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SOAP CRYSTALS

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CONTENTS

ABSTRACT

Although soap is crystalline, little is known of the characteristics of soap crystals This paper records an x-ray and optical investigation of certain soaps which have been prepared in single crystal condition. These include the α form of the neutral sodium soaps, and the α and β forms of the 1:1 acid sodium soaps. The x-ray investigation was carried out by the new precession method of photographing the reciprocal lattice, which is especially adapted to the investigation of crystals with very large cell dimensions. The large cell dimension of soap crystals ranges in the neighborhood of 50 to 100 Å. All data are collected in Table 1.

The several kinds of soap crystals examined to date display great similarities in optical properties, in clastic and plastic properties, and in twinning, in spite of great differences in cell dimensions, cell shape, and cell symmetry. This is a consequence of the layer nature of the structures of the crystals.

INTRODUCTION

It has recently been established that commercial soaps are aggregates of crystals. This knowledge has brought with it the realization that the properties of various kinds of soaps depend not only on the chemical composition but also on the kinds of crystalline phases present, together with their fabric. Soap manufacture may accordingly be guided by a science of phase fields and phase textures somewhat similar to the science of metallography.

The properties of the various phases of soap are comparatively unknown. One reason for this is that the crystalline nature of soaps has been recognized for a rather short time, but there are also properties inherent in soap which by their very nature hinder the investigation of its crystals. The first is that soap crystals, as a rule, are extremely difficult to prepare in large enough and perfect enough individuals to permit critical examination. The second is that the ordinary methods of x-ray investigation, suitable to the simple inorganic crystals of modest cell dimensions, fail when applied to crystals having the comparatively large cell dimensions of soap crystals.

The present paper reports some crystallographic and optical properties of certain soap crystals which it has been possible to prepare in single crystals suitable for investigation. The crystals used by the writer for the investigation herein reported were prepared at the Research Laboratory of Lever Brothers, Cambridge, under the direction of Dr. L. B. Smith. The writer is especially indebted to Messrs. F. V. Ryer and K. W. Gardiner for their patient efforts to provide suitable material.

METHODS OF INVESTIGATION

X-ray investigation. The symmetry and cell dimensions were obtained by means of a novel x-ray diffraction method, the *precession method.*[1] This technique is ideally suited to the study of very large unit cells such as occur among soap crystals. This is because *precession photographs* are simply scaled replicas of levels of the reciprocal lattice. To interpret them, one needs but inspect them for symmetry, lattice type, systematic absences of points (for space group determination), and, finally, make comparatively simple measurements of certain dimensions of the re-

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[1] Buerger, M. J., The photography of the reciprocal lattice: *ASXRED Monograph* 1 (August, 1944).

ciprocal lattice for transformation into direct cell dimensions.

Soap crystals have such large cells that the reciprocal cells are composed of rows of very closely spaced points. If a reciprocal cell of this kind is recorded by the usually powerful Weissenberg method, the interpretation of the photographs is tedious, and there is very real danger of misinterpretation because the errors in transforming a Weissenberg projection into a map of the reciprocal lattice are of about the same order of magnitude as the spacing of points in the reciprocal lattice rows themselves. Transformation errors are entirely avoided in the precession method because no transformation is necessary; the photographs themselves are scaled replicas of the various levels of the reciprocal lattice.

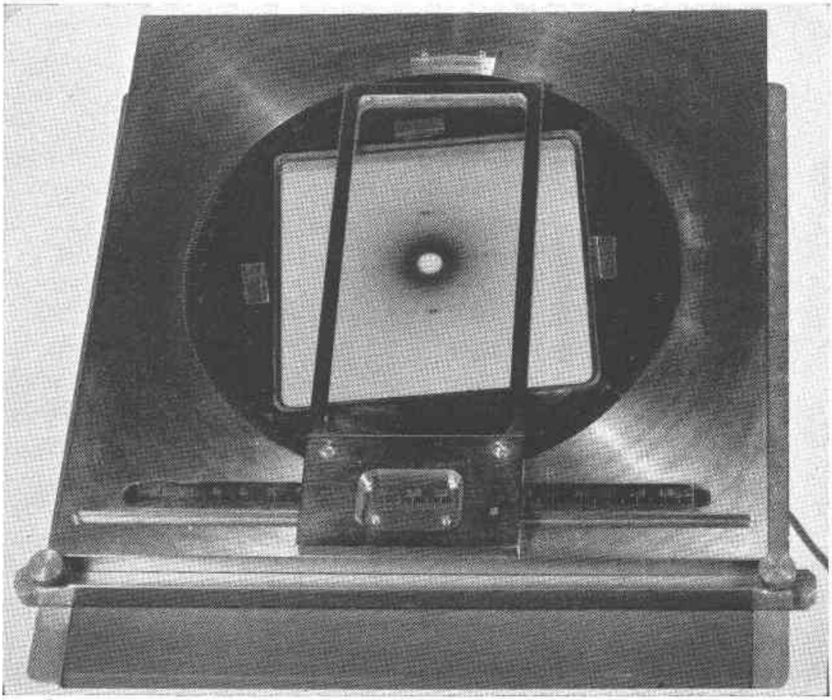

FIG. 1

Inter-row angles and inter-row spacings on precession photographs are measured with the aid of a device which is similar to an instrument described previously[2] for measuring distances and spacings on films. The new device can also measure angles. In both the earlier instrument and

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[2] Buerger, M. J., *X*-ray Crystallography (John Wiley, New York, **1942**) Fig. 229, p. 446.

the new one, spacings are measured as follows: The photograph to be measured is placed under a movable glass plate in such a way that a row of spots in the photograph is aligned along a hair line engraved on the under surface of the glass plate. The coordinate of the line is then measured by means of a millimeter scale and vernier. The plate is then moved parallel with itself until the engraved line comes to coincide with another parallel row of spots on the film, and the coordinate of the line is again read. The difference in the two coordinates is the spacing of the parallel rows on the photograph.

In the new device, Fig. 1, this principle is the same, but the photograph may also be rotated beneath the glass plate by means of a rotating stage similar to a rotating microscope stage. By means of this motion, reciprocal lattice rows of any direction can be brought into parallelism and coincidence with the line of fixed direction engraved on the glass plate. By reading the initial and final angular positions of the stage, the angle between two reciprocal lattice rows can be determined. Thus, in general, the interaxial angles α^*, β^*, and γ^* can be selected and directly measured on the a axis, b axis, and c axis precession photographs respectively. In the monoclinic case, since $\beta = 180° - \beta^*$, the interaxial angle of the direct lattice can be directly measured on the b axis precession photographs.

Optical investigation. The refractive indices α and β for the several soap crystals were determined by the immersion method, using soap crystals which appeared large in the microscope field of view. Liquids which provided final matches in index were immediately standardized on an Abbe refractometer. The α and β indices are believed to be accurate to .003 or better.

To find the index γ directly by the immersion method requires placing the soap flake on edge. This is difficult to accomplish with crystals as plastic and as fragile as soap crystals. The index γ was therefore computed in each case from the measured values in the refractive indices α, β, and the optic angle, V, in the usual way.

Optic angles were measured by the method of Mallard. The values probably contain errors of the order of 5°.

THE α NEUTRAL SODIUM SOAPS

Symmetry and cell. The geometrical features of the "alpha" form of the neutral sodium soaps have already been discussed.[3] This form was first regarded as anhydrous,[4] but has subsequently been shown to be a

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[3] Buerger, M. J., The characteristics of soap hemihydrate crystals: *Proc. Nat. Acad.* Sci., **28**, 529–535 (1942).

[4] Thiessen, Peter A., and Stauff, Joachim, Feinbau and Umwandlungen kristallisierter Alkalisalze langkettiger Fettsäuren: *Zeit. Physikal. Chem.*, (*A*) **176**, 397–429 (1936).

hemihydrate.[5] There is now abundant unpublished evidence confirming the hydrated character of the so-called "alpha" form of the neutral sodium soaps. Sodium palmitate, stearate, behenate, and arachidate have been produced[7] in the "alpha" form.

"Alpha" sodium stearate hemihydrate has been restudied by the powerful precession method. Precession photographs of the reciprocal lattice are shown in Fig. 2. The following plane symmetries are evident:

Precessing axis	Level	Symmetry
c	zero	*ll*
b	zero	2
	n	2
a	zero	*ll*
	n	*l*

These data fix the point group as $2/m$ and consequently place the crystal in the monoclinic system.

By laying a horizontal straight edge on the *a* axis *n* level photographs, it is evident that the (100)* nets are diamond, which calls for an *A*-centered lattice. The zero level (010)* net has alternate [100]* rows missing, which requires a glide *a*. There are no other systematic omissions of reciprocal lattice elements. This information fixes the diffraction symbol as $2/mA-/a$. This diffraction symbol permits either of the space groups Aa or $A2/a$ as possibilities. If the crystal is indeed a hemihydrate, the number of water molecules per unit cell is exactly enough to fill the general positions of the more symmetrical space group, but too many to fill the general positions of the less symmetrical space group. The most likely space group is therefore $A2/a$.

The cell dimensions for "alpha" sodium stearate hemihydrate are:

a	9.16 *kX*
b	8.00
c	103.96
β	$93\frac{1}{4}°$
cell content	$16\text{NaSt.}\frac{1}{2}\text{H}_2\text{O}$
computed density	1.10

The morphological and plastic properties of these crystals have already been reported.[3]

Optical properties. The optical properties of the "alpha" form of the stearate[6] and palmitate[6] are as follows:

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[5] Buerger, M. J., Smith, L. B., de Bretteville Jr., A., and Ryer, F. V., The lower hydrates of soap: *Proc. Nat. Acad. Sci.*, **28**, 526–529 (1942).

		α NaSt $\cdot \frac{1}{2}H_2O$	α NaP $\cdot \frac{1}{2}H_2O$
refractive indices	α	1.507	1.505
	β	1.517	1.517
	γ	1.56*	1.57*
optic angle			
$2V$ (in crystal)		49°	50°
$2E$ (in air)		78°	80°
dispersion		$r>v$ marked	$r>v$ strong
optical orientation		$X=b$	$X=b$
		$Y\approx a$	$Y\approx a$
		$Z\approx c$	$Z\approx c$

* Computed from α, β, and V.

THE α 1:1 ACID SODIUM SOAPS

Introduction. The 1:1 acid soaps such as HSt·NaSt, occur in two forms, here designated α and β. Such soaps can be prepared,[7] for example, by cooling solutions made by dissolving equimolar portions of fatty acid and soap in 95% alcohol. If the precipitation takes place above a critical temperature, the β form appears; if below the critical temperature, the α form appears. The critical temperature for HSt·NaSt is about 50°C.

The α form has been prepared[7] for HMy·NaMy, HP·NaP, HSt·NaSt, HBh·NaBh, HAr·NaAr, and for the mixed acid soaps HP·NaSt and HSt·NaP.

Habits. The habit of HSt·NaSt crystals precipitated from 95% alcohol solutions is somewhat elongated tabular, with the ratio of length ($\|a$) to width ($\|b$) about 2:1. When precipitated from a solution containing excess fatty acid, this ratio increases so that the crystals become acicular, and tend to occur in sheaves. Crystals precipitated from solutions containing an excess of dissolved soap, on the other hand, tend to have a length to width ratio perhaps slightly smaller than for those precipitated from exactly equimolar solutions.

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[6] The following abbreviations are used in this paper for organic radicals:

Composition	Name	Abbreviation
$C_{12}H_{24}O_2$	laurate	L
$C_{14}H_{28}O_2$	myristate	My
$C_{16}H_{32}O_2$	palmitate	Pa
$C_{18}H_{36}O_2$	stearate	St
$C_{20}H_{40}O_2$	arachidate	Ar
$C_{22}H_{44}O_2$	behenate	Bh

[7] The preparations of all crystals discussed in this paper were carried out by Messrs. F. V. Ryer and K. W. Gardiner, to whom the writer is indebted for this information.

Since an elongated tabular habit is also one of those exhibited by "alpha" NaSt·$\frac{1}{2}H_2O$, it will be useful to point out that these two crystals, though somewhat similar in habit, can be distinguished on the basis of optical elongation. NaSt·$\frac{1}{2}H_2O$ is customarily elongated parallel to the optical direction X, and consequently has negative elongation as seen looking normal to the tablet. On the other hand, the α HSt·NaSt and α HP·NaP crystals are elongated parallel to the optical direction Y and consequently exhibit positive elongation when viewed normal to the tablet. (Not only are the neutral hemihydrates monoclinic, but the symmetry studies, noted beyond, prove that the alpha acid soaps are also monoclinic. The neutral soaps are customarily elongated parallel to the two-fold axis, while the acid soaps are customarily elongated at right angles to the two-fold axis.)

Symmetry and cells. For the precession method, these crystals are most easily investigated by mounting them so that the axis of greatest elongation is parallel with the glass capillary to which the crystal is attached. When the crystal is mounted in the usual adjusting crystal holder and placed on the precession instrument, it can accordingly be rotated about the zone of elongation. Thus, the flat surface of the crystal can be brought either normal or parallel to the precessing axis.

As a matter of general strategy in the precession investigation of any soap crystal, the normal to the flat surface (which has never proven to be a rational direction, although in cases studied so far, it has always turned out to be within a few degrees of c) is first brought parallel with the precessing axis. In the case of the α acid soap crystals, this gives a photograph shown in Fig. 3*A* (photographs of acid palmitate and acid stearate cannot be distinguished). This photograph records the projection in this nearly rational direction, not only of the zero level, but also of the first level, since in the particular instrumental adjustment employed, a wide layer-line opening was used. From this photograph, symmetry information and dimensional information can be obtained which is especially valuable for making n-level settings for subsequent photographs. When the flat surface of the crystal is adjusted parallel with the precessing axis, a cone axis photograph[1] proves to be centered, showing that this new direction is rational. The zero and first levels of the reciprocal lattice normal to this axis and as photographed by the precession method are shown in Figs. 3*B* and 3*C*.

FIG. 2. Precession photographs of α NaSt. Figs. 2*A*, 2*B*, and 2*C* represent three central sections of the reciprocal lattice, in correct relation: Figs. 2*A* and 2*B* have a central horizontal line in common, and Figs. 2*A* and 2*C* have a central vertical line in common. Fig. 2*D* is a section parallel to that of Fig. 2*C*, but at another level. Note the symmetries of the levels, and compare Fig. 2*C* with Fig. 2*D* for extinguished rows.

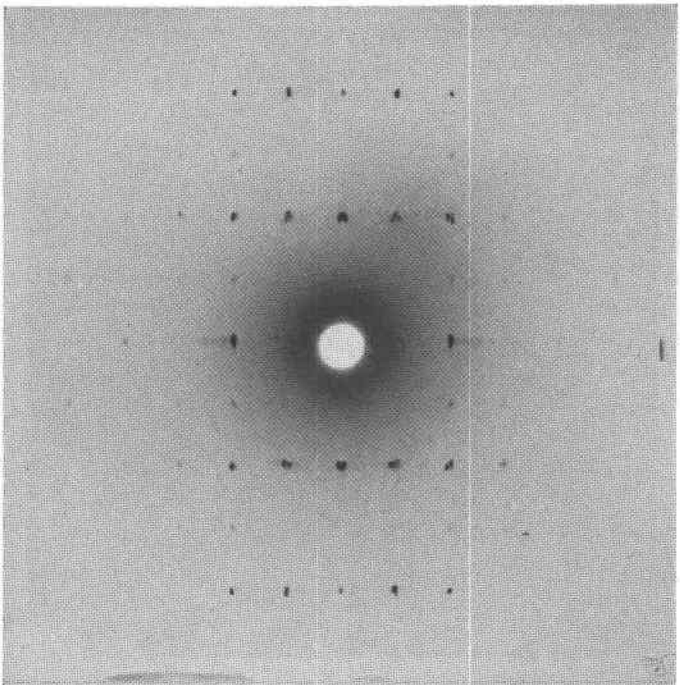

Fig. 2A.
c axis,
several levels.

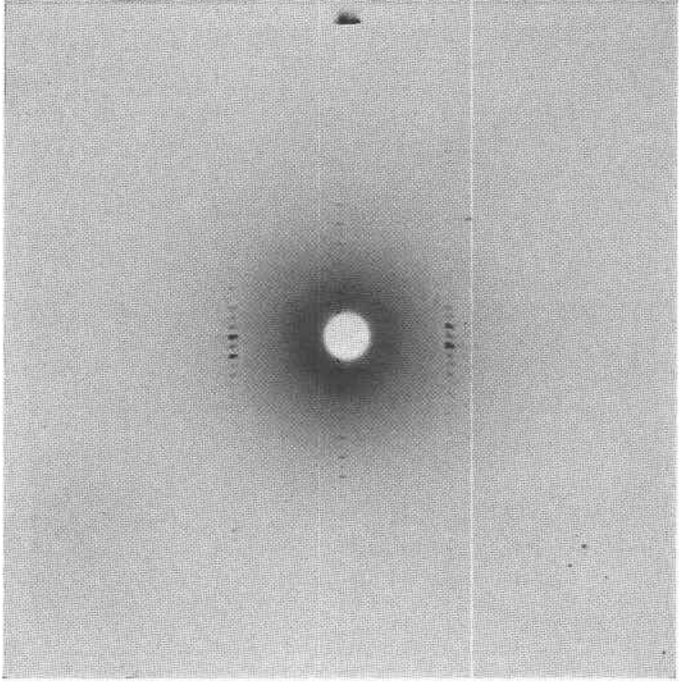

Fig. 2B.
b axis,
zero level.

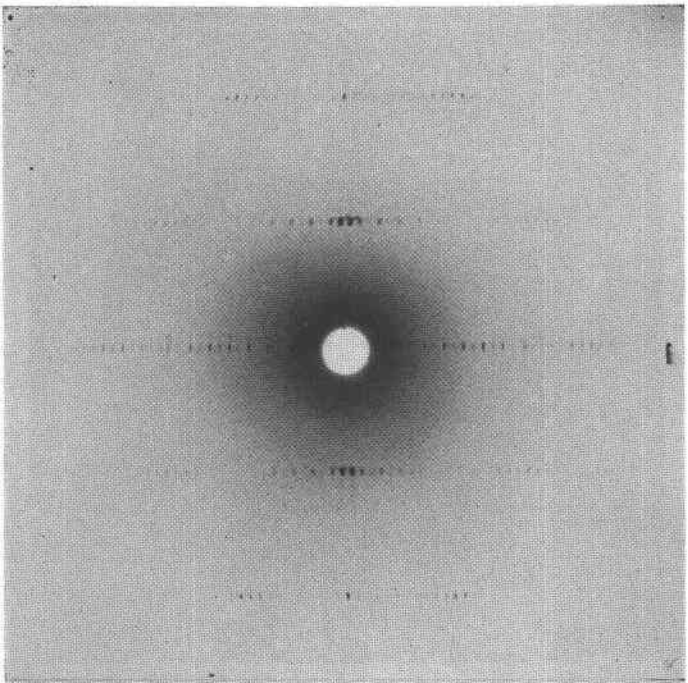

Fig. 2C.
a axis,
zero level.

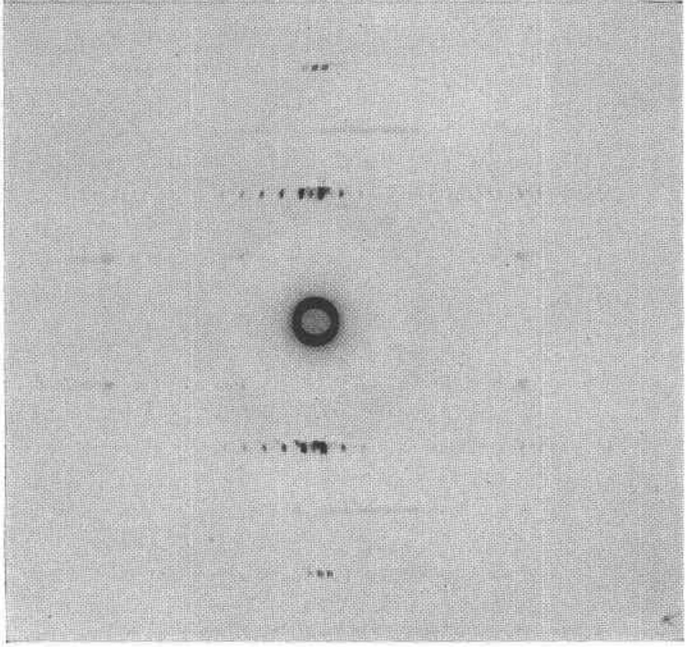

Fig. 2D.
a axis,
1st level.

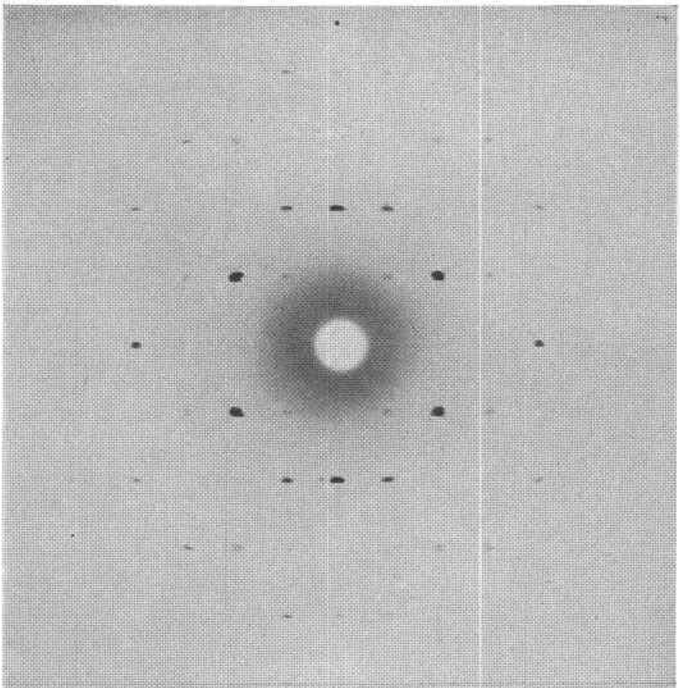

Fig. 3A.
c axis,
several levels.

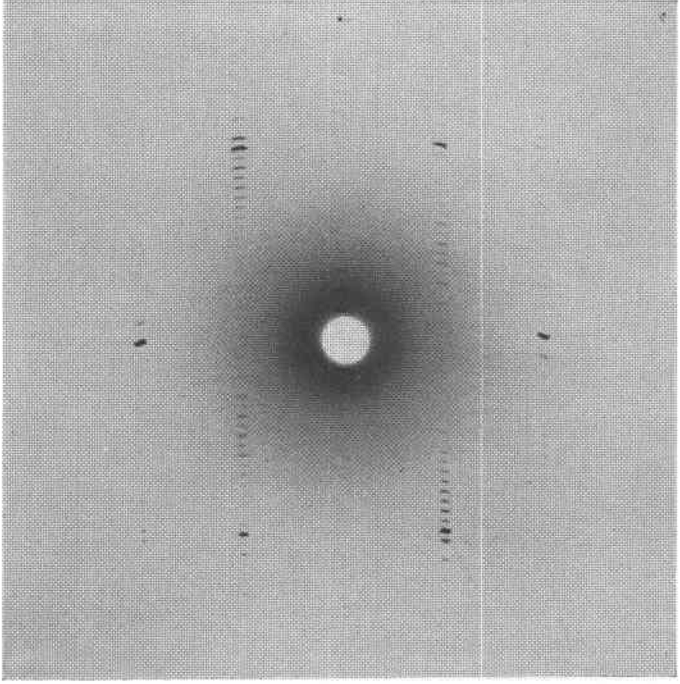

Fig. 3B.
b axis,
zero level.

Fig. 3. Precession photographs of α HSt·NaSt. Figs. *3A* and *3B* represent central sections of the reciprocal lattice, in correct relation; they have a central horizontal line in common. Fig. *3C* is a section parallel to that of Fig. *3B*, but at another level. Note the symmetries of the levels, and compare Fig. *3B* with Fig. *3C* for extinguished lattice rows.

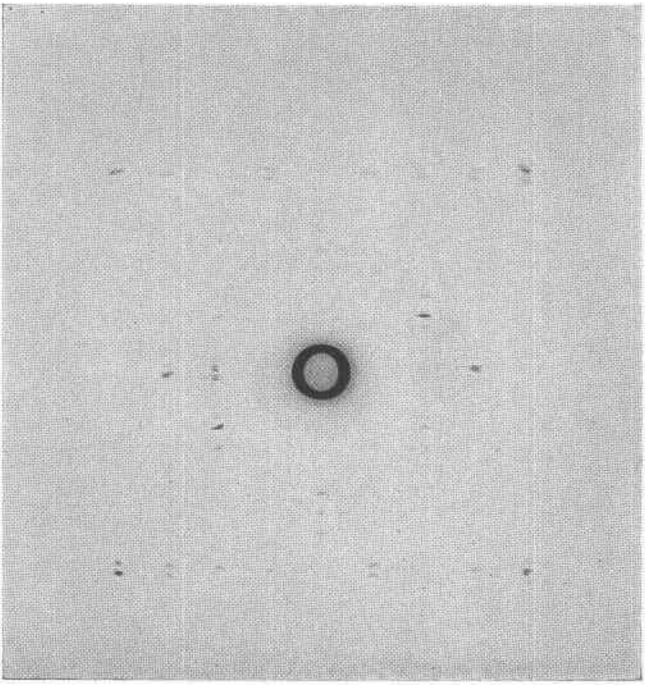

Fig. 3C.
b axis,
1st level.

The symmetries displayed by these three photographs are evidently as follows:

Fig.	precessing axis	level	symmetry	axial label
3*A*	⊥ plate	0+1	*ll*	$\approx c$
3*B*	‖ plate	0	2	*b*
3*C*	‖ plate	1	2	

These symmetry data are sufficient to prove the diffraction point group to be $2/m$. (This symmetry was confirmed by transferring the crystal, as mounted, to a de Jong-Bouman apparatus and rotating about the long, or *a*, axis of the plate. The zero level symmetry was *ll* while the first level symmetry was *l*.)

By superposing the zero level and *n*-level, *b* axis precession photographs (Figs. 3*B* and 3*C*) it is evident that the cell is not centered, hence primitive. Comparing the two photographs shows that the a^* translations are doubled on the zero level, indicating a glide, *a*. Also, the b^* translation on the central line of the *c* axis photograph (Fig. 3*A*) is doubled, indicating a screw 2_1. The diffraction symbol is accordingly $2/mP2_1/a$. This embraces only one space group, namely $P2_1/a$.

The cell dimensions of the α acid sodium palmitate and α acid sodium stearate, as determined from precession photographs, are as follows:

	α HP·NaP	α HSt·NaSt
a	9.97 *kX*	9.97*kX*
b	7.38	7.38
c	45.7	50.7
β	93°	$92\frac{3}{4}$°
cell contents	4 (HP·NaP)	4(HSt·NaSt)
computed density	1.05	1.05

Mechanical properties. Like $NaP\cdot\frac{1}{2}H_2O$ and $NaSt\cdot\frac{1}{2}H_2O$, the acid sodium soap crystals have perfect (001) cleavage as well as perfect (010) cleavage. Similarly, the acid soaps also display very easy plasticity with translation-gliding plane $T=(001)$. It is difficult, however, to discover a folding axis for the plate; hence it may be assumed that any direction in (001) may function as the gliding direction, *t*.

Optical properties. The optical properties of the α form of the sodium acid soaps are as follows:

		α HP·NaP	α HSt·NaSt
refractive indices	α	1.501	1.506
	β	1.513	1.516
	γ	1.57*	1.56*

optic angle	α HP·NaP	α HSt·NaSt
$2V$ (in crystal)	49°	49°
$2E$ (in air)	78°	78°
dispersion	$r>v$ marked	$r>v$ marked
optical orientation	$X=b$	$X=b$
	$Y\approx a$	$Y\approx a$
	$Z\approx c$	$Z\approx c$

* Computed from α, β, and V.

The β 1:1 Acid Sodium Soaps

Introduction. The higher temperature form of the 1:1 acid soaps is here designated β. This form has been prepared[7] for HP·NaP, HSt·NaSt, HBh·NaBh, HAr·NaAr, and for the mixed acid soaps, HP·NaSt and HSt·NaP. Data are given here for β HSt·NaSt only. This may be prepared, for example, by precipitation from a 95% alcohol solution above about 50°C. The present study was made on cleavage flakes of irregular outline.

Symmetry and cell. A precession photograph was first made with the precessing axis normal to the plate. The photograph is shown in Fig. 4*A*. Evidently the symmetry is 2, which is lower than in the cases of the two soaps previously described. The plane of the cleavage is, of course, rational and therefore contains two possible unit translation vectors. In conformity with usage adopted for other soap crystals, these translations are designated a and b, with c becoming transverse to the plate. Provided that c is approximately normal to the plane of the plate (as, indeed, it subsequently develops), then a^* and b^* are also approximately in the plane of the plate, and Fig. 4*A* then presents a photograph of a projection of (001)* which differs little from a parallel projection. Hence, a^* and b^* can be selected from Fig. 4*A*, and, with the proviso above mentioned, rather good values of a, b, and γ can be measured.

With a^* and b^* selected from Fig. 4*A*, the angle which each of these makes with the horizontal universal joint shaft of the precession instrument can be measured. The measurement required is merely the angle between the reciprocal lattice row and the horizontal edge of the film, and this measurement is easily made with the device shown in Fig. 1. When these angles are known, the crystal can be adjusted by means of an arc of the adjusting crystal holder (with the crystal remounted if the adjustment is beyond the range of adjustment of the arc) so that a^* (say) is parallel with the horizontal edge of the film. If, now, the crystal is rotated 90° about the horizontal axis, a^* remains horizontal, c^* comes approximately into the plane of the film, and b becomes nearly parallel

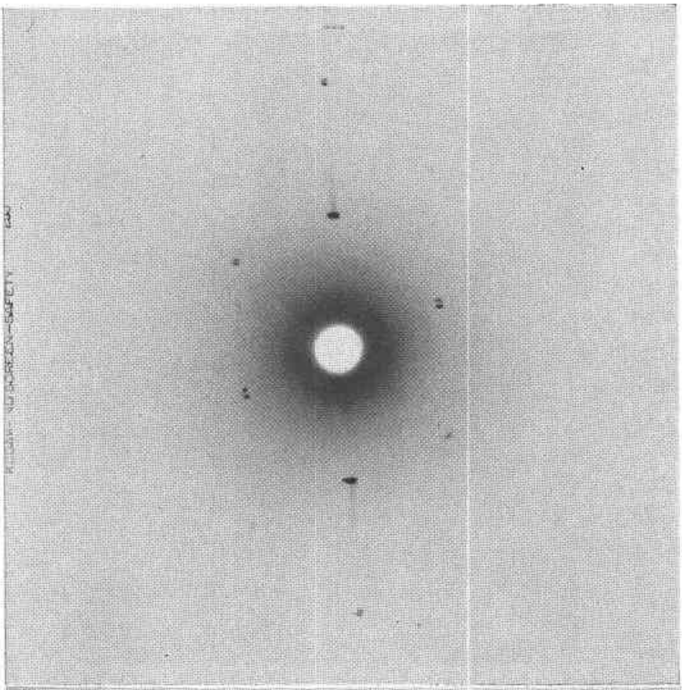

Fig. 4A.
c axis,
several levels.

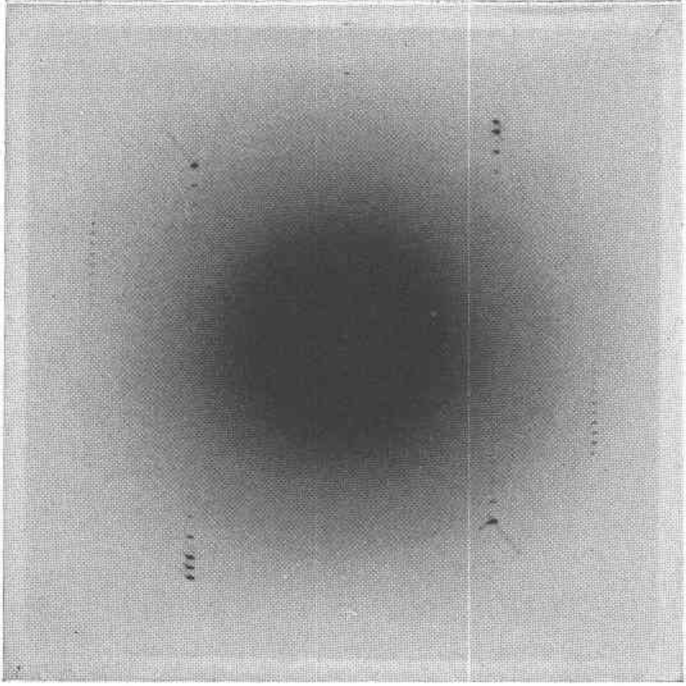

Fig. 4B.
b axis,
zero level.

FIG. 4. Precession photographs of β HSt·NaSt. Figs. 4*A* and 4*B* represent central sections of the reciprocal lattice, in correct relation; they have a central horizontal line in common. Fig. 4*C* is a section parallel to that of Fig. 4*B*, but at another level. Note the symmetries of the levels. Note also the central blind spot in Fig. 4*C*, which is a characteristic of upper-level photographs. Fig. 4*B* was deliberately overexposed in order to record a weak level.

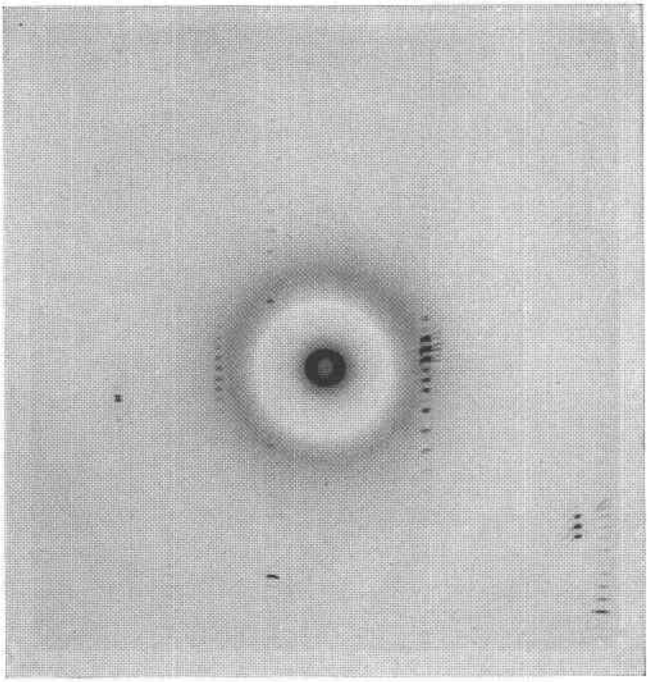

Fig. 4C.
b axis,
1st level.

to the precessing axis. Photographs made with b thus adjusted very approximately parallel to the precessing axis are shown in Figs. 4*B* and *C*.

The symmetries involved in the several photographs of Fig. 4 are evidently 2 for the zero level and 1 for each n-level. The crystal is thus triclinic, with space group either $P1$ or $P\bar{1}$.

Because the crystal used had only one developed surface, namely the (001) cleavage of the flake, and because the distribution of reflections was inappropriate to the precession method of orienting the crystal,[1] small orientation errors, of the order of a few degrees, existed between the reciprocal lattice and its photographs, Fig. 4. Consequently it was impossible to obtain very exact values of the cell dimensions, especially with regard to angles, and the latter may be in error by a degree or so. The cell dimensions so obtained were:

$a = 9.98\ kX$	$\alpha = 90\frac{3}{4}°$
$b = 11.46$	$\beta = 90°$
$c = 50.2$	$\gamma = 94°$

cell contents 6(HSt·NaSt)
computed density 1.02

Mechanical properties. β HSt·NaSt has perfect (001) cleavage, as other soaps, and also perfect (110) cleavage. It is somewhat less plastic than the two previously described crystals, with $T = (001)$, t unknown.

Optical properties. The optical properties of the β form of sodium acid stearate are as follows:

		HSt·NaSt
refractive indices	α	1.498
	β	1.510
	γ	1.59*
optic angle		
$2V$ (in crystal)		42°
$2E$ (in air)		66°
dispersion		$r > v$ marked
optical orientation		$X \wedge b = +40°$
		$Y \wedge a = +36°$
		$Z \wedge c = 90°$
		$X \wedge (110)$ (cleavage) $= -11°$

* Computed from α, β, and V.

REMARKS ON SOME PROPERTIES OF SOAP CRYSTALS

Tabulated data. For convenience, the cell, mechanical, and optical properties of the several soap crystals are brought together in Table 1.

Powder photographs of soap crystals. Powder patterns of soap crystals are easily made with the aid of what amounts to a hollow needle.

TABLE 1

			α Neutral Sodium Soap Hemihydrate		α 1:1 Acid Sodium Soaps		β 1:1 Acid Sodium Soap
			$NaP \cdot \frac{1}{2}H_2O$	$NaSt \cdot \frac{1}{2}H_2O$	HP · NaP	HSt · NaSt	HSt · NaSt
Crystallographic properties	Crystal System Space group		Monoclinic Aa or $A2/a$		Monoclinic $P2_1/a$		Triclinic $C1$ or $C\bar{1}$
	Cell dimensions	a	9.13 kX	9.16 kX	9.97 kX	9.97 kX	9.98 kX
		b	8.01	8.00	7.38	7.38	11.46
		c	91.85	103.96	45.7	50.7	50.2
		α					$90\frac{3}{4}°$
		β	94°	$93\frac{1}{4}°$	93°	$92\frac{3}{4}°$	90°
		γ					94°
	Cell contents Computed density		$16(NaP \cdot \frac{1}{2}H_2O)$ 1.13	$16(NaSt \cdot \frac{1}{2}H_2O)$ 1.10	4(HP · NaP) 1.05	4(HSt · NaSt.) 1.05	6(HSt · NaSt) 1.02
Mechanical properties	Cleavages		(001) perf. (010) perf.	(001) perf. (010) perf.	(001) perf. (010) perf.	(001) perf. (010) perf.	(001) perf. (110) perf.
	Translation-gliding plane, T direction, t		(001) [010]	(001) [010]	(001) many in (001)	(001) many in (001)	(001) ?
Optical properties	Refractive indices	α	1.505	1.507	1.506	1.506	1.498
		β	1.517	1.517	1.513	1.516	1.510
		γ	1.57*	1.56*	1.57*	1.56*	1.59*
	Optical Orientation		$X=b$ $Y \approx a$ $Z \approx c$	$X=b$ $Y \approx a$ $Z \approx c$	$X=b$ $Y \approx a$ $Z \approx c$	$X=b$ $Y \approx a$ $Z \approx c$	$X \wedge b=+40°$ $Y \wedge a=+36°$ $Z \wedge c=\ 0°$
	Optic angle	2V (in crystal)	50°	49°	49°	49°	42°
		2E (in air)	80°	78°	78°	78°	66°
		dispersion	$r>v$ strong	$r>v$ marked	$r>v$ marked	$r>v$ marked	$r>v$ marked

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* Computed from α, β, and V.

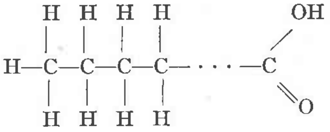
This is simply pressed into the powder, which rises in the cylindrical bore, forming a core. When ejected with a wire plunger, the resulting naked core forms an ideal sample. Any type of powder pattern of soap, unless the sample was exceedingly fine grained, suffers from the effects of preferred orientation due to the platy habit and the extremely plastic nature of soap crystals.

Powder patterns of the three soap types discussed in this paper are shown in Fig. 5.

It should be noted in passing that soaps (as well as other organic crystals with large cells) cannot be identified by the Dow Chemical Company scheme[8] of tabulating the three strongest lines. This is fundamentally due to the fact that the many parameters required to locate the atoms in large cells cannot be represented by three coordinates. Such a scheme can only succeed with crystals having comparatively few atoms in the cell. A number of soaps have the three strongest lines in the same positions. Further, all soaps with the same layer spacing have a sequence or orders of 001 whose locations are identical.

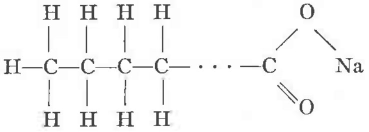
Packing of soap molecules. Many properties of soap crystals are obviously related either directly or ultimately to the characteristics of soap molecules. Molecules entering into the structures of soap crystals are known on chemical grounds to be composed of long paraffin chains of hydrocarbons terminating in COOH groups for the fatty acids and COONa groups for the sodium soaps, thus:

fatty acid molecule



$$\mathrm{H{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\cdots{-}C({=}O){-}OH}$$

soap molecule



$$\mathrm{H{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\cdots{-}C({=}O){-}O{-}Na}$$

The palmitate chain contains 16 total carbon atoms, the stearate chain, 18 carbons.

The packing of such molecules to form crystals requires:

(a) that the molecules pack with long directions in parallel position in response to van der Waal's forces;

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[8] Hanawalt, J. D., Rinn, H. W., and Frevel, L. K., Chemical analysis by x-ray diffraction: *Ind. and Eng. Chem.*, **80** (1938). (*Analytical Edition*, **10**, 457–512.)

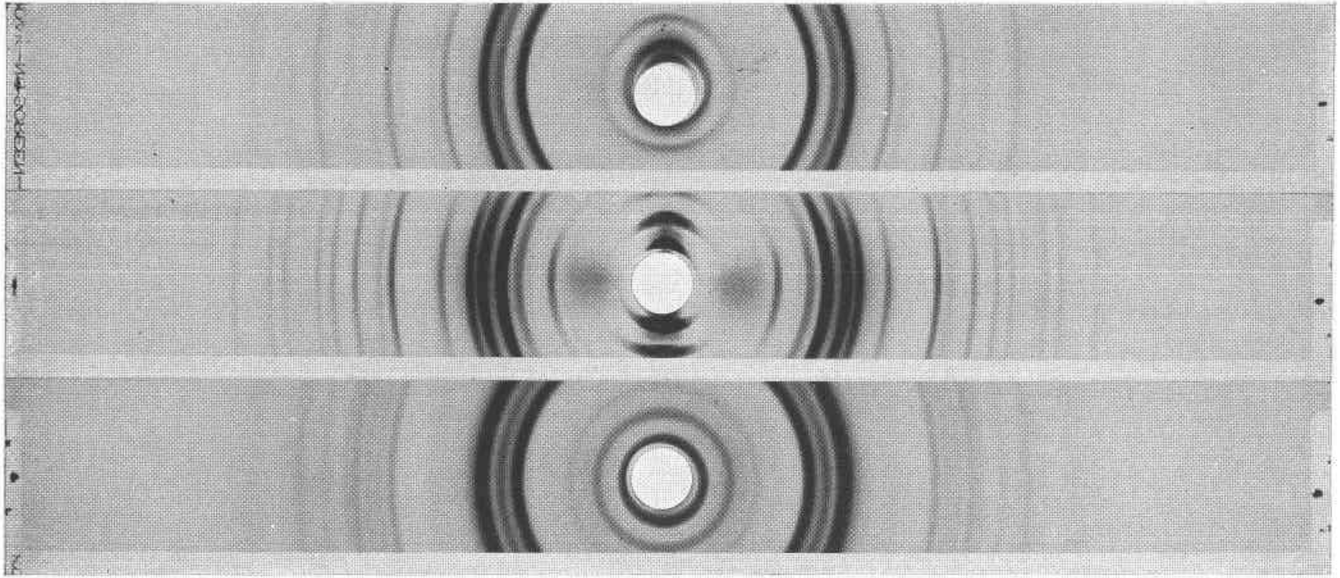

FIG. 5. *X*-ray powder photographs of representatives of the soap crystal types discussed in this paper. These photographs were taken with a camera having the standard diameter of 114.6 mm. (on which 1 mm. film distance corresponds to 1° for the deviation angle, 2θ, and to $\frac{1}{2}°$ for the Bragg angle, θ). For purposes of comparison by others, these photographs are reproduced here to exactly natural size. (The middle photograph displays severe orientation which cannot be eliminated by fine-grinding the sample, since grinding causes the transformation $\alpha \rightarrow \beta$ to occur.)

Upper photograph: α NaSt.
Middle photograph: α HSt · NaSt.
Lower photograph: β HSt · NaSt.

(b) that the packing of neighboring parallel molecules be such as to distribute the positive charge concentrations of the hydrogens on the side arms of the chains;
(c) that a hydrogen bond is possible for the acid end of the acid molecule; and
(d) that the coordination requirements of the sodium in the terminations of the molecules be taken care of by an environemnt of six oxygens.

Requirements (a) and (b) are also found in crystals of paraffin molecules, whose packing has been studied by Müller.[9] Additional requirements (c) and (d) cause soap in general to utilize more complicated modes of packing than paraffins. They are also responsible for the tendency of soaps to form hydrates.[5]

Requirement (a) gives rise to the packing of soap molecules into layers, with the molecules transverse to the layers. The intermolecular forces within layers are strong while the forces between layers are comparatively weak, so that soap crystals, on heating, assume a smectic liquid crystalline condition. The layers thus act as units (transformations within layers are known, however).

Clastic and plastic properties. The layer nature of soap crystals is responsible for their most important mechanical properties. The layers can be separated, giving rise to the perfect {001} cleavages of soap crystals. They can also be slipped along one another, giving rise to the easy gliding with $T = \{001\}$. While there is a tendency toward slippage in preferred directions, as in the case of the sodium stearate and palmitate hemihydrate, this is not always discernible, and, in all cases studied, gliding can occur in any direction in the (001) plane with nearly or actually equal ease.

An *x*-ray study of preferred orientation in commercial soap showed that when soap is passed in heated condition past a streamlined fin, orientation results in the soap which had been in the neighborhood of the obstruction. The orientation is such that some line in (001) of the crystals tends to align itself parallel with the direction of movement of the soap past the obstruction. This is consistent with the gliding of soap layers over one another without a preferred direction in the layer.

Twinning. No twins have been observed in crystals of the α neutral soaps. Twins have been encountered in crystals of both the α and β modifications of the 1:1 acid soaps by mistaking twins for single crystals to be used in making photographs by the precession method. Studies of the precession photographs of such twins show that the twin law is reflection across (001). This implies that the crystallization of soap crystals may be attended by errors of growth in respect to the superposition of

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[9] Müller, Alex. A further *x*-ray investigation of long chain compounds (*n*-hydrocarbon): *Proc. Roy. Soc.*, **120A**, 437–459 (1928).

one layer over another. This kind of error is a reasonable one to expect to occur during the growth of a layer structure.

Optical properties. The several soap crystals discussed, as well as certain crystals found in commercial soaps (as far as they can be investigated) have remarkably similar optical properties. All are biaxial positive with optic angles in the neighborhood of 45°. All have refractive indices with α and β in the neighborhood of 1.51. Optical properties thus do not constitute good criteria by which to distinguish between soap crystals.

It might be mentioned in passing that the positive optical sign is a direct consequence of the soap structure containing separated linear molecules.