

THE EFFECT OF ELECTRIC FIELD UPON THE STRUCTURE OF THIN FILMS OF SOME DIPOLAR LONG-CHAIN MOLECULES

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ABSTRACT

The effect of static electric field applied to thin films of stearic acid and octadecyl alcohol upon the structure of the films was investigated by the method of electron diffraction. The electric field was applied when the films were formed by evaporation of solution or by melting. In the case of stearic acid, some definite relation between the orientation of the crystals in the film and the direction of the applied field was found. While, in the case of octadecyl alcohol, the applied field affected the lattice dimension of the crystals.

1. Introduction

The investigation of crystal structure of long-chain compound was initiated by A. Müller (1) in his X-ray diffraction analysis of a paraffin. Later, C. A. Murison (2), J. J. Trillat and H. Motz (3), C. H. MacGillavry (4) and others examined, by the method of electron diffraction, the molecular arrangement in thin films of some long-chain compounds formed on solid substrates. The structure of built-up films and polymorphism of these substances were also investigated by L. H. Germer and K. H. Storks (5) and P. A. Thiessen and T. Schoon (8) respectively. Temperature dependence of the molecular structure of such films were observed by K. Tanaka (6). Y. Kakiuchi (7) and M. Ida (9) have examined the crystal arrangement in the specimen of some long-chain compounds prepared by cooling from molten state under the presence of strong electric field. In the following, some results of observation on the effect of electric field applied upon the molecular arrangement in the films of stearic acid and octadecyl alcohol.

2. Experimental method

As the specimen holder, we prepared a narrow parallel slit of 0.2~0.3 mm width and 8 mm length with two metal plates, and covered it with thin film of Formbar. Static electric field of about 9 kV/cm was applied between these two metal plates. Various test specimens were prepared by dropping a drop of freshly prepared benzene

solution of the compound on the holder and then letting it to evaporate, or by melting a small piece of the compound on the holder. The specimens thus prepared were investigated by the transmission method of electron diffraction. The applied voltage to the electron-gun was about 40 kV.

3. Results and discussion

Case of stearic acid

(a) *Thin films prepared by evaporation of benzene solution*

Diffraction patterns of thin films prepared from benzene solution in the absence of an electric field are shown in Plates 1 and 2, while those of films prepared under the presence of an electric field are shown in Plates 3, 4 and 5, as examples. Thin films prepared in the absence of an electric field have different structures according to some condition of preparation. In most cases the film consists of two crystal groups: one with their c -axes inclined to the surface of the film, while in the other the said axes are nearly parallel to the same surface.

It is known that there are various types of structure of the crystal. In the present case the crystals in the film seemed to be somewhat deformed from the known ϵ_2 -type whose monoclinic unit cell has the dimensions of $a=9.12\text{\AA}$, $b=4.94\text{\AA}$ and $\beta=56^\circ 11'$. The observed lattice spacings for various thin films examined are tabulated in Table 1 in the columns 1~4. The values in the sixth column are the spacings

Table 1. (\AA -unit)

1	2	3	4	5	ϵ_2 -type
	4.56 s				4.57(112)
		4.46 s			
4.35 s	4.35 s	4.35m	4.30 s		4.36(111)
4.17 s					4.17(201)
4.13 ss	4.12 ss	4.12 ss	4.12 ss	4.15 s	4.12(110)
		3.75m		3.78 s	3.79(200)
3.35m			3.31m		3.33(019)
3.27m		3.22 w	3.23m		3.25(114)
3.17m					3.15(201)
2.48 s	2.49 s	2.48 s	2.47 s	2.47 w	2.47(020)
2.38m	2.375 w		2.38 w		2.38(01, 15)
2.33m			2.34m		2.34(120)
2.16 w	2.17 w		2.16 w		2.18(222)
2.05m	2.06 m	2.06 m	2.04 m		2.06(220)
	1.63 w		1.61 w		
1.59m					
1.44 w					1.44(510)
1.28 w					1.24(430)

calculated for ϵ_2 -type. Some of these thin films show relatively simple diffraction patterns as shown in Plate 2. The observed spacings for such a film are shown in the fifth column. This crystal is considered as the elementary type, i. e. the crystal having the unit cell of $a=4.94\text{\AA}$, $b=7.58\text{\AA}$ and $\beta=90^\circ$ assumed by T. Schoon. In each case, the crystals in the thin film cannot be considered as to be composed of crystals of a single type.

When thin films of stearic acid are prepared under the presence of an electric field, the small crystals in the film have a general tendency of definite orientation in which the b -axis or the a -axis of the crystal is arranged perpendicularly to the applied electric field. The values of the lattice spacings observed in the cases of

Table 2. (\AA -unit)

1	2	3	Müller	Germer
		4.35m		
		4.07m		
3.86 s	3.87m	3.87m		3.88(200)
	3.67m	3.70m	3.69(020)	
4.16 s	4.16 s	4.16 s		4.18(110)
	4.12 s	4.12 s	4.12(110)	
	2.96m	2.97m	2.96(120)	
2.47m	2.48 s	2.47m	2.48(200)	2.48(020)
		2.33w		
2.05w		2.13w	2.11(220)	2.09(220)
1.61w		1.60w	1.61(310)	1.62(130)

Plates 3, 4 and 5 are shown in Table 2 in the columns 1, 2 and 3 respectively. From the observed spacings, the crystals in a film which has comparatively regular arrangement of crystals as shown in Plate 3 are considered to be similar to those found by Germer and Storck in a built-up film of stearic acid, which was investigated by them in detail. The values in the fourth and the fifth columns in Table 2 are respectively the calculated spacings for the values $a=5.546\text{\AA}$, $b=7.38\text{\AA}$, $c=48.84\text{\AA}$ and $\beta=63^\circ38'$, which were given to the unit cell of a single crystal of stearic acid by Müller as the result of his X-ray examination, and those calculated for the unit cell of the crystal in the built-up film, whose dimensions were given by Germer and Storck as $a=8.27\text{\AA}$, $b=4.96\text{\AA}$, $c=49.0\text{\AA}$ and $\beta=63^\circ38'$. As can be seen in Table 2, a lattice plane having a spacing 3.87\AA is found in all diffraction patterns examined and the plane is perpendicular to the applied electric field. And a lattice plane 3.7\AA also appears perpendicularly to the field. Occasionally, lattice planes 4.05\AA and 4.35\AA appeared.

From these observations it can be seen that the crystals in a thin film prepared in an electric field have tendencies to lie in such a manner that their b -axes are

perpendicular to the applied field when the crystals are of Müller type, while their a -axes are perpendicular to the field when the crystals are of Germer type. Frequently, these two types of crystals appeared in a film. In every case, the axes of the long-chain molecules have a tendency to arrange themselves perpendicularly to the applied field.

(b) *Thin films prepared by melting*

Plates 6 and 7 show diffraction patterns of specimens prepared by heating a film of stearic acid on the holder up to about 85°C in air and by successive cooling-down

Table 3. (Å -unit)

Plate 6	Plate 7
7.86 w	
4.83 w w	
4.50 m	4.58 s (spot)
4.42 s	4.42 w (ring)
4.32 s (diffuse)	4.38 s (spot)
4.12 m	4.12 w (ring)
	4.11 s (spot)
3.93 w	3.95 w (spot)
3.84 s	3.83 s (spot)
	3.81 w (ring)
3.77 s (diffuse)	3.79 w (ring)
3.67 s	3.65 s (spot)
2.48 w	2.56 s (spot)

to room temperature without an applied electric field. These specimens show ring patterns as shown in Plate 6 and rarely single crystal patterns as shown in Plate 7. The lattice spacings observed in Plates 6 and 7 are shown in Table 3. The spacings obtained from Plate 6 coincide well with those obtained from Plate 7. But, both of these spacings do not coincide with the spacings of crystals prepared by evaporation of benzene solution in the absence of applied field. These films consist of mixtures of two kinds of crystals with slightly different cross-sections. In the case of Plate 7, the c -axes of both crystals are parallel to each

other and their (100) and (010) planes are also parallel to each other respectively. The cross-section of one kind of crystals is shown in Fig. 1. Ring pattern in Plate 6 shows that the film has fibrous structures of two kinds of crystal appeared in Plate 7 and each of them has its c -axis as fiber axis.

A pattern such as shown in Plate 8 is always obtained for

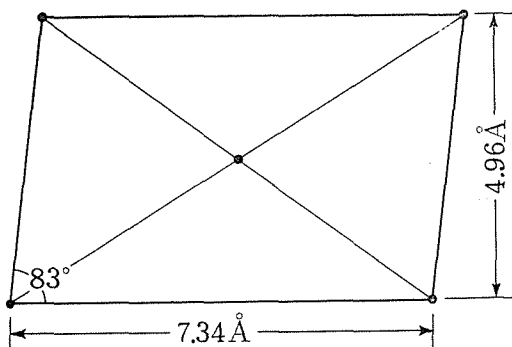


Fig. 1

specimens prepared under an applied electric field of about 9 kV/cm. From this, it is considered that the crystals grown under an electric field always arrange themselves in fibrous structure. As can be seen in Fig. 2, the schematic representation of Plate 8, the pattern consists of spots on parallel lines with equal distances of two groups (K

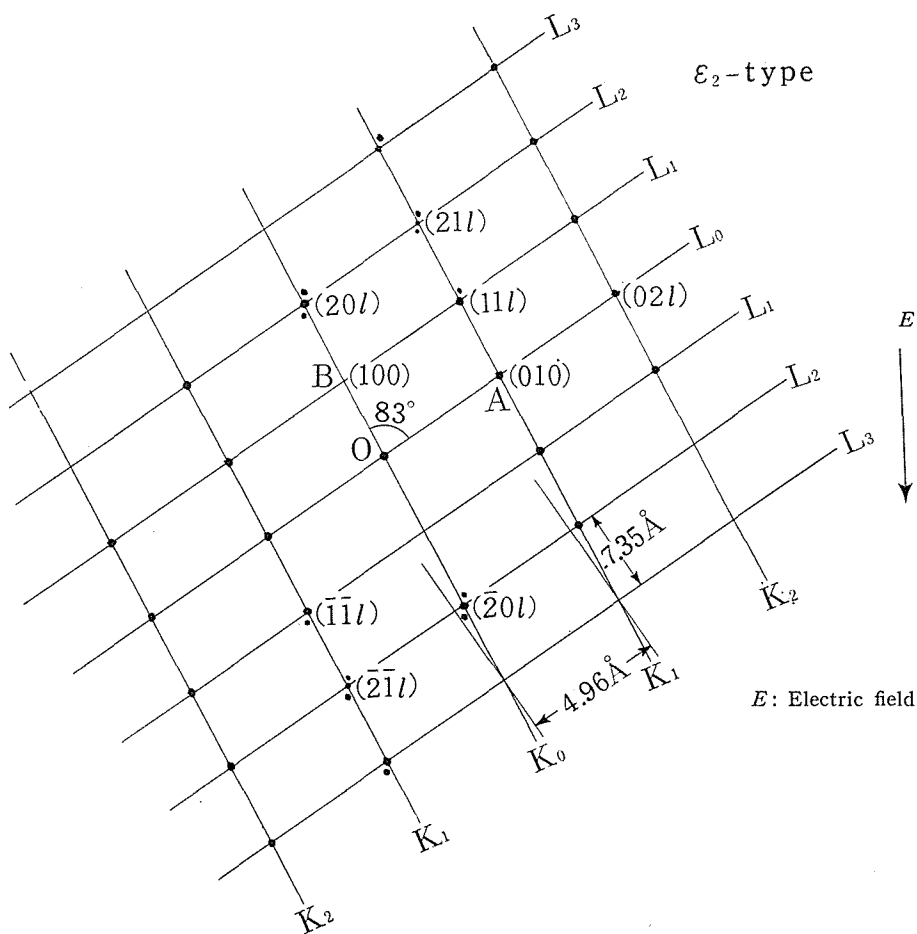


Fig. 2

and L). Each spot on the intersection of these lines is split up into several spots in the direction of applied electric field. In Fig. 2, the spacings corresponding to the lengths of OA and OB are 4.96 \AA and 7.35 \AA respectively. And the angle between K-lines and L-lines is about 83° . Therefore, the film contains mostly the crystals of the same dimensions as that shown in Fig. 1 and except them there are a few kinds of crystals with slightly different dimensions as can be seen from the splitting-up of the spots. The orientations of the microcrystals of these kinds are not parallel to each other but distributed in the angular range of about 10° . But there could not be found any definite relation between the orientation of the crystal around its c -axis and the direction of the applied electric field excepting that the splitting-up of each spot always occurred in the direction of the applied field.

Case of octadecyl alcohol

(a) *Thin films prepared by evaporation of benzene solution*

Observed spacings for various thin films prepared by evaporation of benzene solution are shown in Table 4. Mean values of observed (100) and (010) spacings for six films prepared under no applied electric field are shown in the second row. In this case, the differences of the spacings from the mean values were very small

Table 4. (\AA -unit)

Applied voltage V/cm	(100)	(010)	Number of specimens
0	7.44 ± 0.04	5.05 ± 0.02	6
9000	7.21	4.93	1
9000	7.26 ± 0.04	4.95 ± 0.04	4
6000	7.36	5.02	5
6000	7.44	5.04	2

for six specimens. On the other hand, these lattice spacings of the films prepared under an applied electric field took several different values as shown in the same table and all of these spacings are smaller than the corresponding ones of the films prepared without an applied field.

When these films prepared under an applied field are heated in air at an temperature of about 40°C for several minutes, the spacings of (100) and (010) change from the values of 7.26\AA and 4.95\AA to 7.34\AA and 5.03\AA respectively. In the same manner, when the films prepared under no applied field are heated at about 50°C for several minutes, the corresponding spacings 7.44\AA and 5.03\AA turn into the values 7.34\AA and 5.03\AA respectively. From these facts it can be considered that the crystal of orthorhombic system with the dimensions $a=7.34 \text{\AA}$ and $b=5.03 \text{\AA}$ is a stable form of octadecyl alcohol in such films. Plate 9 is an example of the diffraction patterns of thin films prepared under an electric field.

(b) *Thin films prepared by melting*

Plates 10 and 11 are examples of diffraction patterns of thin films prepared by melting without and with an applied electric field respectively. Figs. 3 and 4 are the schematic representations of these plates. In each case, the film contains

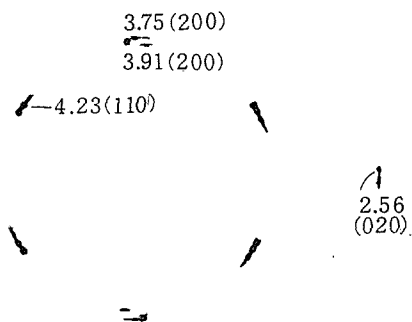


Fig. 3

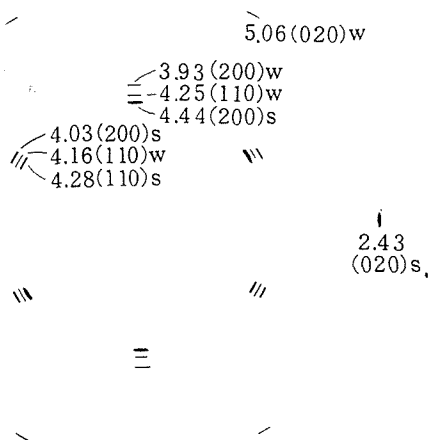


Fig. 4

several crystal forms slightly different from each other. The mean lattice spacings observed for many specimens are tabulated in Table 5. These spacings are different from those observed in the case of films prepared by evaporation. Plate 12 is a reflection pattern of a film and shows that all molecular axes in the film are nearly perpendicular to the surface of the substrate.

As can be seen from Table 5,

Table 5. (\AA -unit)

Applied voltage V/cm	(100)	(010)	(110)
0	7.5 \pm 0.1 7.92 \pm 0.12	5.1 \pm 0.04 "	4.22 \pm 0.06 "
5000	7.3 \pm 0.04 7.48 \pm 0.04 7.72 \pm 0.04 8.12 \pm 0.04	5.05 \pm 0.07 " " "	4.16 \pm 0.03 " " 4.33 \pm 0.02
9000	7.3 \pm 0.04 7.9 \pm 0.04 8.1 \pm 0.06 8.94 \pm 0.06	4.87 \pm 0.02 " 5.06 4.87 \pm 0.02	4.05 \pm 0.03 4.16 \pm 0.02 4.26 \pm 0.03 4.26 \pm 0.03

there are many kinds of crystal forms in the case of applied field and they have larger spacings than those formed under no applied field. It seems from Fig. 4 that the orientations of the orthorhombic crystals are such that they are formed a single high temperature hexagonal crystal through the transition point of the compound. Though we could not find any definite relation between the orientation of the crystals in the film and the direction of the applied electric field as in the case of stearic acid, the variation of the lattice dimensions seems to be caused by the applied field, since the latter affects the interaction between polar molecules of the alcohol when the crystal is formed.

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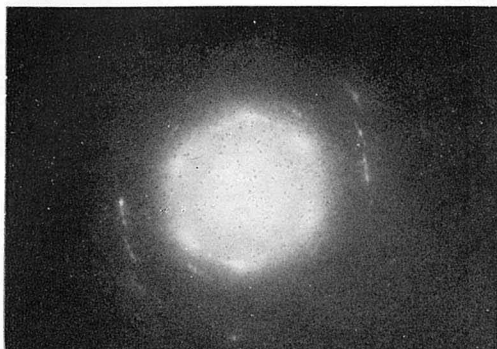


Plate 1

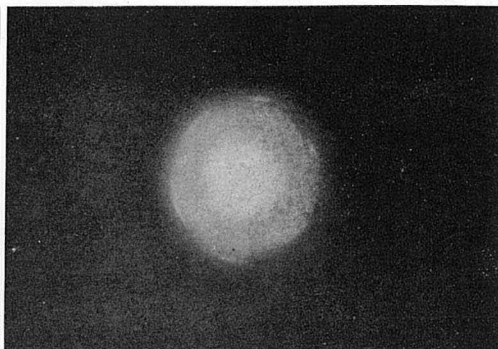


Plate 2

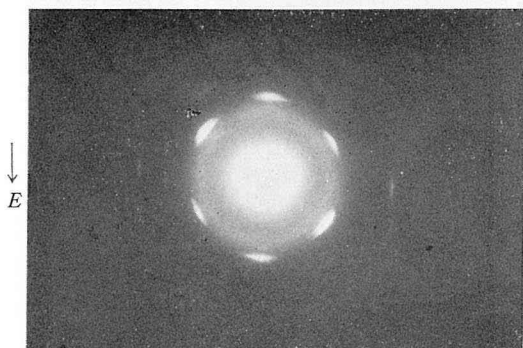


Plate 3

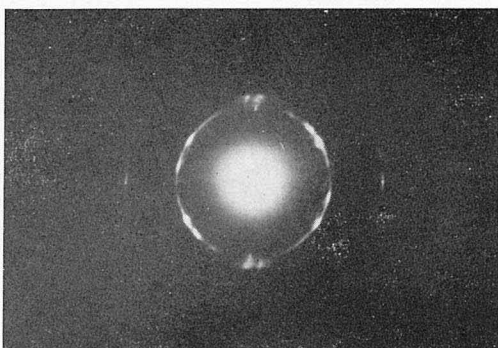


Plate 4

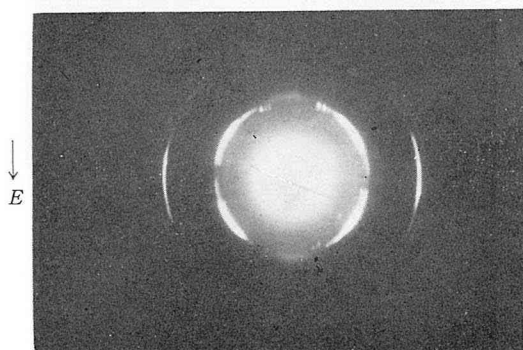


Plate 5

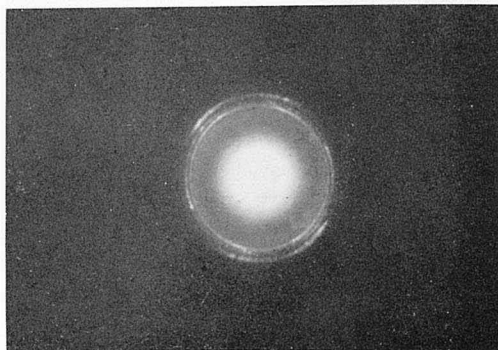


Plate 6

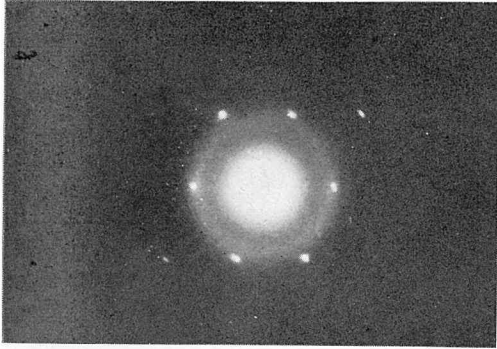


Plate 7



Plate 8

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E



Plate 9

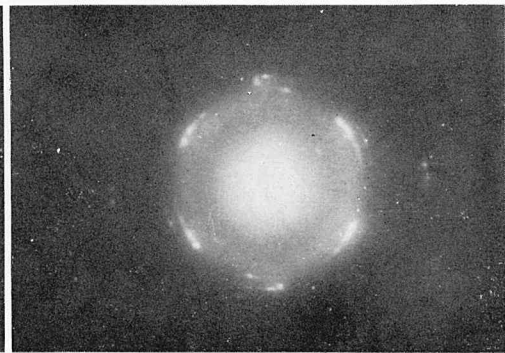


Plate 10

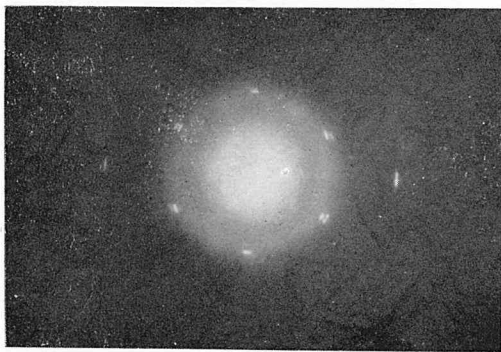


Plate 11



Plate 12