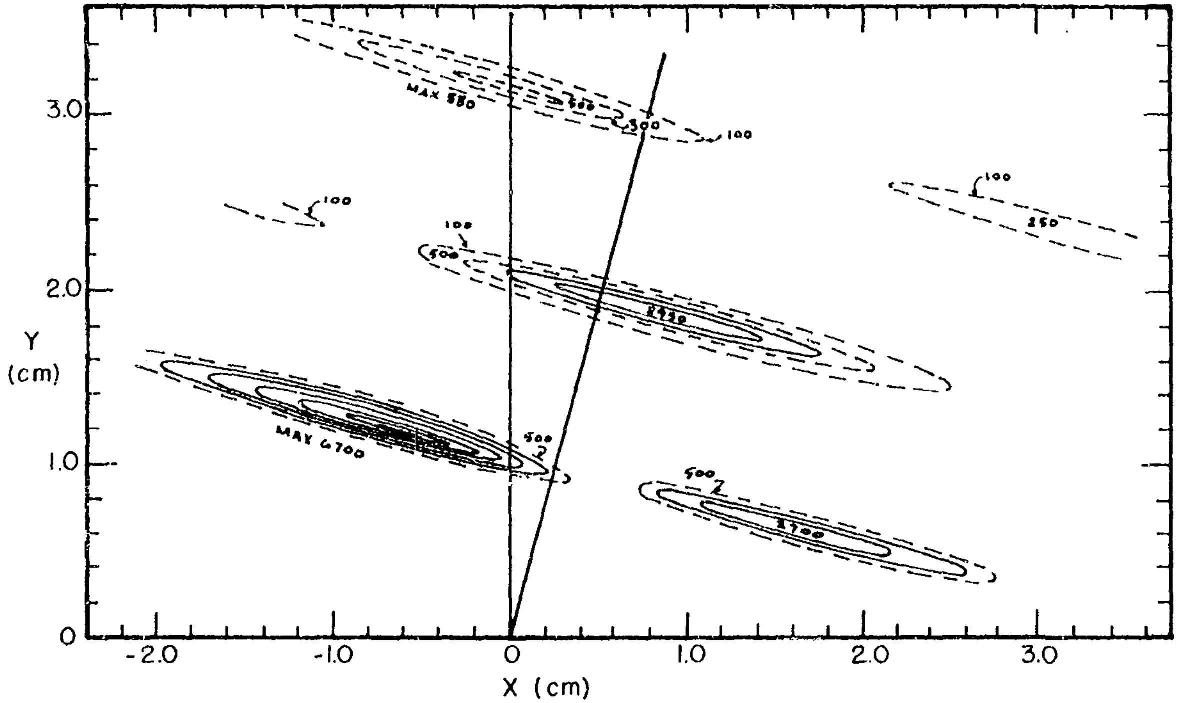

Figure 15. A contour map calculated by Karle and Brockway (20) for the case when $\psi_a = 20°$, $\phi_a = 45°$, and $\delta = 180°$. The projection of the molecular axis and the maxima of the intensity contours are indicated (Journal of Chemical Physics)

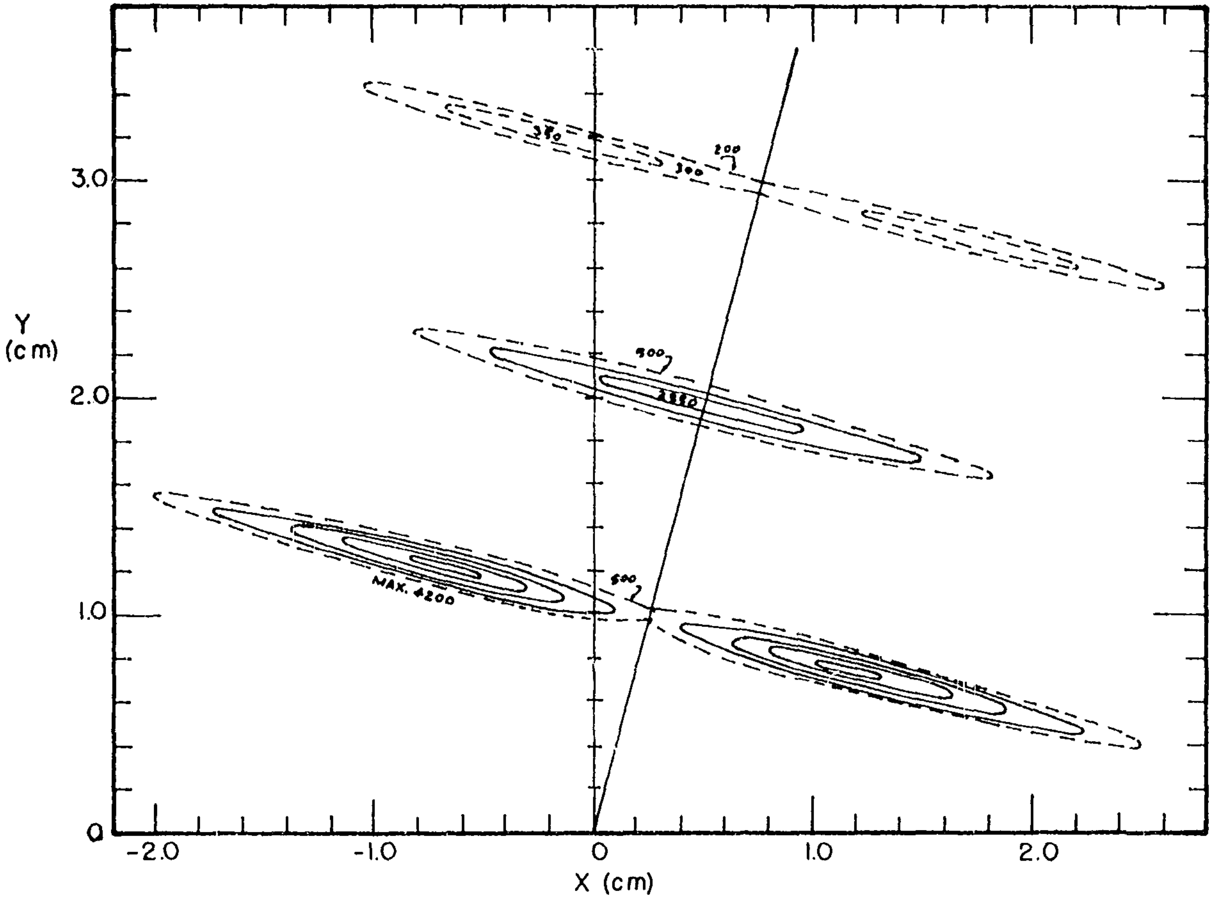

Figure 16. A contour map calculated by Karle and Brockway (20) for the case when $\psi_a = 20°$, $\phi_a = 45°$, and δ is random. The projection of the molecular axis and the maxima of the intensity contours are indicated (Journal of Chemical Physics)

not neglected.

1. Determination of Ψ_a

Let y be the parameter along the perpendicular to the shadow edge of the photographic emulsion with the origin being the burned out spot produced by the undeflected beam. Let x be the parameter along the shadow edge. The intercepts of the layer lines on the y axis are describable by the relation:

$$y = nL\lambda/r_t \cos\Psi_a \tag{1}$$

where n is an integer giving the order of diffraction, λ is the wavelength of the electrons, L is the distance from the specimen to the photographic emulsion, r_t is the alternate carbon to carbon distance along the molecular axis, and Ψ_a is an angular parameter that has already been defined. It should be pointed out that Equation 1 can be used only if Ψ_a is constant for the molecules in the film. This condition holds if the intercepts of the layer lines with the y axis are very nearly evenly spaced.

When Ψ_a begins to assume a range of values for the molecules in the film, the spacing between the layer lines does not remain constant. Karle and Brockway (20) have suggested that an estimate of the average tilt of the molecules can be obtained by using Relation 1 and the spacing between the second and fourth layer lines. A rough estimate of the range on Ψ_a about this average value can be made from the difference between the spacings of the second and third and the third and fourth layer lines.

2. Determination of ϕ_a

When ϕ_a is a constant for the molecules in the film the diffraction pattern will show layer lines perpendicular to the projection of the molecular axis on the photographic plate. When this occurs, one can calculate the value of ϕ_a from the common slope of the layer lines which is given by:

$$dy/dx = \tan \Psi_a \sin \phi_a \quad (2)$$

, (4, 20)

The diffraction pattern is symmetric about the y axis when ϕ_a is random. For Ψ_a equal to zero degrees, ϕ_a has no significance.

3. Determination of δ

The determination of this parameter is very difficult. For fixed values of Ψ_a and ϕ_a, the value of δ determines not only the relative intensities of the even and odd orders, but also the symmetry within an order of diffraction. Assymmetry effects are small when Ψ_a is less than 10°. For fixed Ψ_a, and any value of ϕ_a, the diffraction pattern will be symmetric about the projection of the molecular axis if is random, as shown in Figure 16.

For more information on the determination of this parameter and the use of equations and contour maps, the reader is referred to the literature (19, 20).

B. Patterns of Group II

Reflection patterns of group II contain the diffuse bands or layer lines of the patterns in group I and intense spots, somewhat diffuse and elongated and oftentimes positioned within the contour of the layer lines on the photographic plate. To explain the occurrence of these patterns it is convenient to employ the concepts of reciprocal lattice and the sphere of reflection in reciprocal space (18, 21).

Electrons accelerated by a potential of 35 kilovolts have a wavelength of 0.064 A. The magnitude of the radius of a sphere of reflection, $1/\lambda$, will be about 15.6 A^{-1}. Since the range of diffraction angles recorded by electron diffraction instruments in reflection experiments is generally only a few degrees, the sphere of reflection becomes essentially a plane of reflection. This is illustrated in Figure 17. A consequence of this is that the electron diffraction pattern recorded on a photographic emulsion now can be imagined as the result of the intersection of a plane perpendicular to the incident wave direction through the origin with the appropriate reciprocal lattice.

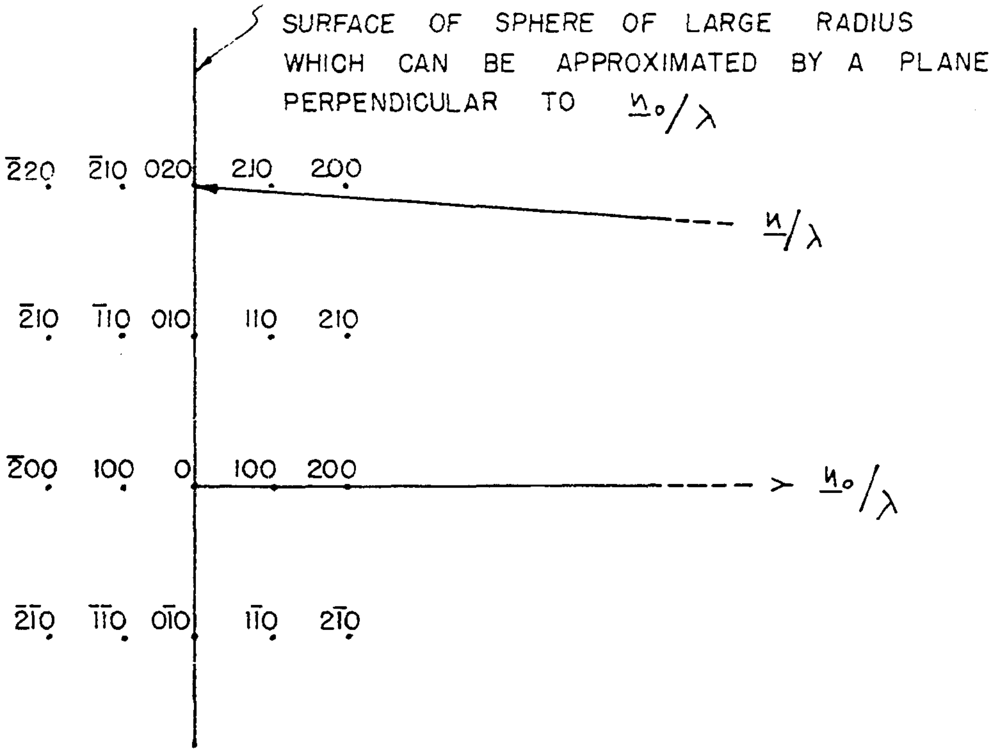

Figure 17. The sphere of reflection in the reciprocal lattice for electrons of wavelength equal to 0.064 A

The phrase, appropriate reciprocal lattice, requires some amplification. For diffraction experiments in which the specimen and film are stationary a comparison of the geometry of the apparatus with the reciprocal lattice indicates that the distances in the reciprocal lattice are smaller than the distances in the diffraction pattern by a factor of $L\lambda$. Moreover, although the reciprocal lattice will generally be different for every crystalline substance, additional factors such as the thickness of the specimen, the crystallite size in the film, the extent of crystalline order, and others must also be considered because of their modifying effect on the reciprocal lattice.

Many long-chain, hydrocarbon derivatives crystallize with the molecular chains parallel to each other. Often a convenient choice of the coordinate axes of a unit cell for these compounds is to select one of the coordinate axes parallel or approximately parallel to the direction of the molecular chains. For compounds containing 18 or more carbon atoms this gives a unit cell with one coordinate axis at least five times greater than either of the other two. Thus, points in the reciprocal lattice along the direction associated with the direction of the molecular chains will be more closely spaced than points along the other two coordinate axes.

Figure 18 is a photograph of a diffraction pattern ob-

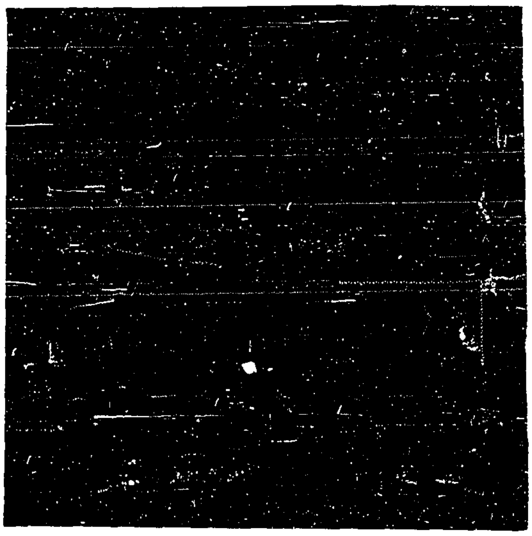

Figure 18. Diffraction pattern from a crystallite in a film of n-octadecyl alcohol

tained from a film of n-octadecyl alcohol, which contains crystallites of orthorhombic form having an 001 orientation in the plane of the metal surface. Through the position of the primary beam and perpendicular to the shadow edge there passes a line containing many closely spaced reflections of alternating intensity. There are also lines parallel to the central line which intersect the first diffuse band and likewise contain spot reflections. The reflections on the central line are caused by scattering from 00ℓ planes of a crystallite. Reflections on the first parallel line to the right of the central line have indices 11ℓ, reflections on the second line have indices 20ℓ, and so on.

The fact that the lines of points having indices 11ℓ, 20ℓ, etc., are most intense on the first diffuse band and do not appear outside of the contour of the band indicates that the diffraction pattern is not simply that of a well-ordered crystallite. The diffraction pattern from a "perfect" crystallite would show no diffuse bands but only spot reflections along the entire length of the parallel lines. Other factors that modify the diffraction pattern must now be considered.

Factors such as the angular spread of the beam, the lack of monochromaticity in the beam and the thermal motion of the molecules (the temperature was about 60° below the melting point of the compound) do not account for the appearance of the diffuse bands or the extinction of many of the reflections on the parallel lines. These factors tend to make the reflections somewhat more diffuse and often allow many reflections to appear for one position of the crystal.

In this case the crystallite contains many small crystalline regions that are not perfectly aligned with respect to each other in 00ℓ planes but with the 00ℓ spacing still preserved. Because these regions do not include more than a few layers of molecules scattering from the regularly spaced CH_2 units within the molecules exercises a very dominant influence on the diffraction pattern. The intensity of many of the weaker reflections of the 00ℓ line and the intensity of all the reflections on parallel lines is controlled by a function very much like that derived for an oriented, long-chain hydrocarbon with ψ_a equal to zero degrees. Thus, the reflections on lines parallel to the 00ℓ line occur only within the contour of the layer lines. The weak, 00ℓ reflections for higher orders are ultimately extinguished only to appear again in the region of maximum intensity of the contour of the second layer line. The small size of the crystalline regions also explains the apparent elongation of reflections on lines parallel to 00ℓ. These regions do not include many layers of molecules and, therefore, include only a few, repeated 00ℓ spacings. The reflections on all lines except 00ℓ are not well resolved and appear to merge into a line.

It is worthwhile to point out that the loss of resolution along lines parallel to 00ℓ cannot be caused by the small penetrability of electrons in the direction perpendicular to 00ℓ planes of the crystallite. If this were responsible for the loss in resolution, then even the 00ℓ reflections would not be resolved. Instead, they would appear as continuous lines. However, well resolved 00ℓ reflections are observed in Figure 18. Nor does the pattern occur because the electron beam strikes a region of film containing a well formed crystallite and a layer of disarranged but oriented, long-chain hydrocarbon molecules. If this occurred, the resulting diffraction pattern would be a superposition of a well resolved spot pattern with spots along the entire length of the parallel lines together with a pattern of group I for molecules having ψ_a approximately equal to zero degrees. This diffraction pattern is apparently a chance occurrence of the electron beam passing through a projecting, single crystallite in the film.

Figures 19 and 20 are photographs of diffraction patterns more typical of those obtained from multilayer films of long-chain, hydrocarbon derivatives. Both figures are examples of a polycrystalline film with the crystallites having an 001 orientation on the metal surface. The photographs illustrate the pronounced diffuseness of reflections along lines perpendicular to the shadow edge caused principal-

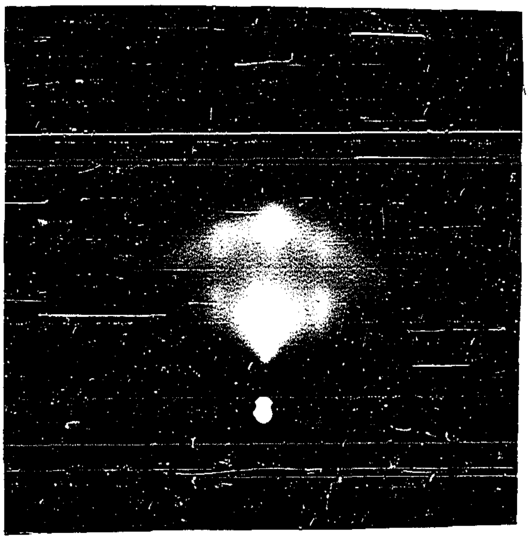

Figure 19. Diffraction pattern from a film of n-octadecyl stearate, approximately 1000 A thick

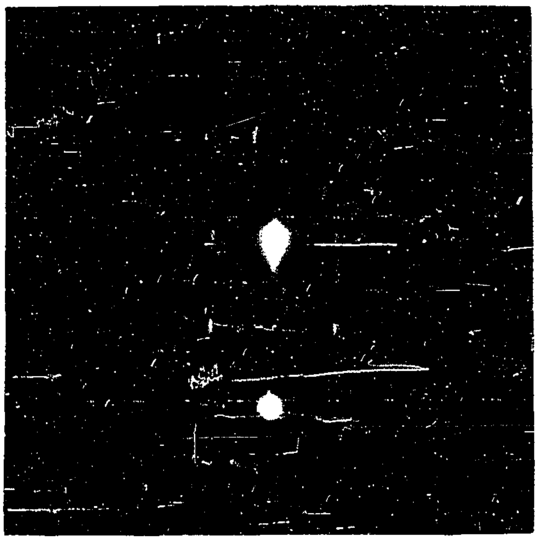

Figure 20. Diffraction pattern from a film of n-octadecyl stearate, approximately 1000 A thick

ly by the small penetration of the electron beam in the direction perpendicular to 00ℓ planes of the crystallites. Spot reflections are not at all visible and only elongated lines positioned within the contour of a layer line can be seen. The diffraction patterns of Figures 19 and 20 are thus strikingly different from Figure 18 in which the electron beam passed through a projecting crystallite. It is estimated that the penetrability of electrons in a direction perpendicular to the plane of the metal surface does not usually exceed about 50 A in hydrocarbon films for an accelerating voltage of about 35 KV. A film of this thickness will often completely mask even an intense pattern from a metal substrate.

The explanation of the occurrence of layer lines and reflections positioned within the contour of the layer lines in Figures 19 and 20 is very similar to that already presented. However, in this case scattering from the regular array of CH_2 units in the molecule is an important factor in the diffraction pattern because the electrons penetrate only the top one or two layers of the molecules in the film.

1. Example 1 - analysis of diffraction patterns from multilayer films of n-octadecyl stearate

Figures 19 and 20 show photographs of typical diffraction patterns obtained from multilayer films of n-octadecyl stearate. The films were approximately 1000 A thick. Both patterns shown are clearly of group II and the following procedure which was used to analyze these is typical of that used throughout this investigation.

All the diffraction patterns obtained from unrubbed films of n-octadecyl stearate indicated the presence of oriented crystallites in the films. Ignoring the elongated reflections on the layer lines for the moment, the positions of the contours of the layer lines on the photographic plate show that the molecular chains are inclined to the metal surface. The value of this angle is estimated later[1].

The position of the reflections on the layer lines is now determined. This is done by measuring the distance to each reflection from a line perpendicular to the shadow edge and passing through the position of the undeflected beam. Then a table is compiled which includes the distance and an estimate of the relative intensity for every reflection measured in the patterns. The average distances for n-octadecyl stearate from Figures 19 and 20 and from other patterns are shown in Table 2.

With the aid of a good compass and closely ruled graph paper, a series of concentric circles are drawn using the

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[1] Note that Figure 20 indicates that the molecular chains are in the plane of incidence of the electron beam but does not establish whether the molecular chains are inclined or are perpendicular to the metal surface. To establish ψ_a accurately it is necessary to examine the pattern at another value of ϕ_a.

measured distances as the radii. This is shown in Figure 21.

If the c axis of the crystallites is chosen parallel to the direction of the molecular chains and if the crystallites are assumed to be monoclinic then the series of concentric circles can be considered as an approximate representation of the cross section of the reciprocal lattice, perpendicular to $\underline{c}^*$, for the crystallites in the film. The cross section of the reciprocal lattice, so obtained, may be more general than required by the structure of the film, or by that shown by any one diffraction pattern. This can be understood by considering that the same cross section would be obtained if the reciprocal lattice for a single crystallite, containing

Table 2. Observed distances to reflections occurring in patterns of n-octadecyl stearate

Reflection number	Distance	Relative intensity[a]
1	0.73	v.d.
2	0.85	v.d.
3	1.05	d
4	1.15	d
5	1.23	f
6	1.42	v.d.
7	1.70	d
8	1.78	f
9	1.84	f
10	1.94	f
11	2.30	f
12	2.55	f

[a] Intensity scale: v.d.> d > f.

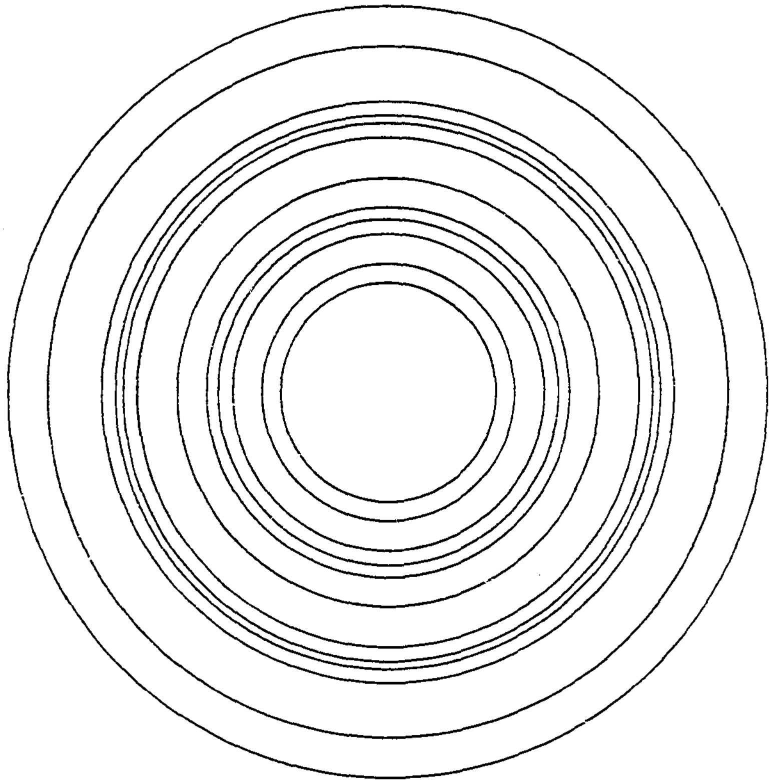

Figure 21. A preliminary cross section of the reciprocal lattice for crystallites in a multimolecular film of n-octadecyl stearate

only one to two layers of molecules, were rotated about $\underline{c}^*$. In effect, the cross section of the reciprocal lattice generated by this operation and the cross section shown in Figure 21 would be identical with a cross section of the reciprocal lattice for a film of oriented crystallites having their basal axes randomly arranged in the plane of the metal surface. This difficulty does not seriously limit the analysis for other information is often available from the patterns that is helpful in determining the basal parameters.

Patterns such as Figure 20 do not show inclined layer lines whereas patterns at different orientations of the film with respect to the incident radiation do show layer lines inclined to the shadow edge. Figure 20 qualitatively supports the assumption that the crystallites are monoclinic and furthermore indicates that the one coordinate axis of the crystallites which is perpendicular to the other two was approximately perpendicular to the incident radiation in this orientation of the film. This information is included in the cross section of the reciprocal lattice by drawing a straight line through the origin of the concentric circles and blackening the intersections of the line with the circles that correspond to especially intense reflections in the pattern.

When this is correctly done, there will be a series of about three to four equally spaced distances along the line, as is shown in Figure 22. The unit distance along this line represents $|\underline{b}^*|$ or a multiple of $|\underline{b}^*|$, and $\underline{a}^*$ for the monoclinic system must be directed perpendicular to this line. Next, lines are drawn perpendicular to $\underline{b}^*$ which also pass through the origin and the various intercepts along $\underline{b}^*$. The intersections of these lines with the circles are carefully noted and are compared with each other and with the distances obtained for the reflections from the patterns. This comparison will often suggest a trial value of $|\underline{a}'^*|$ [1] which is fit into the pattern of concentric circles by drawing lines parallel to $\underline{b}^*$ spaced by the trial value, $|\underline{a}'^*|$. A good fit of $|\underline{a}'^*|$ and $|\underline{b}^*|$ in this cross section of the reciprocal lattice will show all the circles to each have a common intersection with some particular point of the rectangular net determined by the intersections of the straight lines.

Moreover, the fit should account (at least in part) for the relative intensities of these reflections and should agree with all the diffraction patterns obtained for that region of the film. Such a fit for films of n-octadecyl stearate is shown in Figure 23.

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[1] Because $\underline{a}^*$ is, in general, inclined to $\underline{c}^*$ by an angle different from $\pi/2$, it must be remembered that the value being fit to the cross section of the reciprocal lattice is $|\underline{a}^*| \sin\beta$ and not $|\underline{a}^*|$. To avoid confusion we will designate $|\underline{a}^*| \sin\beta$ as $|\underline{a}'^*|$.

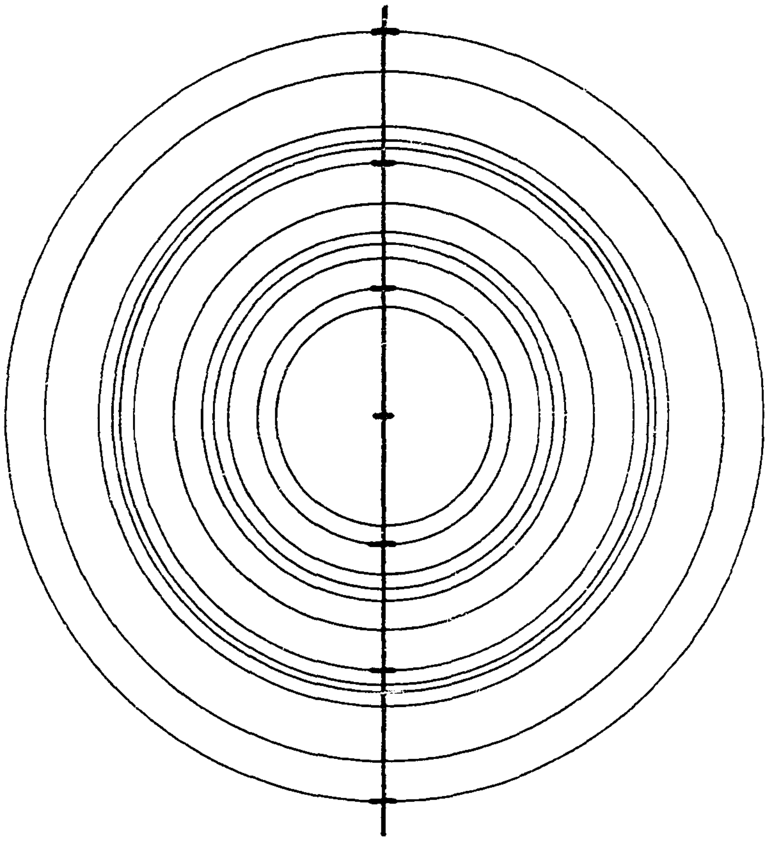

Figure 22. A preliminary cross section of the reciprocal lattice of crystallites in films of n-octadecyl stearate. The unit distance believed to represent $|\underline{b}^*|$ has been indicated

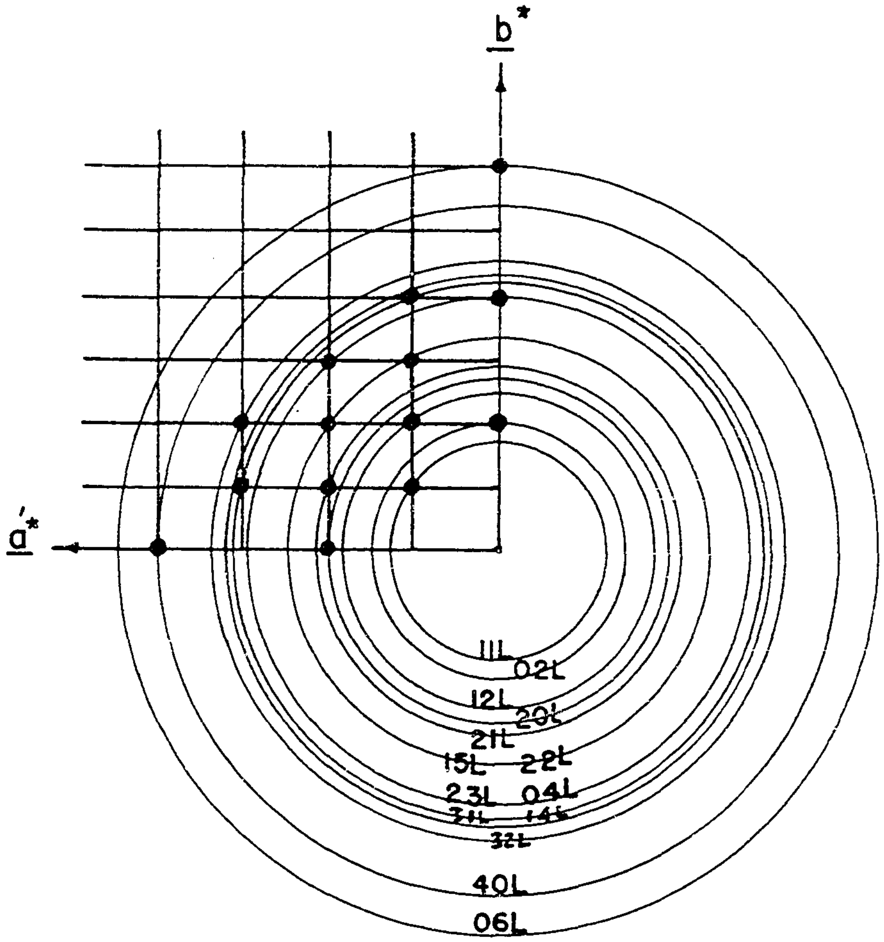

Figure 23. The "best fit" for the cross section of the reciprocal lattice of crystallites in films of n-octadecyl stearate

The basal parameters of the unit cell can be obtained from the relations:

$$|\underline{a}| = \frac{1}{|\underline{a}^*| \ \sin\beta} = \frac{1}{|\underline{\acute{a}}^*|}$$

$$|\underline{b}| = \frac{1}{|\underline{b}^*|}$$

Often it is also worthwhile to refine the parameters $|\underline{\acute{a}}^*|$, and $|\underline{b}^*|$, by the relation $|\underline{r}|^2 = h^2|\underline{\acute{a}}^*|^2 + k^2|\underline{b}^*|^2$. Here, $|\underline{r}|$ is the radius of any particular circle and h and k are the Miller indices associated with the reflection represented by the circle.

Because of the assumptions made ψ_a is a measure of β, the monoclinic angle, which is given by the relation $\beta = \psi_a + 90°$. ψ_a is best determined for patterns from crystallites in which the b axis of the crystallites is parallel to the direction of the incident radiation. The reflections on the layer lines are ignored and the intercepts of the layer lines with the y axis are measured. This has already been discussed in the section on patterns of group I.

In Table 3 the final refined parameters are summarized and compared with those determined for single crystals of n-cetyl palmitate by R. Kohlhaas (22) using x-rays as the incident radiation. The molecules of the two compounds are expected to be arranged in a similar fashion. The agreement for the parameters that were determinable is good.

Table 3. Comparison of the lattice constants of n-octadecyl stearate and n-cetyl palmitate

Parameter	n-octadecyl stearate observed	n-cetyl palmitate by Kohlhaas, R. (22)	n-cetyl palmitate by Schoon, Th. (23)
$\lvert \underline{a} \rvert$	5.56 A	5.61 A	5.60
$\lvert \underline{b} \rvert$	7.53 A	7.42 A	7.49
$c \sin\beta$	——	77.79 A	76.6 A
β	62°	61.3°	60.8°

2. Example 2 - analysis of diffraction patterns from reoriented films of stearic acid

Figures 24 and 25 are photographs of diffraction patterns of films of stearic acid that were reoriented by a mechanical shearing force. The patterns were obtained from a film about 200 A to 300 A thick. In Figure 24 the direction of rubbing was parallel to the direction of the incident radiation. In Figure 25, the direction of the incident radiation was perpendicular to the rubbing direction, the film being rubbed from left to right with respect to the photograph[1].

Diffuse bands of positive slope and containing many reflections are easily visible on the photograph of Figure 25. The "d" spacing of these bands is equal to about 2.54 A which

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[1] Patterns similar to Figure 25 were first well explained by Germer and Storks (13).

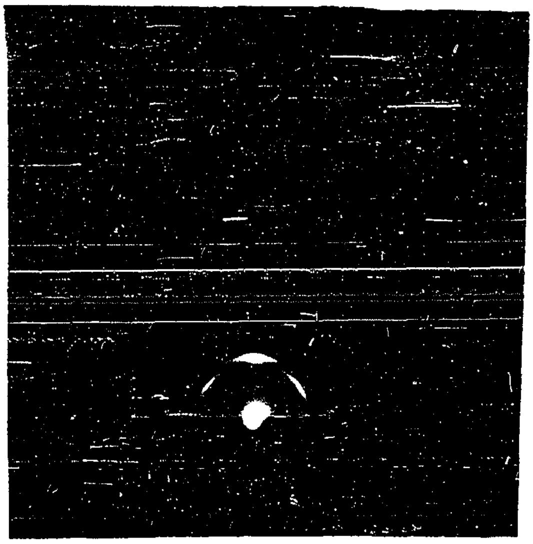

Figure 24. Diffraction pattern obtained from a reoriented film of stearic acid approximately 200-300 A thick. The incident radiation was parallel to the direction of rubbing

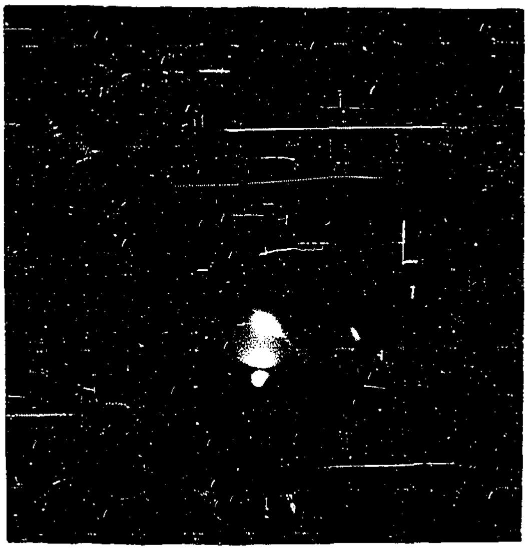

Figure 25. Diffraction pattern obtained from a reoriented film of stearic acid approximately 200-300 A thick. The incident radiation was perpendicular to direction of rubbing. The film was rubbed from left to right with respect to the photograph

agrees very well with that found for the separation of CH_2 units along an n-hydrocarbon chain. The bands apparently are the result of scattering from molecules inclined by 4°-6° to the plane of the metal surface and pointing against the rubbing direction.

On the photograph a line can be seen which passes through the position of the primary beam and which contains many closely spaced reflections. These reflections have been caused by scattering from planes in the crystallites that are separated by about 50A. The only planes in the crystallites that can be expected to be so widely spaced are 00ℓ planes. Therefore, the reflections on this line will be assumed to have indices 00ℓ . Lines parallel to 00ℓ also occur in the pattern. Some of these lines are separated by an equal spacing. The distances to the reflections along the layer lines are measured from a line constructed perpendicular to the layer lines and passing through the position of the primary beam. The distances, so obtained, are tabulated in the same way as shown in Example I.

Patterns such as the one shown in Figure 24 are strikingly different from those usually encountered for films of n-hydrocarbon derivatives. The fact that no layer lines are present is explainable by considering the orientation of the molecular chains with respect to the direction of the incident radiation. The previous discussion has established that the reoriented films of stearic acid contained crystallites in which the molecular chains were inclined by a small angle to the plane of the metal surface. Thus, Figure 24 is qualitatively expected to show an axially symmetric pattern and no layer lines because with the direction of the incident radiation approximately parallel to the molecular chains the row of regularly spaced CH_2 units is in a position which gives diffraction effects of low resolution. Scattering from the basal planes of the crystallites gives a sharp ring pattern which is arced in this photograph because the basal planes of the crystallites are not randomly arranged about the c axis. The radii of all the arcs and circles are measured and also tabulated.

The tabulated values of both photographs, such as those shown in Table 4 are now used as the radii of circles which are constructed with a common origin. This has been done in Figure 26. At this point the crystallites are postulated to have a monoclinic habit with the c axis of the crystallites parallel to the molecular axis. This is but one way of explaining the fact that the 00ℓ line is inclined to the direction of the c axis. The angle between the 00ℓ line and the layer lines is then a measure of β^* and the various planes, $\underline{a}^*$ $\underline{b}^*$, must intersect the pattern in the position of the layer lines.

Now, the circles which correspond to the conspicuous

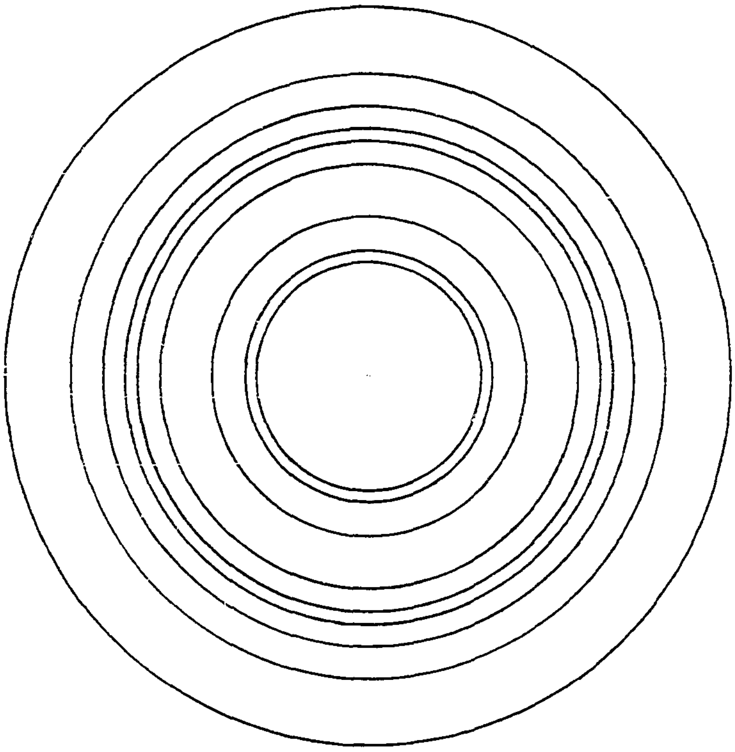

Figure 26. A preliminary cross section of the reciprocal lattice for crystallites in a multimolecular film of stearic acid

Table 4. Observed distances to reflections occurring in patterns of stearic acid

Reflection number	Distance	Relative intensity[a]
1	0.75	v.d
2	0.84	v.d
3	1.05	f
4	1.40	d
5	1.56	d
6	1.66	d
7	1.79	f
8	2.01	f
9	2.48	f

[a] Intensity scale: v.d > d > f.

reflections that occurred on equally spaced lines parallel to the 00ℓ line are marked and a line passing through the origin and intersecting all the circles is constructed, as is shown in Figure 27. The intersections of the marked circles with the line determine a unit distance which will be tried as the distance of one of the coordinate axes in the reciprocal lattice. Lines are constructed perpendicular to the first line and passing through the intersections of the circles with the line. A trial unit distance is again selected which will place each circle in the cross section of the reciprocal lattice at some intersection of the lines

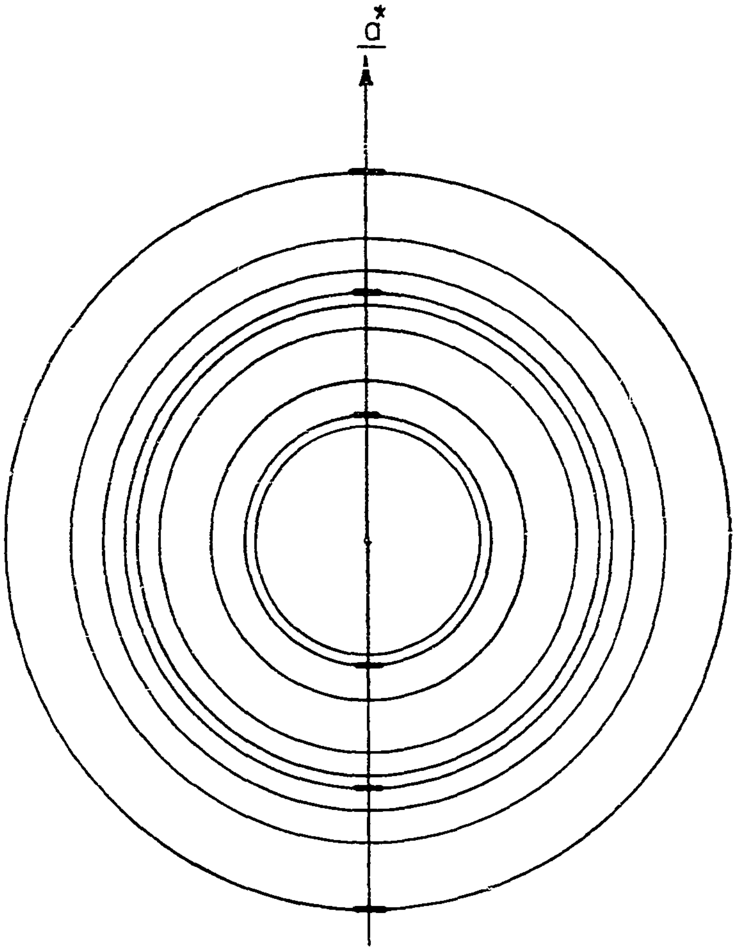

Figure 27. A preliminary cross section of the reciprocal lattice of crystallites in films of stearic acid. The unit distance believed to represent $|\underline{a}^*|$ has been indicated

forming the rectangular net. Such a fit is shown in Figure 28. If agreement is found, the parameters may then be refined. In the case of stearic acid, which has been the subject of numerous studies, three monoclinic modifications are known. The parameters from these modifications should be compared with those found by the above procedure. The equation, $|\underline{r}|^2 = h^2 |\underline{a}^*|^2 + k^2 |\underline{b}^*|^2$ can again be used to refine the parameters.

Table 5 is a summary of the parameters that were found and a comparison with the results of recent x-ray investigation.

Table 5. Comparison of the lattice constants of stearic acid

	Observed	Abrahamsson and von Sydow (24)
$\lvert\underline{a}\rvert$	9.40	9.35
$\lvert\underline{b}\rvert$	5.0	4.96
$\lvert\underline{c}\rvert$	50	50.76
β	128°	128° 14'
Form	monoclinic, form C	monoclinic, form C

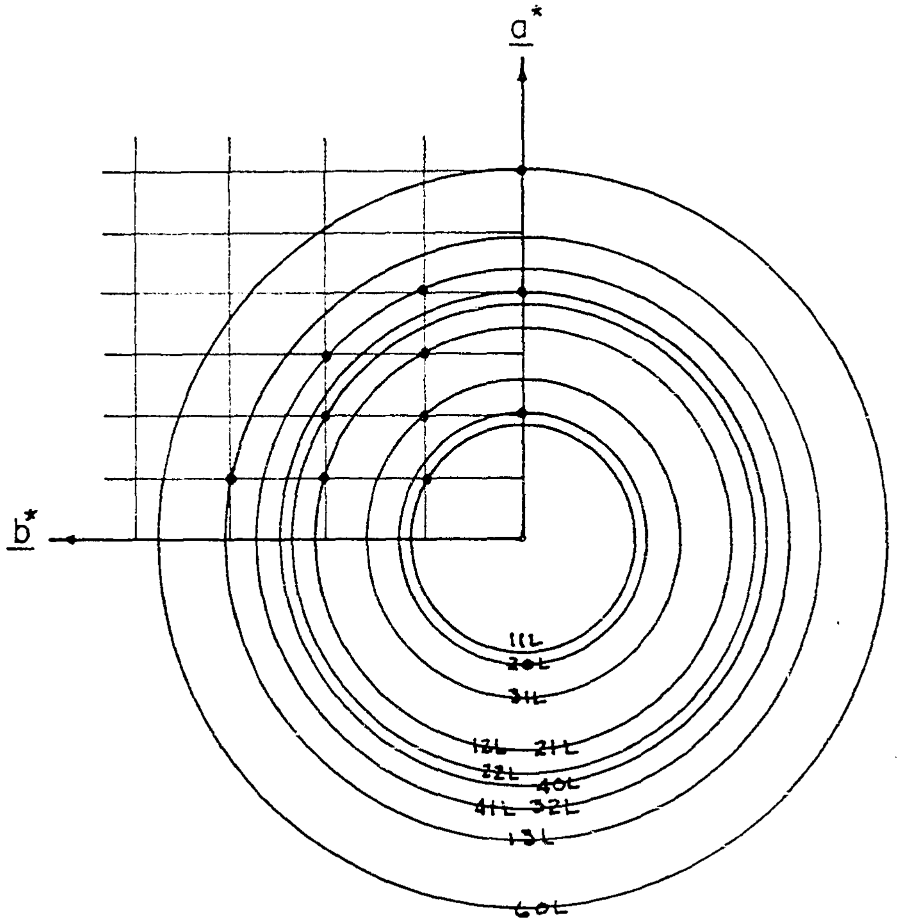

Figure 28. The "best fit" for the cross section of the reciprocal lattice of crystallites in films of stearic acid

VI. EXPERIMENTAL RESULTS

A. The n-Aliphatic Acids

1. Stearic acid

The structure and molecular orientation in multimolecular films of stearic acid have been the subject of several previous investigations (4, 5, 6). Multimolecular films of stearic acid have also been included in this investigation, mainly to confirm and extend the observations of previous studies of these films. Very limited data were available on the reorientation of molecules induced in multimolecular films of stearic acid by a unidirectionally applied shearing force. Germer and Storks (13) observed that reorientation in multimolecular films of stearic acid occurred with a change in crystallite structure from form A to form C. Sutula and Bartell (7) observed that crystallites of form C were also obtained by reorientation of multimolecular films of stearic acid originally containing crystallites of form B. These observations prompted an investigation to determine if reorientation could occur with no change in the structure of the crystallites in the film.

Several attempts were made to prepare films containing exclusively crystallites of form C of stearic acid. Efforts to prepare Langmuir-Blodgett films of form C of stearic acid met with limited success. The difficulties encountered are more fully described in Appendix II. Although form C of stearic acid was known to crystallize when the molten compound was cooled, films obtained by spreading fused stearic acid over a metal surface were too thick for optimum results with electron diffraction.

Acetone, ethyl alcohol, benzene, toluene and n-octane were then tried as solvents in preparing films of stearic acid by evaporation of dilute solutions on platinum surfaces. Various polymorphic forms were obtained in the multimolecular films when these solvents were used. The observations are summarized in Table 6. These results were found to be in agreement with the observations of von Sydow (25) who studied the crystallization behavior of the n-aliphatic acids by x-ray diffraction.

Figure 29 is a photograph of a typical diffraction pattern from a film of stearic acid prepared by evaporating a dilute solution of stearic acid in acetone on a platinum surface. The film contained crystallites of form C of stearic acid in an 001 orientation in the plane of the metal surface. The application of a shearing force to such films of stearic acid effected a reorientation of the molecules in the film. Figure 30 is a typical diffraction pattern obtained with reoriented films of stearic acid when the incident radiation was parallel to the shearing direction. Figure 31 is a diffraction pattern when the incident radiation was perpendicular

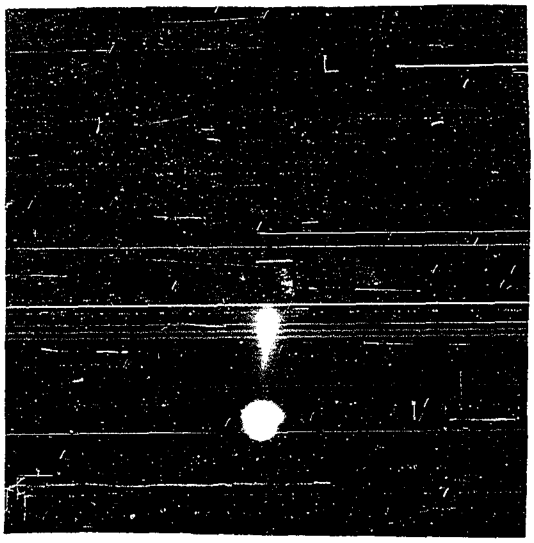

Figure 29. A diffraction pattern obtained with a film of stearic acid about 1000 A thick. The film was prepared by evaporating a dilute solution of stearic acid in acetone on a platinum surface

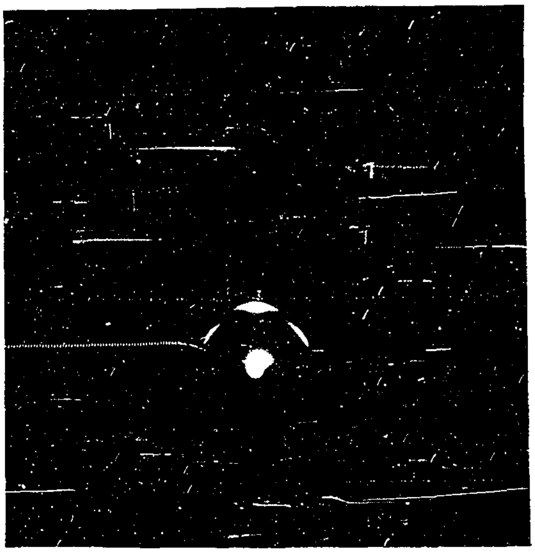

Figure 30. A diffraction pattern obtained with a reoriented film of stearic acid when the incident radiation was parallel to the shearing direction. The thickness of the film was about 280 A

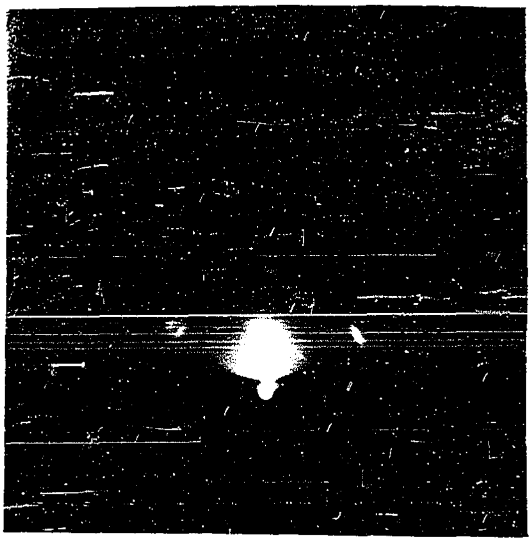

Figure 31. A diffraction pattern obtained with a reoriented film of stearic acid when the incident radiation was perpendicular to the shearing direction. The thickness of the film was about 280 A. Shear was applied from left to right with respect to the pattern as reproduced here

Figure 32. A diffraction pattern obtained with a film of arachidic acid, about 320 A thick. The incident radiation was perpendicular to the shearing direction. Shear was applied from left to right with respect to the pattern as reproduced here

Table 6. The polymorphic forms found in films of stearic acid prepared by the evaporation of various solutions

Solvent	Crystal form(s) observed Temperature, 20-25°C	Crystal form(s) observed by von Sydow (25) Temperature, above 18°C
Acetone	C	C
Ethyl alcohol	C	C
Benzene	C and B	C and B
Toluene	C and B	---
n-Octane	C and possibly A or B or both	C and A

to the shearing direction. The crystallites in these reoriented films were also of form C of stearic acid. They were arranged in the film so that the molecular chains were inclined at 3°-8° to the plane of the metal surface and were pointed against the shearing direction. Apparently, a transition in crystal structure was not required for reorientation to occur in multimolecular films of stearic acid.

Subsequently, it was found possible to produce thin films (several thousands of angstrom units) of stearic acid containing crystallites of form C by a thermal method (described in Appendix I). Such films were also reoriented by a unidirectionally applied, shearing force. The structure and molecular orientation of the reoriented films was identical to that previously described.

The molecular chains in films produced by the thermal method were found to be inclined in the same direction over large areas of the film. A shearing force was applied to such films in various directions with respect to the original direction of inclination of the molecular chains. From such experiments it was found that the molecular orientation in reoriented films was unrelated to the original inclination of the molecular chains. Germer and Storks (13) and Finch (11) have made similar observations in their work on films of stearic acid.

2. Arachidic acid

Diffraction patterns from multimolecular films of arachidic acid, $CH_3(CH_2)_{18}COOH$ were of group II and indicated an 001 orientation for the crystallites in the film. However, most patterns were not well resolved. The crystallites in the film were identified as probably of form C of arachidic acid on the basis of the orientation of the molecular chains and the position of a few reflections in the patterns.

Films of arachidic acid were observed to reorient when they were subjected to unidirectional shear. Figure 32 is a typical diffraction pattern obtained with such films in which the incident radiation was perpendicular to the shearing direction. The patterns are very similar to those obtained with reoriented films of stearic acid. The crystallites in the reoriented film were of form C of arachidic acid with the molecular chains pointed up against the shearing direction and inclined at 2-3° to the substrate surface.

3. n-Heptadecanoic acid

Diffraction patterns from multimolecular films of n-heptadecanoic acid were not well resolved. Nevertheless, they indicated the presence of crystallites with an 001 orientation. Attempts at indexing these patterns were unsuccessful mainly because of the poor resolution and the fact that the particular crystal form in the film was probably triclinic. Long-chain n-aliphatic acids containing an odd number of carbon atoms have been found to exist in at least three polymorphic forms, A', B', and C' (26). The first two forms are triclinic and the last form is monoclinic.

Although the structure of the multimolecular films could not be satisfactorily established, reorientation of the molecular chains was observed to occur with the application of a shearing force. The molecular chains, originally so inclined that Ψ_a had a value of approximately 20° were found to be inclined at 5°-6° to the metal surface after the application of the shearing force. As in reoriented films of stearic acid, the molecular chains in reoriented films of n-heptadecanoic acid pointed up against the shearing direction. Figures 33 and 34 show diffraction patterns of re-

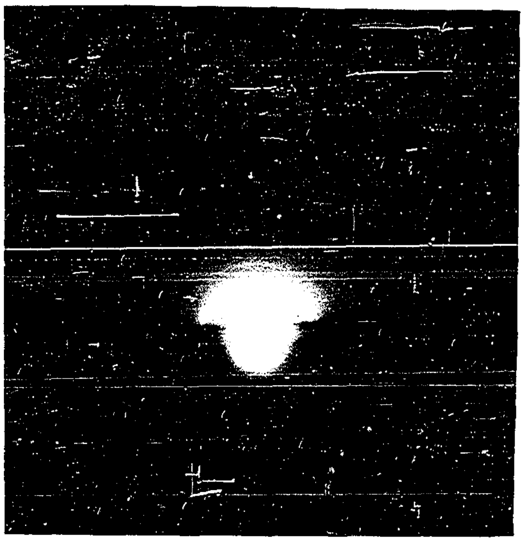

Figure 33. A diffraction pattern obtained with a reoriented film of n-heptadecanoic acid about 24 A thick. The incident radiation was parallel to the shearing direction

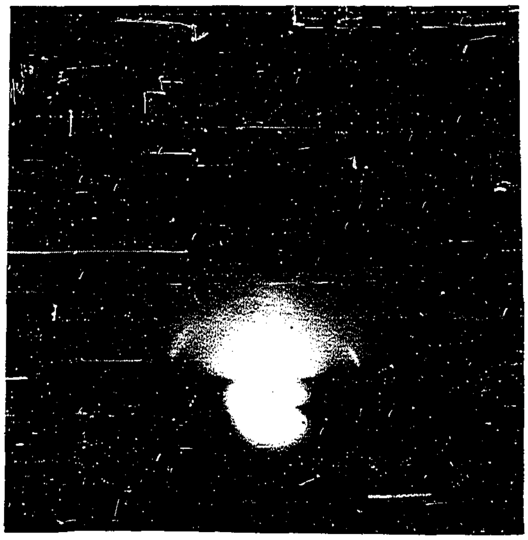

Figure 34. A diffraction pattern obtained with a reoriented film of n-heptadecanoic acid about 24 A thick. The incident radiation was perpendicular to the shearing direction. The direction of shear was from the left to the right with respect to the pattern reproduced here

oriented films of n-heptadecanoic acid in which the incident radiation was respectively parallel and perpendicular to the shearing direction. The patterns clearly show that the molecular chains were arranged in crystallites in the reoriented films, but it has not been possible to establish their crystalline form.

4. Palmitic acid

Preliminary studies by Sutula and Bartell (7) on multimolecular films of palmitic acid were performed with material that was not too pure. Diffraction patterns from films of palmitic acid of improved purity (better than 99 per cent) indicated that the molecular chains were inclined to the perpendicular to the plane of the metal surface. The crystallites were of form C of palmitic acid and had an 001 orientation in the plane of the metal surface. The previous study reported the molecular chains to be perpendicular to the plane of the metal surface. Figure 35 is a photograph of a diffraction pattern from a multimolecular film of palmitic acid obtained during the preliminary investigation whereas Figure 36 is a typical diffraction pattern from a multimolecular film of palmitic acid of improved purity.

The application of a shearing force to multimolecular films of palmitic acid induced a reorientation of the molecules in the film. The molecular chains in reoriented films

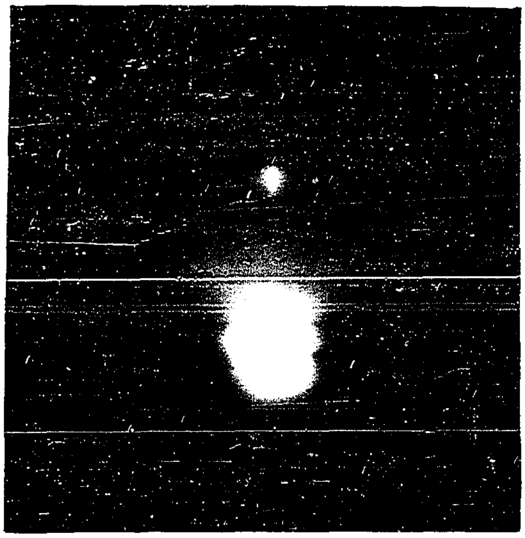

Figure 35. A diffraction pattern obtained from a film of palmitic acid about 1000 A thick. The purity of the palmitic acid was about 95 per cent

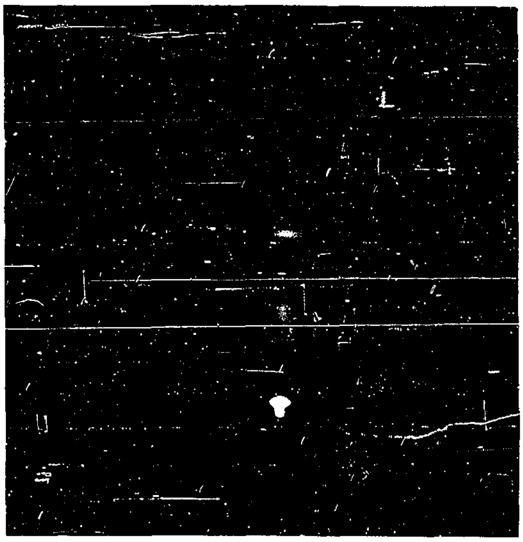

Figure 36. A diffraction pattern obtained from a film of n-palmitic acid about 1000 A thick. The purity of the palmitic acid was better than 99 per cent

of palmitic acid were inclined at 4°-9° to the plane of the metal surface and were pointed up against the shearing direction. Figure 37 is a diffraction pattern from a reoriented film of palmitic acid in which the incident radiation was parallel to the shearing direction. In Figure 38, the incident radiation was perpendicular to the shearing direction. The crystallites of the reoriented film were identified as form C of palmitic acid.

It is instructive to compare diffraction patterns from reoriented films of impure palmitic acid with those obtained with films of purer material. Figure 39 is a diffraction pattern obtained with a film of impure palmitic acid in which the incident radiation was perpendicular to the shearing direction. $h0\ell$ lines of reoriented crystallites are present in the patterns from films of both the pure and impure material. These reoriented crystallites are of form C of palmitic acid. However, Figure 39 also shows layer lines with reflections parallel to the shadow edge. These indicate the presence of crystallites in an 001 orientation in the film. Patterns of this character have also been observed for a few other compounds. They are presented and discussed below.

5. Miscellaneous acids

Multimolecular films of isostearic acid approximately

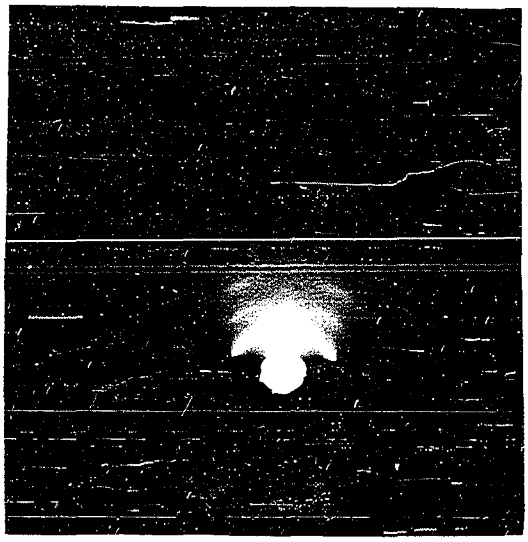

Figure 37. A diffraction pattern obtained with a reoriented film of palmitic acid about 320 A thick. The incident radiation was parallel to the shearing direction

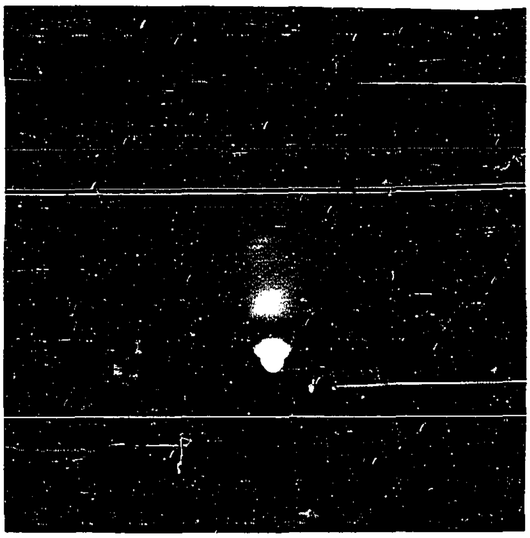

Figure 38. A diffraction pattern obtained with a reoriented film of palmitic acid about 320 A thick. The incident radiation was perpendicular to the shearing direction. Shear was applied from right to left with respect to the pattern as reproduced here

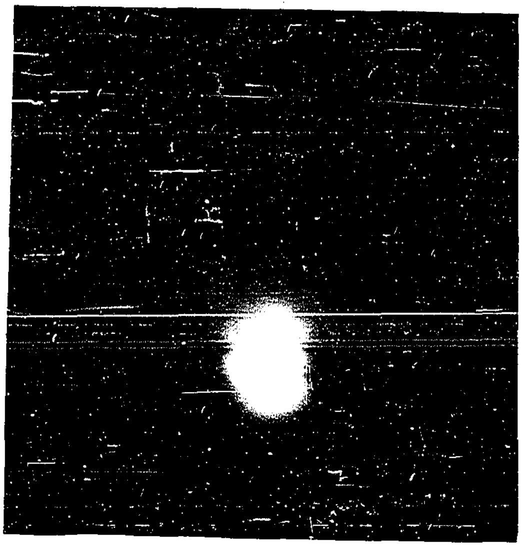

Figure 39. A diffraction pattern from a reoriented film of palmitic acid about 100 A thick. The incident radiation is perpendicular to the shearing direction. Shear was applied from left to right with respect to the pattern as reproduced here

Figure 40. A diffraction pattern from a film of isostearic acid approximately 120 A thick

120 A in average thickness gave electron diffraction patterns such as Figure 40 and Figure 41. The patterns are clearly of group II and indicate an 001 orientation for the crystallites in the film. Although the patterns are well resolved, they have not been successfully indexed and it is possible that the form of the crystallites is triclinic.

Sutula and Bartell (7) have reported that multimolecular films of isostearic acid did not reorient when subjected to unidirectional shear. In more extensive work with films of this compound, reorientation of the molecules by a shearing force was observed. Figures 42 and 43 show diffraction patterns obtained with reoriented films of isostearic acid in which the incident radiation was respectively parallel to and perpendicular to the shearing direction. The crystallite form in the reoriented films appeared to be identical to that of the unrubbed, multimolecular films. As was observed for reoriented films of other compounds, the molecular chains pointed up against the shearing direction and in this case were inclined at 2°-5° to the plane of the metal surface.

Rubbing a film of a hydrocarbon derivative with soft tissue rapidly decreases the thickness of the film in the first few rubs. Because the films of isostearic acid that were rubbed in the preliminary investigation were quite thin it seems reasonable that reorientation could have been unobserved. It has been observed with hydrocarbon films that

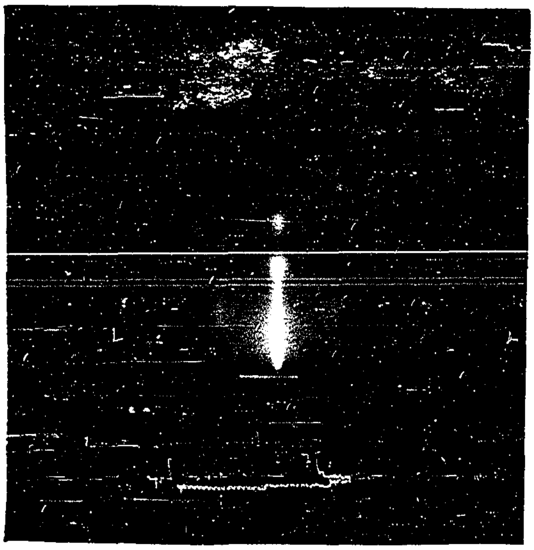

Figure 41. A diffraction pattern from a film of isostearic acid approximately 120 A thick

Figure 42. A diffraction pattern obtained with a film of isostearic acid about 280 A thick. The incident radiation was parallel to the shearing direction

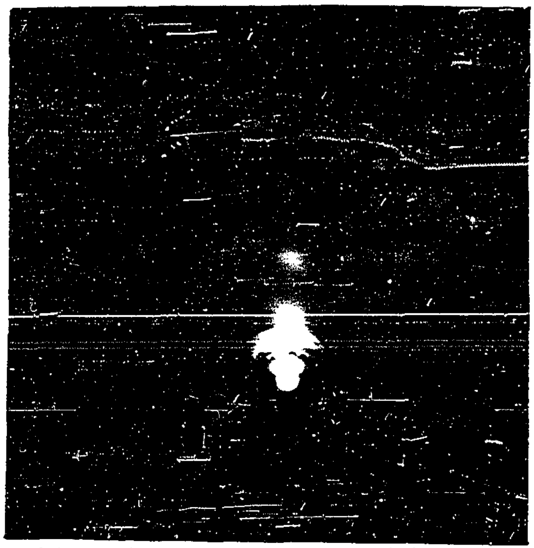

Figure 43. A diffraction pattern obtained with a film of isostearic acid about 280 A thick. The incident radiation was perpendicular to the shearing direction. Shear was applied from left to right with respect to the pattern as reproduced here

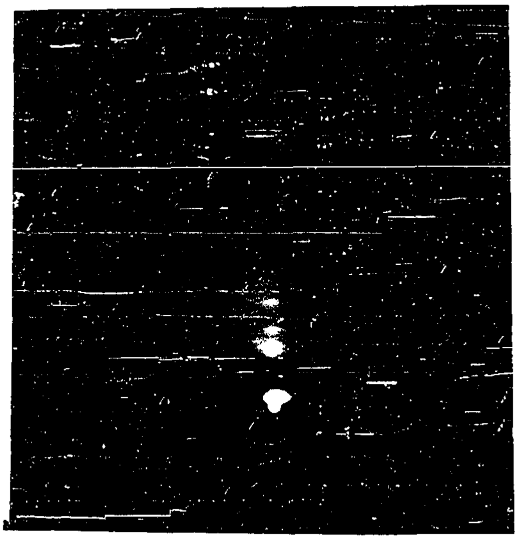

Figure 44. A diffraction pattern obtained with a film of sebacic acid about 250 A thick. The incident radiation was perpendicular to the shearing direction. Shear was applied from left to right with respect to the pattern as reproduced here

it is more effective to use much thicker films (about 1000 A) in tests of mechanically induced reorientation.

Films of isopalmitic acid have been previously investigated by Sutula and Bartell (7). The results obtained in this investigation confirm the earlier observations. The multimolecular films were polycrystalline with probably triclinic crystallites in an 001 orientation. ψ_a had the value of approximately 35°. The molecules in the film were reoriented with the application of a mechanical shearing force. The molecular chains in the reoriented film were inclined by about 4°-7° to the metal surface and were pointed up against the shearing direction.

Multimolecular films of dodecanoic acid were difficult to study by electron diffraction. The principal reason for this difficulty was that the films would sublime while being examined in the vacuum chamber of the electron diffraction unit. Films of dodecanoic acid which were subjected to mechanical shear did not appear to reorient. Diffraction patterns of such films indicated only that applied shear disordered the molecular arrangement in the film.

Multimolecular films of azelaic and sebacic acid were also included in this investigation. Films prepared by the evaporation of solutions of the compounds in acetone or by the spreading of the fused compounds over a metal surface were polycrystalline and apparently not oriented. A shearing force, unidirectionally applied, however, did orient the crystallites in the film so that the molecular chains were approximately parallel to the shearing direction and parallel to the plane of the metal surface. The diffraction patterns from these "oriented" films are quite striking for they show layer lines even though molecules of sebacic acid contain only ten carbon atoms. Figure 44, a pattern from a film of sebacic acid, obtained with the incident radiation perpendicular to the shearing direction, is typical of the patterns obtained with rubbed films of these two dicarboxylic acids.

Table 7 summarizes the parameters determined for the crystallites in multimolecular films of the aliphatic acids. Data from x-ray studies of these compounds, when available, have been included in the table. The results of experiments in which a mechanical shearing force was applied to the films are summarized in Table 8.

B. The Saturated n-Hydrocarbons

Multimolecular films of eleven members of the saturated n-hydrocarbons were studied in this investigation. The films were prepared by evaporating solutions of the compounds in n-tetradecane or benzene or by spreading the fused material on a polished platinum surface. In general, the multimolecular films were made-up of crystallites having an 001 orientation in the plane of the metal surface. Crystallites of

Table 7. The parameters determined for crystallites in multimolecular films of the n-aliphatic acids

Compound	a	b	c	β	ψ_a	Crystal form
Stearic acid	9.40	5.0	50	128°	38°	monoclinic, form C
Abrahamsson and von Sydow (24)	9.35	4.96	50.76	128°14'	---	monoclinic, form C
Arachidic acid	----	----	-----	128-9°	38-9°	monoclinic, form C
extrapolated (24)	9.4	5.0	-----	128°	---	monoclinic, form C
n-Heptadecanoic acid	----	----	-----	---	20°	possibly triclinic
Palmitic acid	9.48	5.0	-----	127-9°	37-9°	monoclinic, form C
Verma (28)	9.68	5.05	46.86	128°57'	---	monoclinic, form C
Thibaud and Dupre La Tour (29)	9.41	5.00	45.9	129°10'	---	monoclinic, form C
Isostearic acid	----	----	-----	---	40-5°	possibly triclinic
Isopalmitic acid	----	----	-----	---	35°	possibly triclinic
Dodecanoic acid	----	----	-----	no reliable data obtained		
Sebacic acid	----	----	-----	---	random	monoclinic
Morrison and Robertson (30)	10.10	5.00	15.10	133.8°	---	monoclinic
Azelaic acid	----	----	-----	---	random	monoclinic
Caspari (31)	5.61	9.58	27.20	136°30'	---	monoclinic

Table 8. Observations on reorientation in multimolecular films of n-aliphatic acids

Compound	Unrubbed film		Rubbed film	
	Ψ[a]	Crystal form	α[a]	Crystal form
Stearic acid	38°	monoclinic, C	3-8°	monoclinic, C
Arachidic acid	38-9°	monoclinic, C	2-3°	monoclinic, C
n-Heptadecanoic acid	20°	possibly triclinic	5-6°	possibly triclinic
Palmitic acid	37-9°	monoclinic, C	4-9°	monoclinic, C
Isostearic acid	40-5°	possibly triclinic	2-5°	possibly triclinic
Isopalmitic acid	35°	possibly triclinic	4-7°	possibly triclinic
Dodecanoic acid	--	----	random	disordered film
Sebacic acid	random	monoclinic	0°	monoclinic
Azelaic acid	random	monoclinic	0°	monoclinic

[a] α is the angle of inclination of the molecular chains with the metal surface.

orthorhombic form were found in films of the pure, odd-numbered saturated hydrocarbons. Crystallites of monoclinic form were found in films of the pure, even-numbered n-hydrocarbons except for films of n-octadecane, n-eicosane, and n-docosane.

1. The odd-numbered saturated n-hydrocarbons

The multimolecular films of the odd-numbered, saturated n-hydrocarbons were found to be very similar in their structure and molecular orientation. The members of this series that were investigated were n-tricosane ($C_{23}H_{48}$), n-heptacosane ($C_{27}H_{56}$), n-nonacosane ($C_{29}H_{60}$) and n-hentriacontane ($C_{31}H_{64}$). The films contained crystallites of orthorhombic form having an 001 orientation in the plane of the metal surface. Figures 45, 46, 47 and 48 are typical diffraction patterns from the multilayer films of each of these compounds. The basal parameters which were determined for the crystallites in each of these films were identical to within the experimental error of the determination. The average values were $|\underline{a}| = 5.0$ A; $|\underline{b}| = 7.5$ A.

When a mechanical shearing force was applied unidirectionally to films of n-heptacosane, n-nonacosane and n-hentriacontane the molecules were found to reorient. Films of n-tricosane, however, were disarranged by the mechanical shear.

Figure 49 is a diffraction pattern from a rubbed film of n-tricosane. Only diffuse bands can be seen on the pattern. Figures 50, 51 and 52 show respectively diffraction patterns from films of n-heptacosane, n-nonacosane and n-hentriacontane in which the incident radiation was perpendicular to the direction of rubbing. The difference between Figure 49 and Figures 50, 51 and 52 is very striking.

The principal features of the diffraction patterns from the reoriented films of n-heptacosane, n-nonacosane and n-hentriacontane are very similar to the patterns obtained

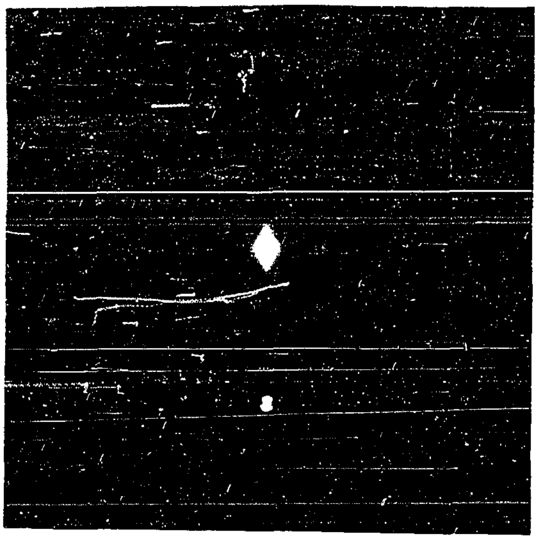

Figure 45. A diffraction pattern obtained with a film of n-tricosane about 1000 A thick

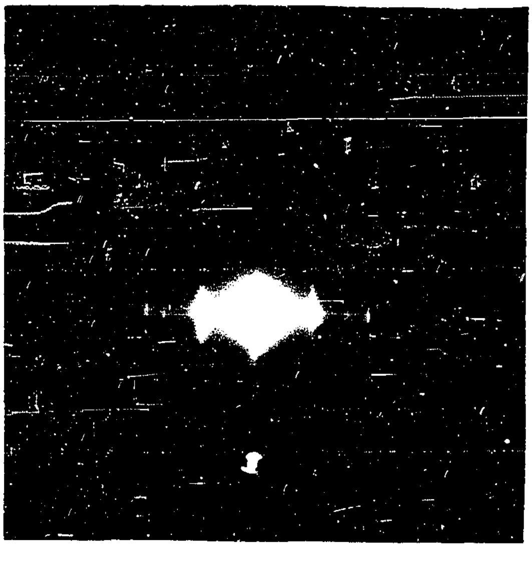

Figure 46. A diffraction pattern obtained with a film of n-heptacosane about 1000 A thick

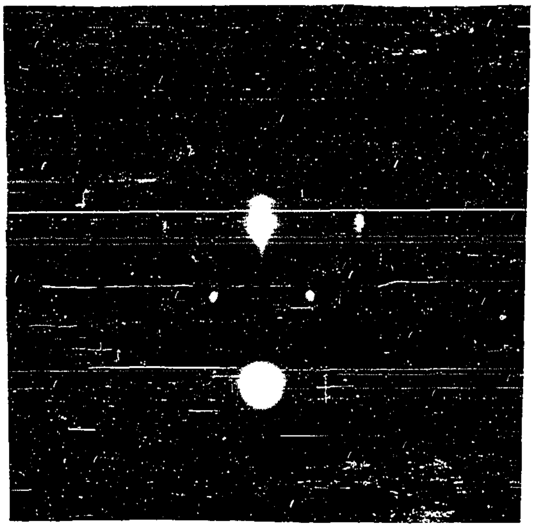

Figure 47. A diffraction pattern obtained with a film of n-nonacosane about 1000 A thick

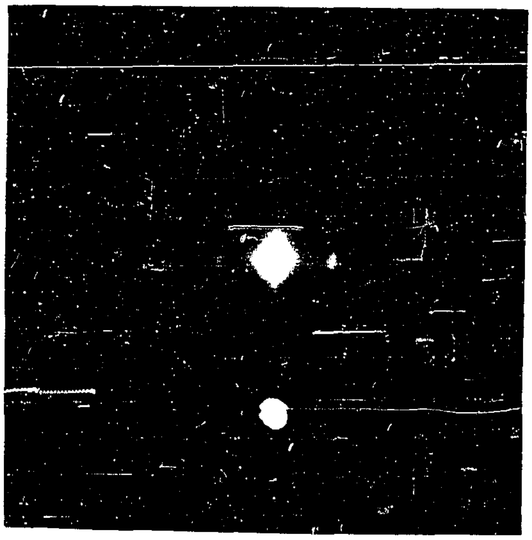

Figure 48. A diffraction pattern obtained with a film of n-hentriacontane about 1000 A thick

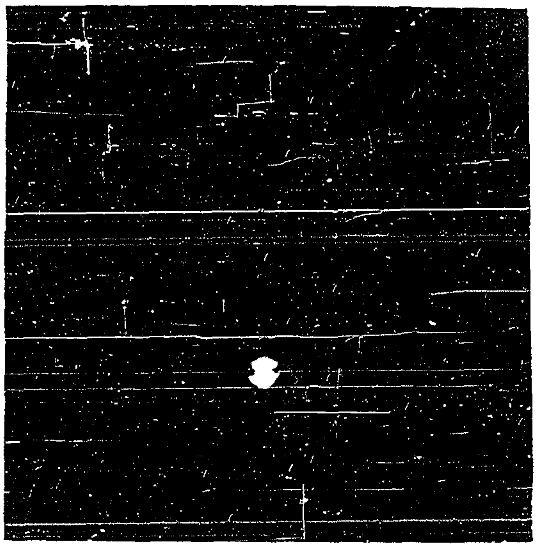

Figure 49. A diffraction pattern obtained with a reoriented film of n-tricosane after application of a shearing force. The thickness of the film was 160 A

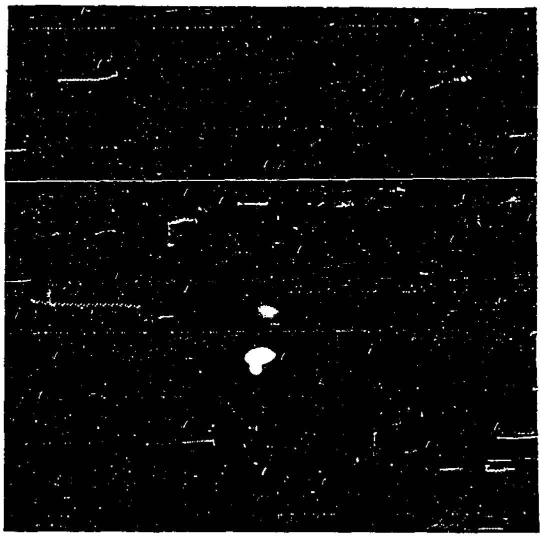

Figure 50. A diffraction pattern obtained with a reoriented film of n-heptacosane when the incident radiation was perpendicular to the shearing direction. The thickness of the film was about 330 A. Shear was applied from left to right with respect to the pattern as reproduced here

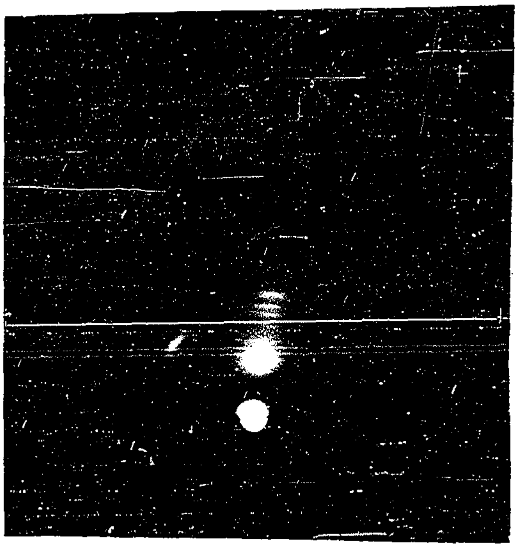

Figure 51. A diffraction pattern obtained with a film of n-nonacosane about 300 A thick. The incident radiation was perpendicular to the shearing direction. Shear was applied from left to right with respect to the pattern as reproduced here

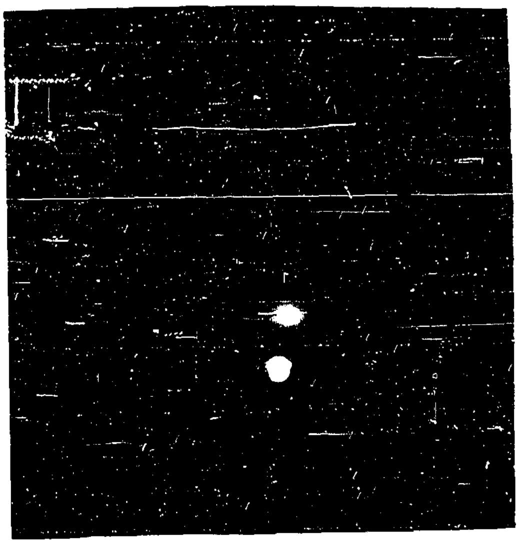

Figure 52. A diffraction pattern obtained with a reoriented film of n-hentriacontane about 250 A thick. The incident radiation was perpendicular to the shearing direction. Shear was applied from left to right with respect to the pattern as reproduced here

from the reoriented films of the aliphatic acids. The reoriented crystallites, however, were of orthorhombic form and were positioned in the plane of the metal surface so that the molecular chains were inclined by 12°-14°, 10°-11°, and 8°-10°, to the metal surface, respectively, for films of n-heptacosane, n-nonacosane and n-hentriacontane. As in other reoriented films, the molecular chains were pointed up against the shearing direction.

2. The even-numbered saturated n-hydrocarbons

Multimolecular films of seven members of the even-numbered n-hydrocarbons were studied in this investigation. These members were: n-octadecane ($C_{18}H_{38}$), n-eicosane ($C_{20}H_{42}$), n-docosane ($C_{22}H_{46}$), n-hexacosane ($C_{26}H_{54}$), n-octacosane ($C_{28}H_{58}$), n-triacontane ($C_{30}H_{62}$) and n-dotriacontane ($C_{32}H_{66}$).

Diffraction patterns from multimolecular films of n-octadecane contained very few features ascribable to the presence of crystallites in the films. Figure 53 shows a typical pattern from a film of n-octadecane. From such diffraction patterns it was inferred that the films of n-octadecane were polycrystalline with probably orthorhombic crystallites in approximately an 001 orientation. The purity of the n-octadecane used to prepare the films was about 95 per cent. A typical diffraction pattern from a disordered

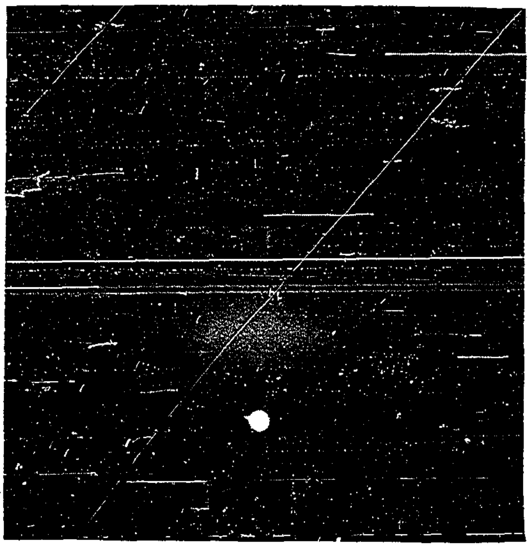

Figure 53. A diffraction pattern obtained with a film of n-octadecane about 1000 A thick

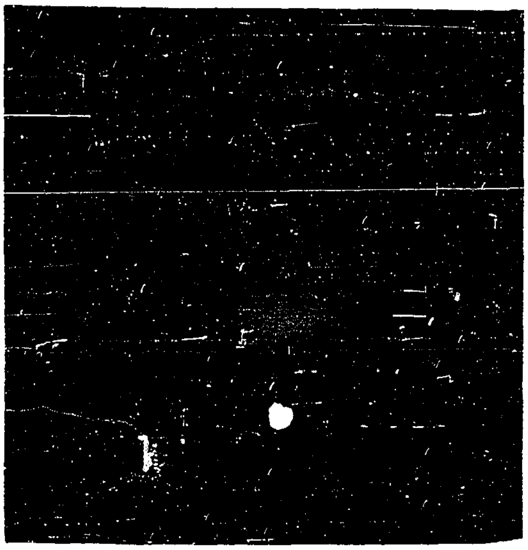

Figure 54. A diffraction pattern obtained with a film of n-octadecane after applying shear. The thickness of the film was about 95 A

film of n-octadecane is shown in Figure 54.

Multimolecular films of n-eicosane were noticeably more crystalline than those of n-octadecane. The crystallites had an 001 orientation in the plane of the metal surface. As in films of n-octadecane, the crystallites appeared to be of orthorhombic form with basal parameters $|\underline{a}| = 7.4$ A, $|\underline{b}| = 5$ A. The purity of the n-eicosane used to prepare the films was about 95 per cent.

A unidirectionally applied shearing force did not effect disorder quite as rapidly in films of n-eicosane as in films of n-octadecane. Even at a thickness of about two molecular layers reflections of the type 11ℓ , 20ℓ were still visible. Prolonged rubbing finally gave diffraction patterns interpretable in terms of a random distribution of the molecules in the film.

Diffraction patterns from multimolecular films of n-docosane were strikingly different from those of films of n-octadecane and n-eicosane. The crystallites in these films had an 001 orientation in the plane of the metal surface and appeared to be of triclinic form. Figure 55 is a typical diffraction pattern from a multimolecular film of n-docosane. Multimolecular films of n-docosane were less rapidly disordered by shear than films of either n-octadecane or n-eicosane. Nevertheless, prolonged application of a shearing force to films of n-docosane appeared to completely dis-

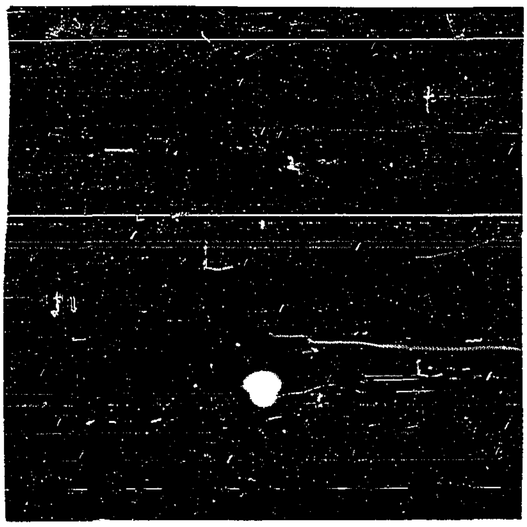

Figure 55. A diffraction pattern obtained with a film of n-docosane about 1000 A thick

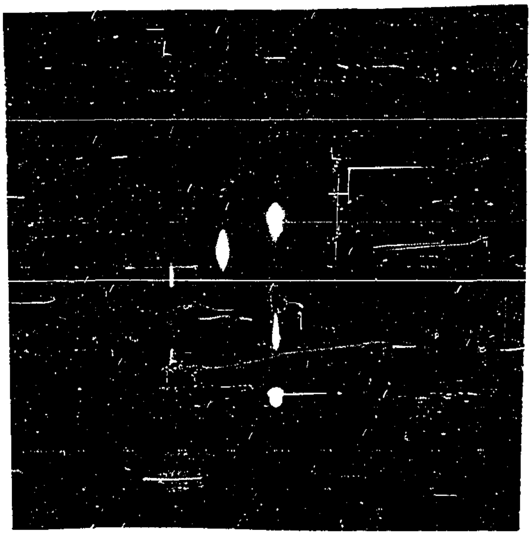

Figure 56. A diffraction pattern obtained with a film of n-hexacosane about 1000 A thick

order the structure and molecular orientation in the films.

Diffraction patterns from multimolecular films of n-hexacosane, n-octacosane and n-triacontane were very similar. These films were found to contain monoclinic crystallites in an 001 orientation in the plane of the substrate surface. The average parameters which were determined for these crystallites were $|\underline{a}| = 5.5$ A, $|\underline{b}| = 7.4$ A. Figures 56, 57 and 58 show, respectively, typical diffraction patterns from films of n-hexacosane, n-octacosane and n-triacontane.

When a shearing force was unidirectionally applied to the multimolecular films of the above compounds, reorientation of the molecules in the film occurred. The crystallites in the reoriented films were identical to those in the unrubbed, multimolecular films in their crystal form and in their basal and angular parameters. Figures 59, 60, and 61 are, respectively, diffraction patterns from reoriented films of n-hexacosane, n-octacosane and n-triacontane in which the incident radiation was perpendicular to the shearing direction. As in other reoriented films the molecular chains were inclined at a small angle to the metal surface and were pointed up against the shearing direction. The angles by which the molecular chains were inclined to the plane of the metal surface were 4°-6° for n-hexacosane, 3°-4° for n-octacosane and 3°-6° for n-triacontane.

Multimolecular films of n-dotriacontane were found to

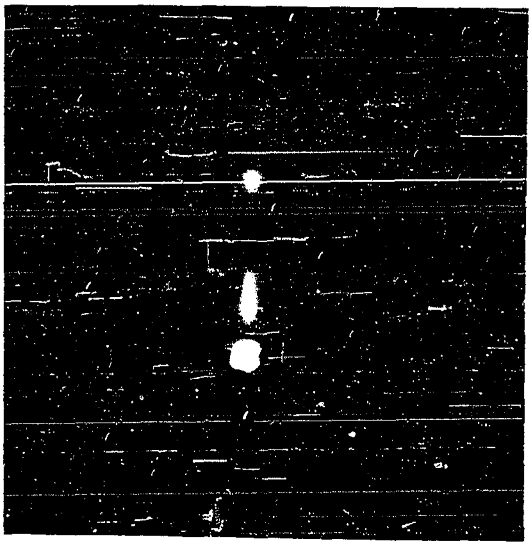

Figure 57. A diffraction pattern obtained with a film of n-octacosane about 1000 A thick

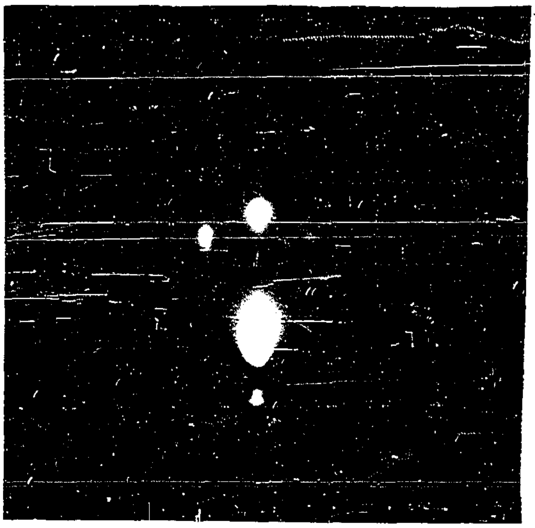

Figure 58. A diffraction pattern obtained with a film of n-triacontane about 1000 A thick

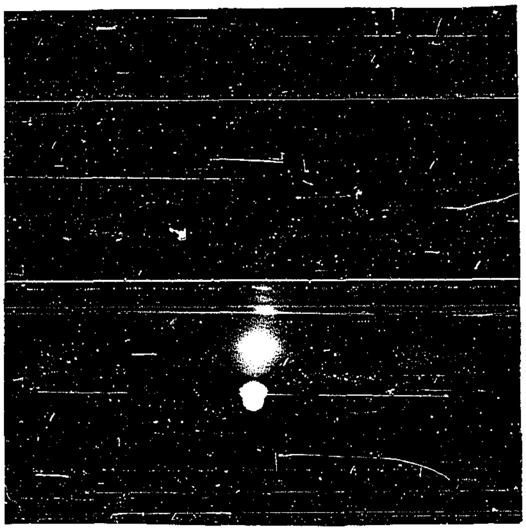

Figure 59. A diffraction pattern obtained with a reoriented film of n-hexacosane when the incident radiation was perpendicular to the shearing direction. The thickness of the film was about 280 A. Shear was applied from left to right with respect to the pattern as reproduced here

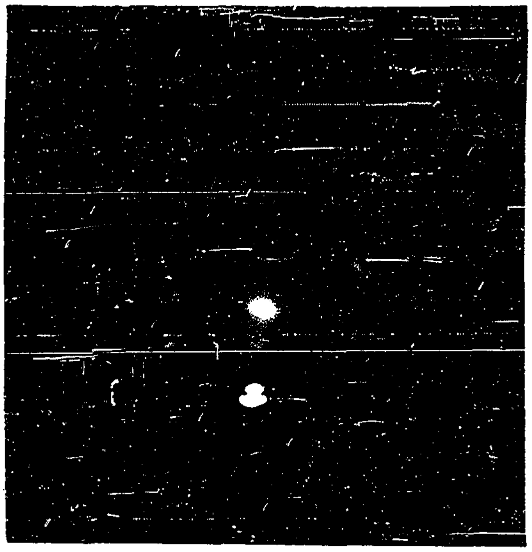

Figure 60. A diffraction pattern obtained with a reoriented film of n-octacosane about 190 A thick. The incident radiation was perpendicular to the shearing direction. Shear was applied from left to right with respect to the pattern as reproduced here

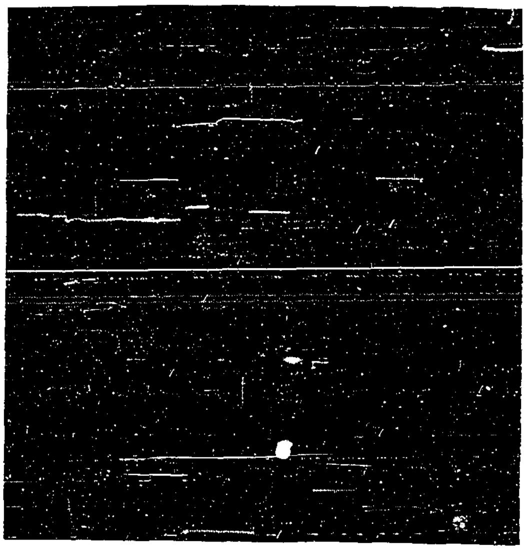

Figure 61. A diffraction pattern obtained with a reoriented film of n-triacontane about 300 A thick. The incident radiation was perpendicular to the shearing direction. Shear was applied from left to right with respect to the pattern as reproduced here

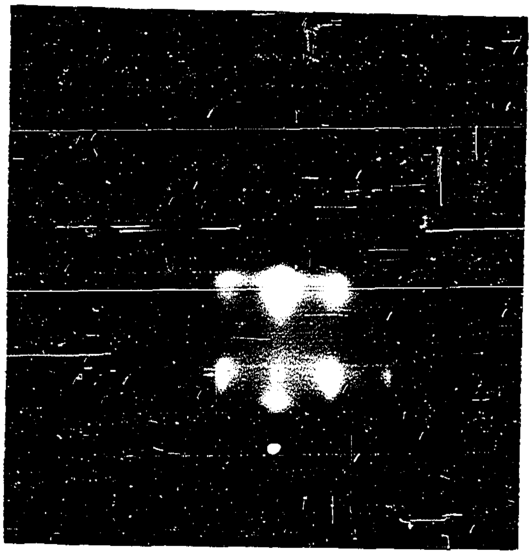

Figure 62. A diffraction pattern obtained with a film of impure n-dotriacontane about 1000 A thick

contain orthorhombic crystallites in an 001 orientation in the plane of the metal surface. The purity of the n-dotriacontane used to prepare the films was probably no better than 95 per cent. Figure 62 is a typical diffraction pattern from a multimolecular film of n-dotriacontane. The basal parameters of the crystallites were $|\underline{a}| = 7.35$ A, $|\underline{b}| = 5.0$ A.

When multimolecular films of n-dotriacontane were subjected to unidirectionally applied shear, only a fraction of the molecules in the film were observed to reorient. Patterns such as Figure 63 were obtained for these films, which incidentally are very similar to those obtained by Brummage (14) during his investigation of the effect of shear in multimolecular films of three n-hydrocarbons. The patterns indicate that a large fraction of the crystallites in the film have retained their 001 orientation. However, small arcs occur quite near the position of the primary beam. The arcs are caused by reoriented crystallites. These reoriented crystallites are arranged so that the molecular chains are inclined by $\sim 3°$ to the plane of the metal surface and are pointed up against the rubbing direction.

Table 9 summarizes the parameters that have been determined for the crystallites which were found in multimolecular films of the saturated n-hydrocarbons. Data from x-ray studies of these compounds, when available, have been in-

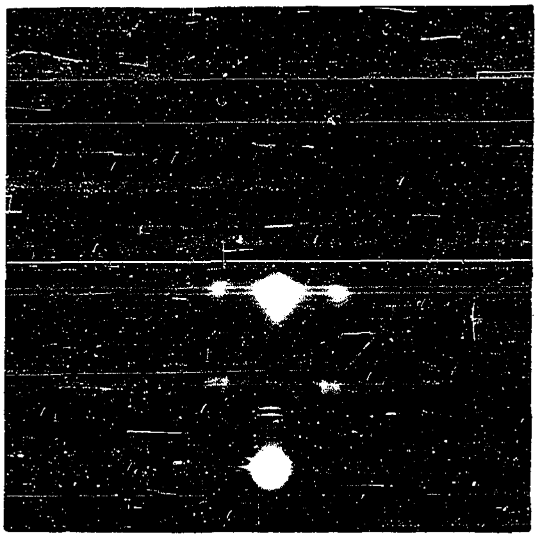

Figure 63. A diffraction pattern obtained with a film of n-dotriacontane after applying shear. The incident radiation was parallel to the shearing direction. The thickness of the film was about 150 A

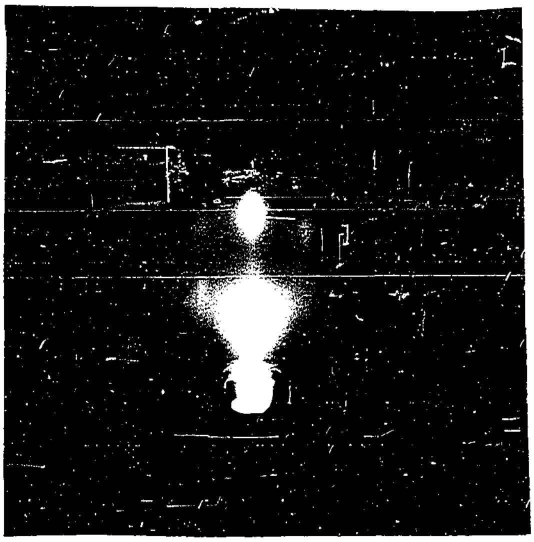

Figure 64. A diffraction pattern obtained with a film of n-octadecyl stearate about 1000 A thick

Table 9. The parameters determined for crystallites found in multimolecular films of saturated n-hydrocarbons

Compound	a	b	c	β	ψ_a	Crystal form
n-Octadecane	----	----	-----	---	0°	orthorhombic
extrapolated (32)	7.43	4.96	-----	90°	---	orthorhombic
n-Eicosane	7.4	5	-----	90°	0°	orthorhombic
extrapolated (32)	7.43	4.96	-----	90°	---	orthorhombic
n-Docosane	----	----	-----	---	---	triclinic
Data from films of n-docosane fit extrapolated results of Mazee (33)						
n-Tricosane	5.0	7.5	-----	90°	0°	orthorhombic
Smith (35)	4.97	7.48	62	90°	---	orthorhombic
n-Hexacosane	5.5	7.4	-----	118°	28°	monoclinic
extrapolated (34)	5.57	7.42		119°	---	monoclinic
n-Heptacosane	5.0	7.5	-----	90°	0°	orthorhombic
Smith (35)	4.97	7.48	72.59	90°	---	orthorhombic
n-Octacosane	5.5	7.4	-----	118°	28°	monoclinic
extrapolated (34)	5.57	7.42	-----	119°	---	monoclinic
n-Nonacosane	5.0	7.5	-----	90°	0°	orthorhombic
Smith (35)	4.97	7.48	77.70	90°	---	orthorhombic
n-Triacontane	5.5	7.4	-----	118°	28°	monoclinic
extrapolated (34)	5.57	7.42	-----	119°	---	monoclinic
n-Hentriacontane	5.0	7.5	-----	90°	0°	orthorhombic
Smith (35)	4.97	7.48	-----	90°	---	orthorhombic

Table 9. (Continued)

Compound	a	b	c	β	ψ_a	Crystal form
n-Dotriacontane	7.35	5.0	-----	90°	0°	orthorhombic
extrapolated (32)	7.43	4.96	-----	90°	---	orthorhombic

cluded in the table. The results of experiments in which a mechanical shearing force was applied to the films are summarized in Table 10.

C. The Long-Chain Esters

The multimolecular films of three esters, n-octadecyl stearate, n-hexadecyl stearate and n-dodecyl laurate were included in this study. The diffraction patterns from the multimolecular, unrubbed films were quite similar. Crystallites of monoclinic form with an 001 orientation in the plane of the metal surface were found in the films of the three compounds. The parameters determined for these crystallites are quite similar to those found for form B of stearic acid. They are also similar to the parameters determined by Kohlhaas (22) and Th. Schoon (23) who studied single crystals of hexadecyl palmitate by x-ray and electron diffraction. Figures 64, 65 and 66 illustrate the type of diffraction patterns obtained, respectively, from multimolecular films of n-octadecyl stearate, n-hexadecyl stearate and n-dodecyl laurate.

Unidirectionally applied shear was found to reorient the molecules in multimolecular films of n-octadecyl stearate and n-hexadecyl stearate. The films of n-dodecyl laurate were disarranged by shear.

Figure 67 is a typical diffraction pattern obtained from

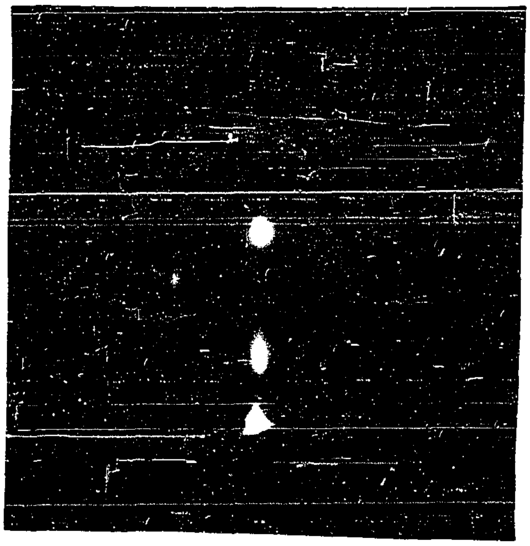

Figure 65. A diffraction pattern obtained with a film of n-hexadecyl stearate about 1000 A thick

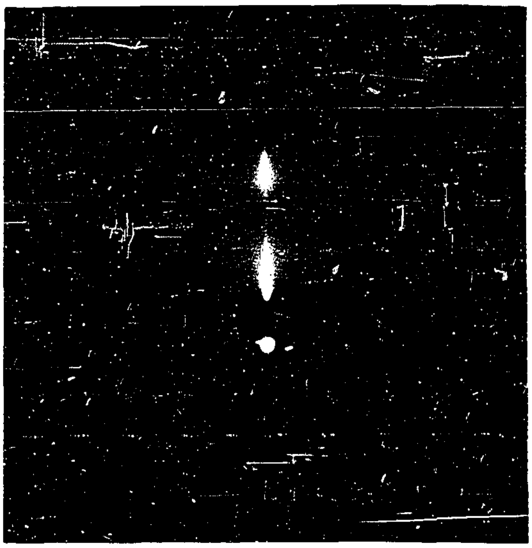

Figure 66. A diffraction pattern obtained with a film of n-dodecyl laurate about 1000 A thick

Figure 67. A diffraction pattern obtained with a film of n-dodecyl laurate after applying shear. The thickness of the film was about 48 A

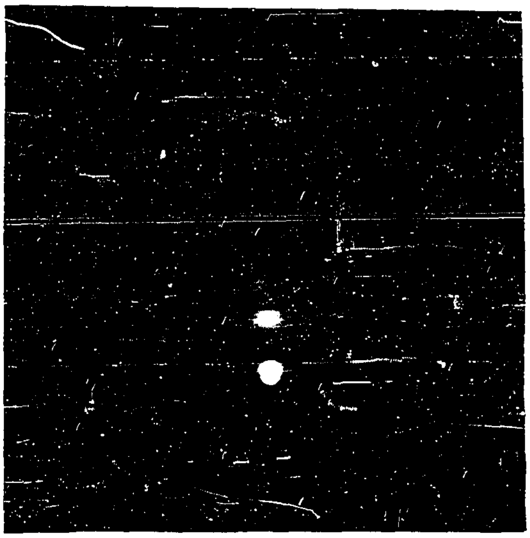

Figure 68. A diffraction pattern obtained with a film of n-octadecyl stearate about 290 A thick. The incident radiation was perpendicular to the shearing direction. Shear was applied from right to left with respect to the pattern as reproduced here

Table 10. Observations on reorientation in multimolecular films of saturated n-hydrocarbons

Compound	Unrubbed film		Rubbed film	
	ψ_a	Crystal form	α	Crystal form
n-Octadecane	0°	orthorhombic	random	disordered film
n-Eicosane	0°	orthorhombic	random	disordered film
n-Docosane	---	triclinic	random	disordered film
n-Tricosane	0°	orthorhombic	random	disordered film
n-Hexacosane	28°	monoclinic	4-6°	monoclinic
n-Heptacosane	0°	orthorhombic	12-14°	orthorhombic
n-Octacosane	28°	monoclinic	3-4°	monoclinic
n-Nonacosane	0°	orthorhombic	10-11°	orthorhombic
n-Triacontane	28°	monoclinic	3-6°	monoclinic
n-Hentriacontane	0°	orthorhombic	8-10°	orthorhombic
n-Dotriacontane	0°	orthorhombic	3°	orthorhombic (partially reoriented)

films of n-dodecyl laurate after prolonged rubbing.

Figures 68 and 69 are diffraction patterns from reoriented films of n-octadecyl stearate in which the incident radiation was, respectively, perpendicular and parallel to the shearing direction. Figures 70 and 71 are diffraction patterns from reoriented films of n-hexadecyl stearate. The incident radiation was perpendicular to the shearing direc-

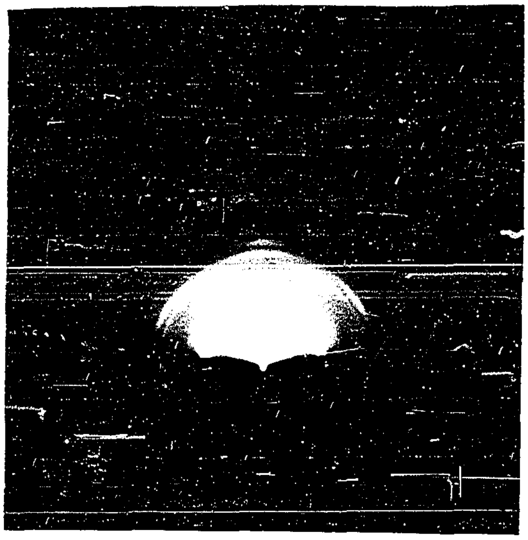

Figure 69. A diffraction pattern obtained with a reoriented film of n-octadecyl stearate about 290 A thick. The incident radiation was parallel to the shearing direction

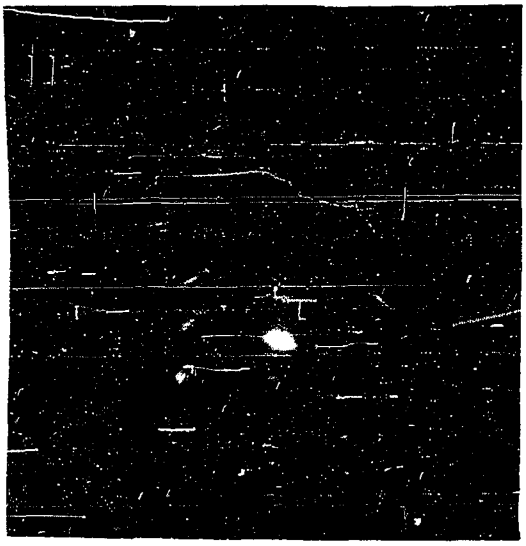

Figure 70. A diffraction pattern obtained with a reoriented film of n-hexadecyl stearate about 300 A thick. The incident radiation was perpendicular to the shearing direction. Shear was applied from left to right with respect to the pattern as reproduced here

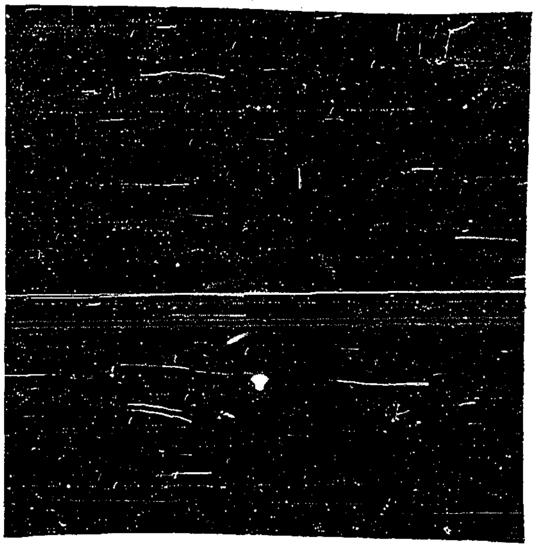

Figure 71. A diffraction pattern obtained with a reoriented film of n-hexadecyl stearate about 300 A thick. The incident radiation was parallel to the shearing direction

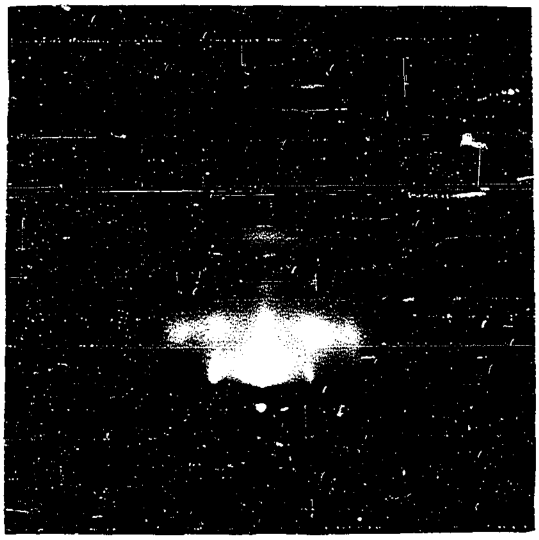

Figure 72. A diffraction pattern obtained with a film of stearamide about 90 A thick. The incident radiation was perpendicular to the shearing direction. Shear was applied from left to right with respect to the pattern as reproduced here

tion in Figure 70 and parallel to the shearing direction in Figure 71. As in other reoriented films, the molecular chains of n-octadecyl stearate and n-hexadecyl stearate were found to be inclined by a small angle to the plane of the metal surface and were pointed up against the shearing direction. This angle of inclination was 0-6° for n-octadecyl stearate and 0-5° for n-hexadecyl stearate. The crystallites in the reoriented films were identical to the crystallites in the multimolecular, unrubbed films.

Table 11 contains a summary of the parameters that were determined for the crystallites in multimolecular films of the esters. Table 12 summarizes the observations on reoriented films of these compounds.

D. Miscellaneous Compounds

1. n-Octadecyl alcohol

Sutula and Bartell (7) have studied multimolecular films of n-octadecyl alcohol. Films of this substance were included in the present study mainly to observe the effect of a shearing force on the structure and molecular orientation in the films. The results obtained in this investigation confirm the earlier observations.

Multimolecular films of n-octadecyl alcohol contained orthorhombic crystallites in an 001 orientation in the plane of the metal surface. The parameters of the crystallites

Table 11. The parameters determined for crystallites found in multimolecular films of some long-chain esters

Compound	a	b	c	β	ψ_a	Crystal form
n-Octadecyl stearate	5.56	7.53	-----	118°	28°	monoclinic
n-Hexadecyl stearate	5.65	7.40	-----	118°	28°	monoclinic
n-Dodecyl laurate	5.68	7.5	-----	120°	30°	monoclinic
n-Cetyl palmitate by Kohlhaas (22)	5.61	7.42	92.8	118.7°	---	monoclinic
n-Cetyl palmitate by Schoon (23)	5.60	7.49	93	119.2°	---	monoclinic

Table 12. Observations on reorientation in multimolecular films of some long-chain esters

Compound	Unrubbed film		Rubbed film	
	ψ_a	Crystal form	α	Crystal form
n-Octadecyl stearate	28°	monoclinic	0-6°	monoclinic
n-Hexadecyl stearate	28°	monoclinic	0-5°	monoclinic
n-Dodecyl laurate	30°	monoclinic	random	disordered film
n-Octadecyl alcohol	0°	orthorhombic	random	disordered film

were $|\underline{a}| = 4.97$, $|\underline{b}| = 7.45$. The purity of the n-octadecyl alcohol used in preparing the films was estimated to be about 98 per cent. A shearing force applied unidirectionally to the films rapidly disarranged the structure and molecular orientation in the films. Films of alcohols of long chain length, however, are expected to reorient with applied shear. Sanders and Tabor (27) have obtained a striking diffraction pattern from a reoriented film of melissyl alcohol ($C_{31}H_{63}OH$) when the film was prepared by rubbing the material onto a metal surface.

2. Stearamide

The diffraction patterns from multimolecular films of stearamide were not well resolved. The films were polycrystalline and the crystallites were possibly in an 001 orientation in the plane of the metal surface. Attempt to index the diffraction patterns were not successful. However, the molecular axis was found to be inclined to the metal surface, ψ_a having a value of about 20°.

When a shearing force was applied to the multimolecular films a reorientation of the molecules in the film did not appear to occur. Rather complex diffraction patterns, which are not as yet fully understood, were obtained such as the one shown in Figure 72. The purity of the stearamide used to prepare the films was about 95 per cent.

Table 13 summarizes the data obtained with films of n-octadecyl alcohol and stearamide. Table 14 contains the observations made when the films were subjected to shear.

Table 13. The parameters determined for crystallites found in multimolecular films of n-octadecyl alcohol and stearamide

Compound	$\lvert \underline{a} \rvert$	$\lvert \underline{b} \rvert$	$\lvert \underline{c} \rvert$	β	ψ_a	Crystal form
n-Octadecyl alcohol	4.97	7.45	49.4	90°	0°	Orthorhombic
n-Stearamide	----	----	----	---	20°	---

E. Rubbing Curves

In order to further investigate the reorientation of molecules in films by a mechanical shearing force, the decrease in the thickness of multimolecular films was observed

Table 14. Observations on the effect of a shearing force on multimolecular films of n-octadecyl alcohol and stearamide

Compound	ψ_a	Crystal form	α	Crystal form
n-Octadecyl alcohol	0°	orthorhombic	random	---
n-Stearamide	20°	---	---	---

with an ellipsometer after each application of a shearing force for a succession of shearing strokes on the films. This was done for films of a variety of n-hydrocarbon derivatives and for several types of films. The rubbing device (described on page 27) was used in these experiments to apply a shearing force to the films. The velocity of sliding was 3-4 centimeters per second and the load or weight of the slider was varied from about 250 grams to about 1250 grams.

Curve I of Figure 73 is representative of the type of curve obtained when the difference in ellipsometer reading, ΔE, was plotted against the number of shearing strokes performed on the film. The vertical scale can be converted to an approximate average thickness of film by using the relation, $\Delta E \doteq 1.5$ mm $\doteq 25$ A.

Curve II in Figure 73 was obtained by applying a shearing force to a film of stearic acid. The film contained 17 layers of stearic acid deposited by the method of Langmuir and Blodgett from an aqueous subphase of pH equal to one and

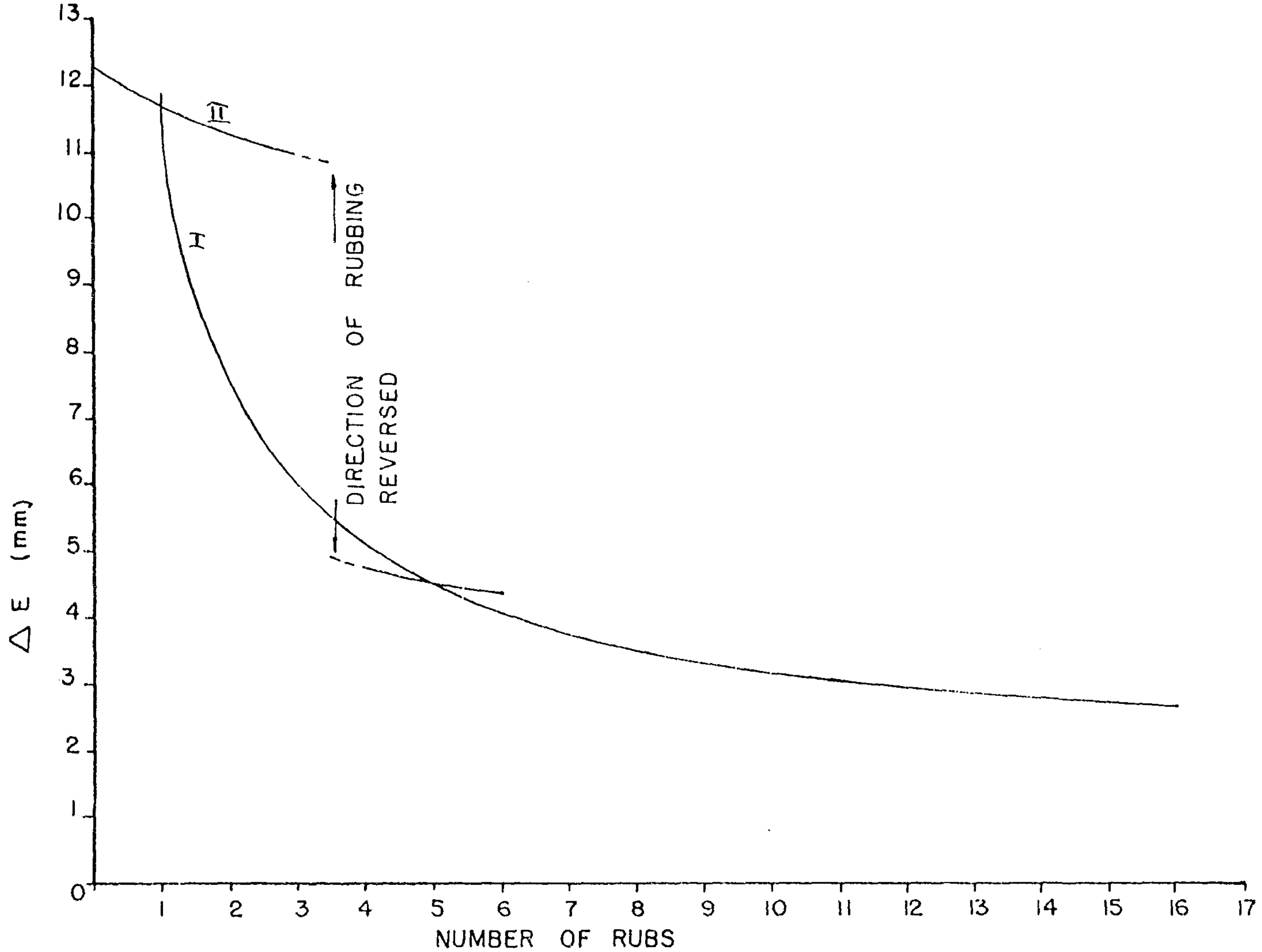

Figure 73. Rubbing curves of films of hydrocarbon derivatives

at a piston pressure of 15 dynes/cm. Three shearing strokes were applied in one direction and then the direction of shear was reversed. The sharp decrease in the thickness of the film confirms a previous observation of Germer and Storks (13). They reported that reoriented films of stearic acid were quite resistant to a further decrease in film thickness if a shearing force was repeatedly applied in one direction. The reoriented films, however, could be easily removed by applying the shearing force in the opposite direction. Curve II illustrates this behavior very well, and also furnishes a more quantitative picture of this effect.

However, curves similar to curve II were not always obtained when multimolecular films of compounds that were known to reorient were subjected to shear. Many of the multimolecular films that were studied were very inhomogeneous in film thickness. The application of a shearing force to such films often moved material over the metal surface in such a way as to give ellipsometer readings that were quite erratic.

VII. DISCUSSION OF THE RESULTS

A. Unrubbed, Multimolecular Films

The parameters that have been determined for the crystallites found in multimolecular films of the n-hydrocarbon derivatives are in good agreement with the results of some investigations of these compounds by x-ray and electron diffraction. In Table 7 a comparison was made of these parameters with those from studies of the n-aliphatic acids. Tables 9, 11, and 13 have shown similar comparisons for saturated hydrocarbons, esters, and some miscellaneous compounds. Several investigators, however, have reported observations which do not agree with the data presented here. Their results also appear anomalous when compared with the results of many investigations of these compounds and films by x-ray diffraction. Various proposals have been made to explain this disagreement, but the only plausible explanation seems to be that based on effects of impurities.

Long-chain hydrocarbon derivatives are obtained very pure only with some difficulty. Rapid standard methods of determining the purity of these derivatives have not been developed. Piper, <u>et</u> <u>al</u>. (36) have shown that the melting point of these derivatives is not always a good indication of their purity.

Therefore, it appears reasonable to suggest that some investigations may have been performed with impure compounds or contaminated films. For example, Germer and Storks (4) have reported infrequent observations of molecular chains perpendicular to the plane of the metal surface in multimolecular films of stearic acid (see also Appendix II). Sutula and Bartell (7) previously reported an orthorhombic form for the crystallites in multimolecular films of palmitic acid. The crystallites in multimolecular films of palmitic acid of improved purity have now been found to be of monoclinic form. Brummage (14) determined that crystallites in films of n-tetracosane, n-triacontane, and n-tetratriacontane were of orthorhombic form. However, the crystallites in films of exceptionally pure n-hexacosane, n-octacosane, and n-triacontane have been found to be monoclinic in this investigation.

A. E. Smith (35) in an x-ray study of single crystals of a series of n-hydrocarbons determined that the even-numbered n-hydrocarbons beginning with n-hexacosane are monoclinic at room temperature. Moreover, the even-numbered n-hydrocarbons below and including n-hexacosane may crystallize in a triclinic form. For example, Mazee (33) has found n-tetracosane to be triclinic at room temperature while Muller and Lonsdale (37) have found a triclinic form for n-octadecane. Indeed, it appears that in pure compounds, the orthorhombic form is found only for the odd-numbered n-hydrocarbons and also for certain n-aliphatic alcohols (38, 39). In this connection, Smith (40) has shown that the presence of even a single homologous impurity in a concentration as low as one per cent gave orthorhombic crystals for the even-numbered n-hydrocarbons. Also, Shearer and Vand (34), while determining the crystal structure of n-hexatriacontane, observed the crystals to change from an orthorhombic form to a monoclinic form with repeated crystallization.

The use of impure compounds may also account for the contradictory results of Natta and Rigamonti (41) who found orthorhombic crystallites in films of many n-aliphatic acids, esters, ethers, etc., and who suggested that the orthorhombic form and a "two-dimensional isomorphism" were characteristic of very thin films (multimolecular) of all these compounds.

Coumolous and Rideal (42) have found orthorhombic crystallites in multimolecular Langmuir-Blodgett films of some long-chain esters whereas the results of this investigation and the results of Germer and Storks (4), Schoon (23), and Kohlhaas (22) indicate a monoclinic form for crystallites of long-chain esters. Knott, Schulman and Wells (43) have also found a monoclinic form for crystallites in multimolecular, Langmuir-Blodgett films of some long-chain esters by x-ray diffraction.

Several investigators who studied multimolecular films of n-hydrocarbon derivatives by electron diffraction have reported results consistent with those obtained in the present study. For example, Germer and Storks (5, 6) found forms A and C of stearic acid in multimolecular, Langmuir-Blodgett films of stearic acid. Trillat and Hirsch (44) have found forms A, B, and C of stearic acid in lenses of stearic acid which were formed on a water surface from benzene solutions.

On the basis of the results from this study it seems reasonable to suggest that crystallites in multimolecular films of pure n-hydrocarbon derivatives exhibit a structure identical to that found in larger crystals of the pure substances. Moreover, this fact is independent of the nature of the substrate and the thickness of the film for films thicker than one molecular layer. The hypothesis appears to be valid for multimolecular films when formed by the method of Langmuir and Blodgett, by the evaporation of dilute solutions or by the spreading of fused material on a substrate.

Although several crystalline forms have been observed in multimolecular films of hydrocarbon derivatives, the observation of crystallites with an 001 orientation has been remarkably constant. Except for films of azelaic and sebacic acids, impure films as well as films prepared from pure compounds have contained crystallites with an 001 orientation on the metal substrate. Moreover, all molecular orientations observed in multimolecular, unrubbed films agree to within

2-3° with the angle(s) that the molecular chains form with the 00ℓ planes in larger crystals of the compounds, as determined by x-ray studies. These facts suggest that the molecular orientation observed in multimolecular films is best described in terms of the structure and orientation of the crystallites in the films. Therefore, in order to understand the relation of molecular structure to the molecular orientation in multimolecular films of n-hydrocarbon derivatives it is necessary to understand:

1. The relation of molecular structure to the crystal structure of n-hydrocarbon derivatives.
2. The occurrence of an 001 orientation for the crystallites in the film.

It must be admitted that the relation of molecular structure to the crystal structure of n-hydrocarbon derivatives is not as yet completely understood. There have been some attempts to derive approximate descriptions of the intermolecular forces in these compounds, as for example that of Muller (45, 46). However, no theory has been proposed that explains all the observations. For example, crystals of pure n-hexacosane can be either triclinic or monoclinic at room temperature. When adulterated with homologous impurities even to only a few per cent, the crystals adopt an orthorhombic form. The orthorhombic, impure crystals transform to an hexagonal form at a temperature near their melting point.

In general, the faces of lowest surface energy will be the most prominent faces of the crystal under a particular set of conditions. For crystals of n-hydrocarbon derivatives, the 001 face is considered to be the face of lowest surface energy. This is supported by much indirect evidence from wetting experiments, adsorbed monomolecular films, and observations of the growth of these crystals. Faces exposing CH_2 units, such as 010, 100, or 110 faces have been shown by the same indirect evidence to be of higher surface energy. In the absence of some disturbing force, such as a shear, it is unlikely that the crystallites would adopt an orientation which would increase the surface energy of the film.

B. Reoriented Films

Multimolecular films of long-chain hydrocarbon derivatives appear to respond in three distinct ways to a mechanical shearing force. First, there are films which are rapidly disordered by shear. These have been found to be films prepared from compounds of relatively few carbon atoms. Examples of such compounds are dodecanoic acid, n-octadecane, n-eicosane and n-octadecyl alcohol. A second type of effect is an almost complete reorientation of the molecules in at least the top layers of the film. This is observed with multimolecular films of many pure compounds. The third type of response is a reorientation of only a fraction of the molecules in the film as in films of some impure compounds. In some cases, neither a reorientation nor a disarrangement is effected by the shearing force, as in films of paraffin wax.

The first kind of response is a disarrangement of the molecular orientation and the structure of the films. Apparently, the lateral attraction of the hydrocarbon chains in the film is not large enough to maintain a crystalline arrangement of the molecules during repeated application of a shearing force. Whether a multimolecular film of a particular n-hydrocarbon derivative will be disordered by a shearing force depends largely on its chain length. In the saturated n-hydrocarbon series films of compounds containing less than 24 carbon atoms were disarranged by a shearing force. Films of n-hexacosane, however, were reoriented by a shearing force. The transition in response to a shearing force appears to occur in this series at a chain length of 24 to 25 carbon atoms at room temperature. It is possible that the critical length depends on temperature, perhaps increasing as the temperature increases. Films of dodecanoic acid were disarranged by shear, whereas films of palmitic acid were reoriented by shear. Because the n-aliphatic acids are arranged as dimers in their crystals, films of the n-aliphatic acids can be considered to change in their response to a shearing force at an effective chain length of about 24 to 25 carbon atoms.

The data for other types of n-hydrocarbon derivatives are less complete. Films of n-octadecyl alcohol were rapidly disordered by shear. However, films of mellisyl alcohol ($C_{31}H_{63}OH$) can be reoriented by shear (27). It is reasonable to expect that a transition in response in this series occurs at a chain length of 23 to 24 carbon atoms.

The second type of response of multimolecular films to a shearing force is illustrated in Figures 74 and 75. Figure 74 shows schematically the relation of monoclinic crystallites in a reoriented film to the shearing direction and to the original orientation of the crystallites in the unrubbed film. Figure 75 illustrates this fact for crystallites of orthorhombic form. In both figures, α is the angle of inclination of the molecular chains to the metal surface.

Mechanically induced reorientation of the molecules in a film occurred abruptly when the molecules exceeded a certain chain length in a variety of long-chan n-hydrocarbon derivatives. The orientation of the molecular chains in reoriented films was found to be unrelated to the original inclination of the molecular chains with respect to the shearing direction.

K. Brummage (14) obtained diffraction patterns such as the one shown in Figure 63 from rubbed, multimolecular films

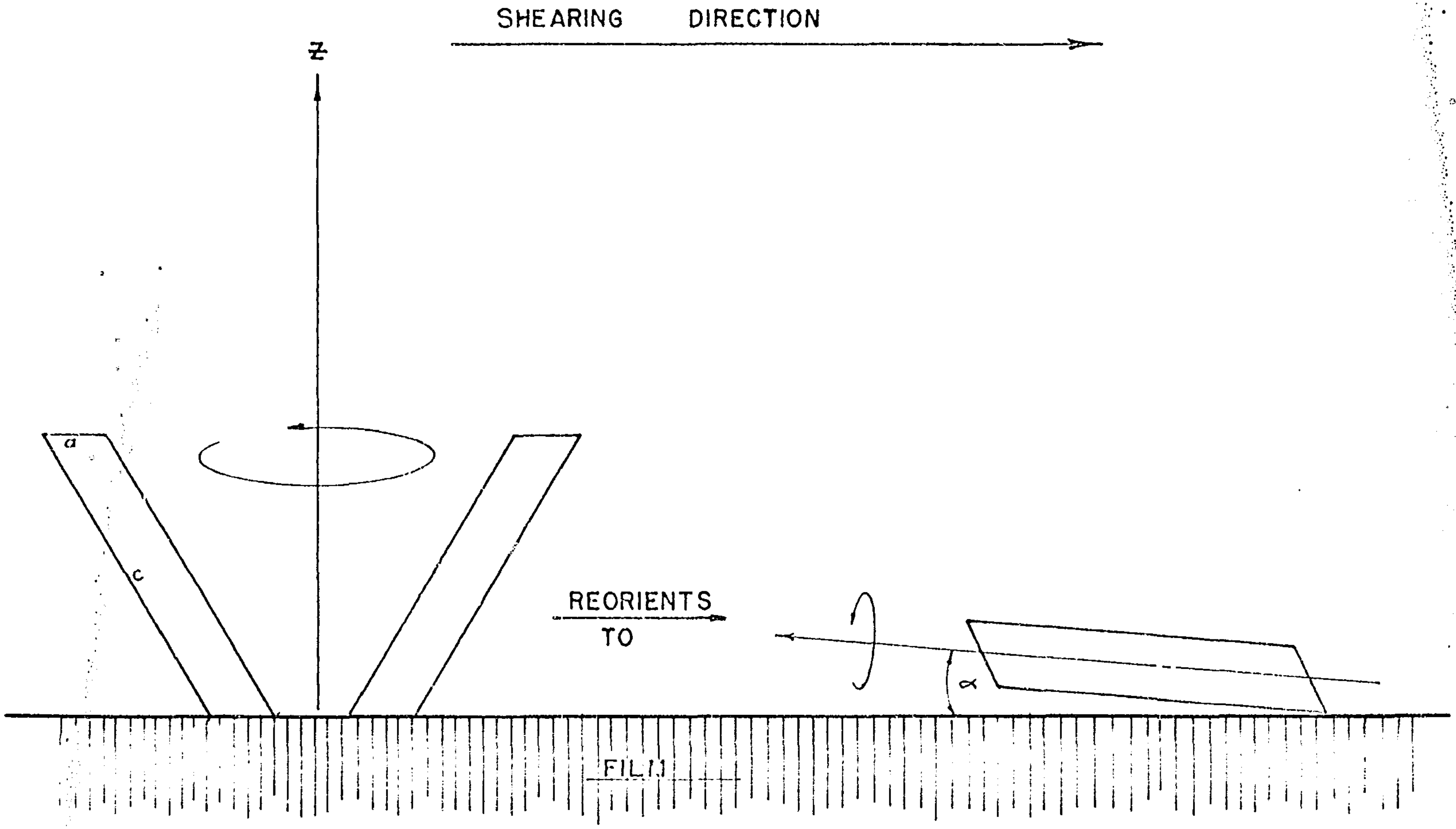

Figure 74. An illustration of the relation of monoclinic crystallites in a reoriented film to the shearing direction and the orientation of the crystallites in the unrubbed film

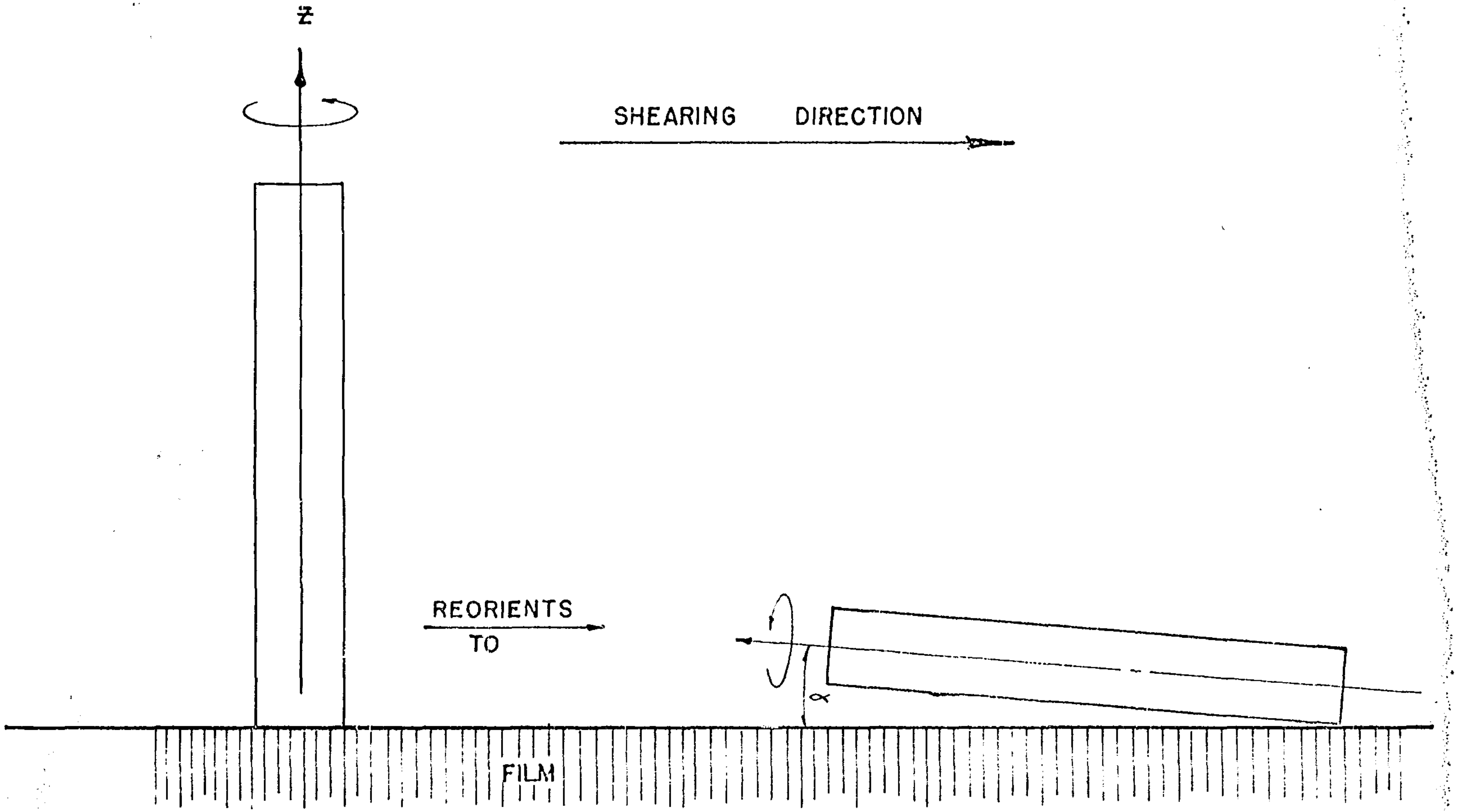

Figure 75. An illustration of the relation of orthorhombic crystallites in a reoriented film to the shearing direction and the orientation of the crystallites in the unrubbed film

of n-triacontane and n-tetracontane. He deduced that the arcs found near the position of the primary beam in these patterns were caused by scattering from reoriented crystallites. These crystallites were so positioned in the plane of the metal surface, that they could be considered to be lying on their 201 planes. Further, the crystallites were so arranged that the molecular chains were inclined by 3° to the metal surface and were pointed against the shearing direction. Brummage proposed that a 201 orientation of the crystallites could be expected for crystallographic reasons along with the often observed 001 orientation. He suggested that rubbing melted the film which then recrystallized under the sliding shear of the departing rubbing surface. Further, he proposed that crystallites in the 001 orientation would adhere more strongly to the substrate than those in the 201 orientation. The shearing force was then likely to remove many crystals in the 201 orientation leaving most of the crystallites with an 001 orientation. Those crystallites pointing against the direction of rubbing would more effectively resist removal by the sliding shear because the presence of a component of the shearing force in that direction would tend to hold them to the surface.

Although this proposal appears to account qualitatively for the patterns obtained by Brummage it does not appear to explain all the results that have been obtained in this and other studies with reoriented films. In most multimolecular films, when reorientation was induced by a shearing force it was found to be much more complete than that observed by Brummage. In fact, evidence for the presence of crystallites in an 001 orientation in reoriented films has generally not been obtained when the compounds were extremely pure. Crystallites in an 201 orientation or similar orientation (as, 011, 101, 021, etc.) have also not been observed in multimolecular films of n-hydrocarbon derivatives when the films were prepared by spreading molten substances over a metal surface.

It is possible that Brummage made his observations on films which were only partially contacted by a shearing force. A stronger possibility is that the response of the films to a shearing force was influenced by impurities present in the films. A similar incomplete response was observed in this investigation in films of impure palmitic acid and impure dotriacontane, even though shear was applied in apparently the same way as for other films. Films of parawax, a mixture of many long-chain hydrocarbons, are neither reoriented nor disordered by a shearing force.

The angle of inclination of molecules implied by the 201 orientation proposed by Brummage is in poor agreement with the results of the present 201 orientation. The patterns obtained made the determination of the angle much more direct than was possible in Brummage's work. It is possible that the roughness of the surface obscures the true angle of inclination because of the disproportionate accumulation of crystallites on the leeward (downhill) slopes of the asperities by the action of rubbing. At the present no altogether acceptable theory exists which accounts for the orientations observed in reoriented films.

VIII. SUMMARY

A study has been made of the structure and the molecular orientation in multimolecular films of a variety of long-chain n-hydrocarbon derivatives by electron diffraction. The films were prepared by evaporating dilute solutions of the compounds or by spreading the fused compounds on polished surfaces of platinum and "chrome" plated steel. A polarimetric method was used to measure the optical thickness of the films to within a few angstrom units.

Interest in this investigation stems from the fact that the orientation of the molecules in films and surface phases often strikingly influences the surface properties of these systems. During a preliminary study of films of a variety of long-chain n-hydrocarbon derivatives, highly oriented polycrystalline films were often observed over a large range of film thickness. This fact was not in agreement with reports of some previous studies. Also, unusual molecular orientations could be induced in these films by a shearing force. These observations prompted the present investigation.

In general, crystallites in multimolecular films were formed with their 001 planes parallel to the metal surface. The structure of these crystallites appeared to be identical to the structure of the bulk substances. This fact was unrelated to the thickness of the films in films thicker than one molecular layer. It was also unrelated to the methods used in preparing the films.

Crystallites of monoclinic form were found in the multimolecular films of pure, even-numbered n-aliphatic acids, long-chain esters, and in films of n-hexacosane, n-octacosane and n-triacontane. Multimolecular films of pure, odd-numbered saturated n-hydrocarbons, n-octadecyl alcohol and films of some impure compounds contained crystallites of orthorhombic form. Multimolecular films of n-heptadecanoic, isostearic and isopalmitic acids and films of n-docosane contained crystallites probably of triclinic form.

The molecular orientation in multimolecular films of many n-hydrocarbon derivatives could be altered by applying a shearing force to the film in one direction. Such reoriented films were composed of crystallites so arranged in the plane of the metal surface that the molecular chains were inclined at a small angle to the metal surface and were pointed up against the shearing direction.

Molecular reorientation was induced mechanically in films of arachidic, stearic, palmitic, isostearic, isopalmitic and n-heptadecanoic acids. It also occurred in films of saturated n-hydrocarbons containing 26 or more carbon atoms and in films of n-hexadecyl stearate and n-octadecyl stearate. Multimolecular films of some substances were disordered rather than reoriented in a new direction by the applied shearing force. Examples of such substances are dodecanoic acid, n-octadecyl alcohol and n-tricosane. Multimolecular films of some impure substances, when subjected to shear, were reoriented only partially while other impure substances were not altered at all in structure. The influence of impurities in mechanically induced reorientation was not systematically studied.

Reorientation often occurred with a change from one polymorphic form of the crystallites to another in multimolecular films. Such a change was not a necessary condition for reorientation, however, and identical structural parameters were often observed in unrubbed and rubbed films.

The molecular orientation in reoriented films was unrelated to the original orientation of the crystallites in the film but depended solely on the shearing direction.

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X. ACKNOWLEDGMENTS

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XI. APPENDIX I: TWO THERMAL METHODS FOR PRODUCING SPECIAL ORIENTATIONS IN MULTIMOLECULAR FILMS OF STEARIC ACID

While studying the reorientation of molecules by mechanical shear in films of hydrocarbon derivatives it was necessary to prepare films containing crystallites of form C of stearic acid. This form of stearic acid could be readily produced in a film by cooling molten stearic acid which was spread over the metal surface. Films prepared in this fashion, however, were too thick for optimum results in electron diffraction experiments. Some experimentation with this method resulted in the production of films that were not too thick for observation with electron diffraction and in which the molecular chains were inclined in a controlled direction over large areas of the film.

Molten stearic acid was spread over the surface of a polished, platinum surface at a temperature of 130-140°C. When one end of the slide was gripped with very cold forceps, a thin crystalline film of stearic acid began to form at the cold end and spread down the slide, pushing in front of it a thick wave of the molten material.

This crystallized film was not homogeneous in thickness over the entire metal surface. Smooth regions of film were found near the end held by the cold forceps whereas thick clusters of material were found at the opposite end and in a few small regions of the film. The thickness of the film in the smooth regions was about 10,000 A.

In order to discuss the structure and molecular orientation in these smooth regions, it is convenient to define a direction of reference. Let D be a vector in the plane of the metal surface, perpendicular to the moving wave of liquid stearic acid and directed away from the cold object. Then, the crystallites in the smooth regions were found to have their a axes approximately parallel to D and their b axes approximately perpendicular to D. Moreover, the molecular chains were inclined by 52° to the plane of the metal surface and were pointed up from the surface in the direction of D.

With more experimentation, it was found that the smooth regions could be made larger. This was done by holding one side of the slide with warm forceps while a very cold (about -50° or lower) and clean metal surface was placed at the edge of the film on the opposite side of the slide. The position of the cold surface and the warm forceps relative to the film and its metal substrate is illustrated in Figure 76.

Diffraction patterns from films prepared in this manner are shown in Figures 77 and 78. Figure 77 was obtained with the film so positioned that the incident radiation was parallel to the vector, D. Figure 78 was obtained with the incident radiation perpendicular to D, the direction of D being from left to right with respect to the photograph.

Crystallites of form C of stearic acid could also be

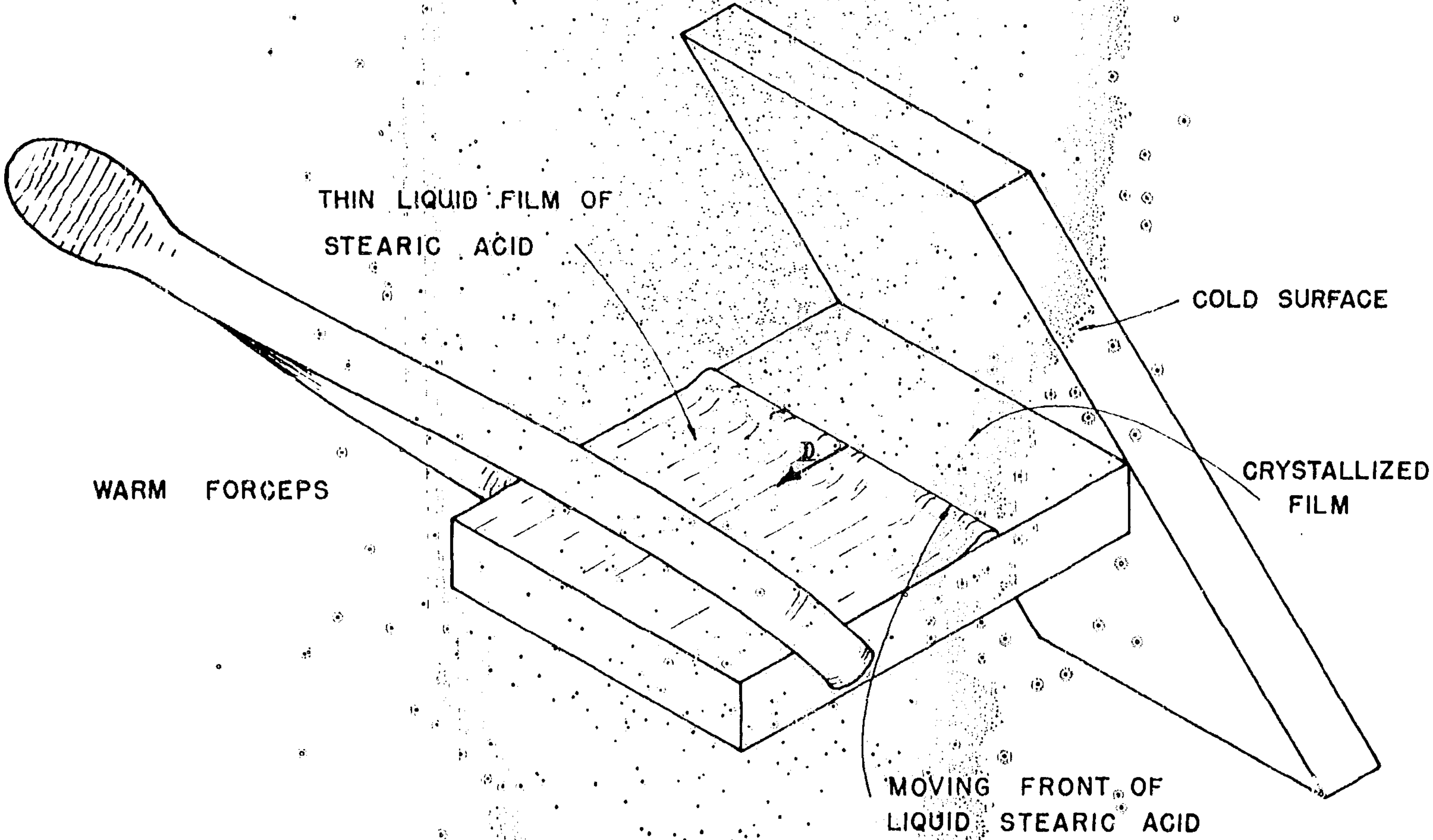

Figure 76. The position of various components while preparing a film by the thermal method

Figure 77. A diffraction pattern obtained with a film of stearic acid prepared by the thermal method. The incident radiation was parallel to D. The inclined bands visible in the pattern are caused by crystallites positioned at the edge of a smooth region in the film

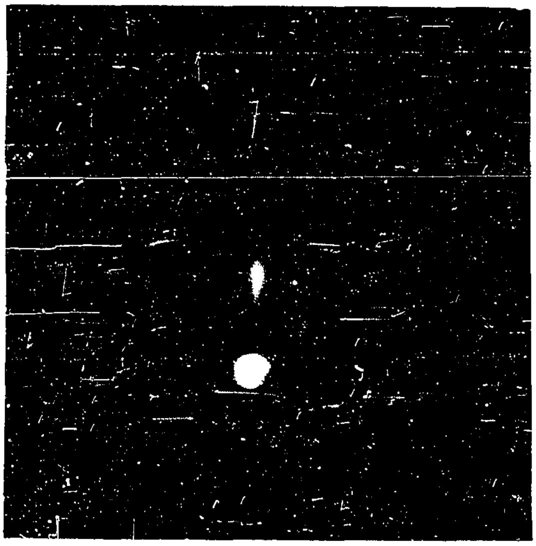

Figure 78. A diffraction pattern obtained with a film of stearic acid prepared by the thermal method. The incident radiation was perpendicular to D. The vector, D, was directed from left to right with respect to the pattern

produced in multimolecular films by evaporating a small amount of a dilute solution of stearic acid in acetone on a metal surface. Generally, the crystallites in such films had an 001 orientation in the plane of the metal surface but were otherwise arranged randomly in this plane. If, however, a drop of solution was spread over the metal surface and a warm, clean surface was placed at the edge of the film, a thin crystalline film of stearic acid began to form at the warm end and spread down the slide, pushing in front of it a wave of solution. The initial temperature of the warm object was slightly less than the boiling point of the solution used to prepare the film.

The direction of progress of the front of solution can be described by a vector, E. The vector, E, is defined to be in the plane of the metal surface, perpendicular to the moving front of solution and directed away from the warm object. The crystallites in the smooth regions of this film were found to have their a axes aligned approximately parallel to E and their b axes approximately perpendicular to E. The molecular chains were inclined by approximately 52° to the plane of the metal surface and were pointed in the direction of the vector, E. Diffraction patterns with these films were very similar to those shown in Figures 77 and 78.

XII. APPENDIX II: SOME OBSERVATIONS ON THE EFFECT OF PURITY IN LANGMUIR-BLODGETT FILMS OF STEARIC ACID

While performing experiments in which an attempt was made to prepare Langmuir-Blodgett films of form C of stearic acid, a series of observations were made which illustrated the need for meticulous technique when preparing films in this way. The observations are presented here because of their relevance to this investigation and because they help to explain some anomalous results reported in the literature. The multimolecular films of stearic acid were deposited on polished chromium plated surfaces. The stearic acid was spread from a dilute benzene solution (approximately 2 mg of stearic acid/ml of benzene) on an aqueous substrate of pH equal to 3. The piston pressure on the stearic acid film during deposition was 30 ± 2 dynes/cm. This pressure was measured by a float assembly coupled to a torsion wire device and was maintained manually by adjusting the position of a paraffined metal barrier.

Fairly homogeneous films of stearic acid, 31 layers thick, were then investigated by electron diffraction. Initial films built in this manner indicated an orientation for the stearic acid in which the molecular axis was perpendicular to the plane of the metal surface. This orientation for films of stearic acid is usually found only for the first layer of molecules next to the metal surface. Germer and

Storks (4), however, have also reported that multimolecular films having this orientation were infrequently observed in their work on stearic acid.

The purity of the benzene used to make the solutions of stearic acid and the technique of spreading these films on the aqueous subphase were critically examined. The benzene was found to give a surface pressure of about 2-3 dynes/cm upon a tenfold decrease in surface area after spreading the same amount of benzene as was normally employed in the spreading of the stearic acid film.

It was also observed that the paraffin coating from the sides of the tray of the surface balance would dissolve and loosen if the benzene was applied in large drops to the aqueous subphase. By applying very small drops of benzene to the water surface (drop volume approximately 0.005 ml) the benzene would spread and evaporate without dissolving enough paraffin to give a noticeable surface pressure or a crumpled paraffin film upon a tenfold decrease in the surface area of the film.

Langmuir-Blodgett films of stearic acid containing 31 molecular layers were prepared again, using refined technique, highly purified benzene as the spreading solvent, and a surface pressure of 30 ± 2 dynes/cm. These films were found to contain crystallites of form B of stearic acid. The c axis of the crystallites was pointed outward from the surface and formed an angle of 62-63° with the plane of the metal surface.

R. Uyeda and S. Takagi (47) have reported observing electron diffraction patterns from which the presence of crystallites in Langmuir-Blodgett monolayers and trilayers of stearic acid was inferred. The crystallites in the films were found to be orthorhombic with axes $|\underline{a}| = 7.30$ A and $|\underline{b}| = 4.98$ A. The a and b axes were parallel to the plane of the metal surface and were distributed nearly uniformly in all directions in this plane. However, Uyeda and Takagi were not certain about the purity of the stearic acid used in their experiments and planned to determine whether these films were prepared with pure material.

Recently, S. Takagi (48) reported that the above diffraction patterns were probably due to a thin film of paraffin or a mixed film of stearic acid and paraffin. This conclusion was reached after it was found that identical diffraction patterns were obtained even if a few drops of pure benzene were spread on the water surface. He found that benzene would dissolve the paraffin at the border of the tray forming a thin film (not monomolecular) of paraffin on the water surface. Such films of paraffin could also be prepared by floating a small piece of paraffin on the water surface and spreading a few drops of pure benzene near the piece of paraffin. The films of paraffin were lifted from the water surface and were studied by electron diffraction (49).

XIII. APPENDIX III: ION BOMBARDMENT CLEANING OF METAL SURFACES

During the course of this investigation it was found necessary to devote a large amount of attention to the preparation of the metal surface and, especially, to the procedure of cleaning the surface. A variety of methods for removing hydrocarbon contamination from metal surfaces were tried and a few of these were found to be particularly successful. One such method was ion bombardment cleaning.

When a voltage is applied between two electrodes in a vacuum of pressure of the order of a few millimeters of mercury, a glow discharge is obtained which is crossed by a series of dark zones (50, 51). Moreover, several workers (52, 53, 54) have found that when a glass or metal surface is placed within the cathode or Crookes dark space of a glow discharge, a cleaning of the surface can be effected. A metal or glass surface treated in this manner has a very high coefficient of friction, gives black "breath figures" and firmly adheres to evaporated films of certain metals. These properties are found normally for "clean" surfaces, that is, surfaces prepared by taking severe precautions to insure the absence of certain contaminants.

In order to determine the efficiency of ion bombardment in removing adsorbed films of hydrocarbon derivatives from metal surfaces a glow discharge was initiated between aluminum electrodes in a bell jar. With the unit employed for these experiments, most efficient removal of the film was determined to take place at bombarding voltages between 500 to 600 volts. Ion bombardment proceeded satisfactorily at these voltages if the pressure in the chamber was about 0.15 mm of mercury and the distance between the electrodes was about four centimeters. Under these conditions and with air as the gas in the chamber the current during ion bombardment was about 10-15 milliamperes.

Because quantitative data on ion bombardment cleaning were not available in the literature, it was decided to perform a simple kinetic study of the removal of adsorbed hydrocarbon films by this method. For this study monomolecular films of n-octadecyl amine were formed on lightly flamed, chromium plated slides by adsorption from 0.1 per cent (by weight) cetane solutions. The amount of film removed by ion bombardment was measured with an ellipsometer.

The general nature of the removal of the film by ion bombardment can be illustrated by plotting the average film thickness versus the time of bombardment. This has been done in Figure 79. The average value of the thickness of the film was obtained from about ten runs for each time value. There was some scatter of values of film thickness at bombarding times from one to three minutes (about ± 4 Å). The scatter at bombarding times of four to five minutes rarely exceeded

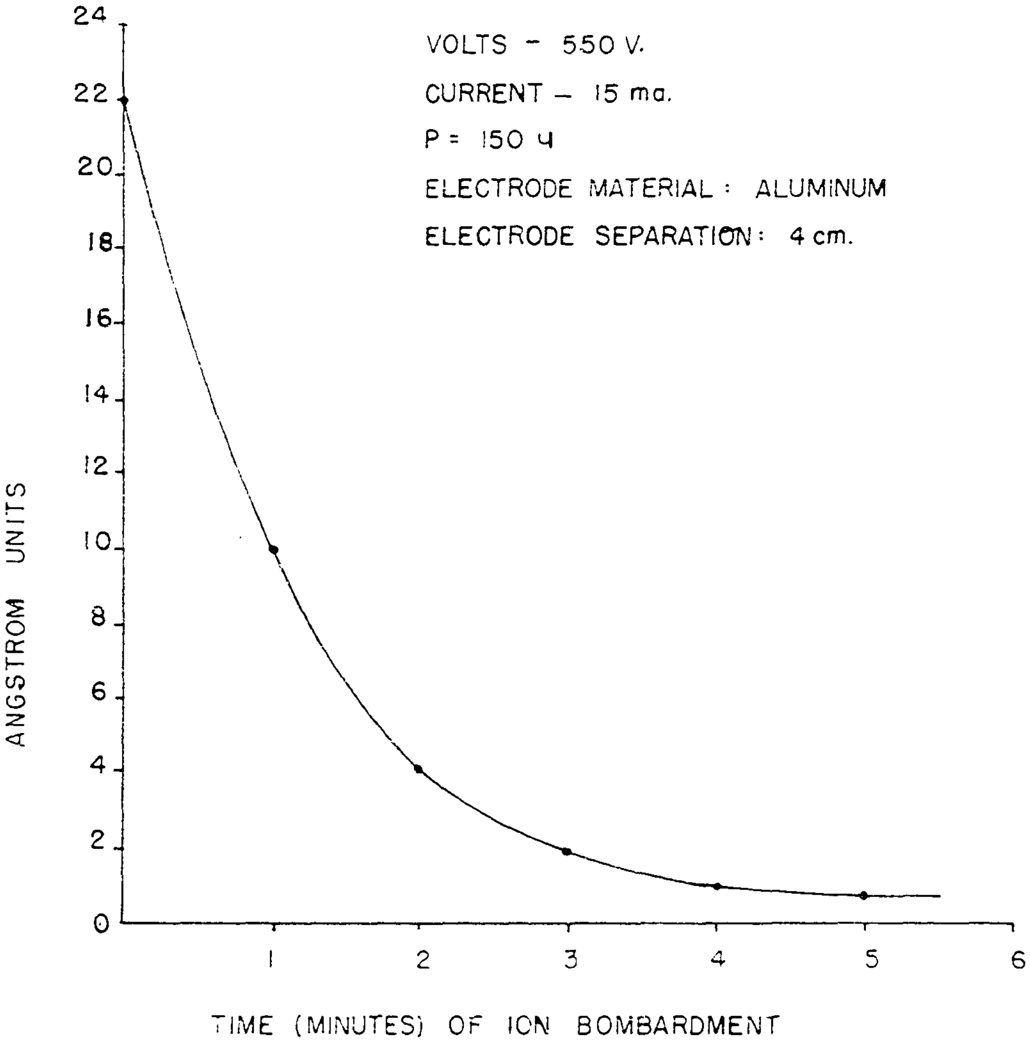

Figure 79. The removal of adsorbed monomolecular film by ion-bombardment

about ± 1 A. In terms of an actual measurement on the ellipsometer, this means that the base reading on the ellipsometer could be reproduced to within its practical sensitivity (about ± 1 A) after formation of the adsorbed film and bombardment for four to five minutes.

Several observations made during this study are pertinent here. The base reading of the metal slides was not found to increase more than about 1 A even after ion bombardment of five minutes duration. This was true for chromium slides with or without a deposited film. It was also noticed that on any particular slide, the formation of films of n-octadecyl amine by the technique of drop retraction was noticeably faster on slides subjected to ion bombardment than on slides that were only cleaned with benzene and mildly flamed for five seconds.

Diffraction patterns of ion bombarded surfaces were found to be different from those of mildly and heavily flamed chromium plated surfaces. Both contained a series of diffuse, concentric rings. The rings on patterns from ion bombarded surfaces were more diffuse than those from flamed surfaces but there was no agreement in "d" spacings for the rings in the two sets of photographs. The data from diffraction patterns of the bombarded slides were then compared with data for all forms reported in the ASTM index of aluminum, chromium, and the oxides, carbides and nitrides of aluminum and chromium to determine whether some agreement could be found. No one substance or simple combination of substances likely to form or sputter onto the slide had "d" spacings that would agree with those obtained from bombarded slides.