(2) If maximum intensity is required, an abrasive treatment should be chosen which limits the misorientations to within the range provided by the incident beam. It was shown in § 9 that if the divergence of the incident beam is greater than the angle over which the crystal reflects, the intensity reflected by the stationary crystal is proportional to the integrated reflexion. Hence a monochromatic beam of large divergence can be used to measure the integrated reflexion from stationary crystals. This method has been used by Renninger (1937).

(3) If the crystal is used as a concentrating monochromator, the surface layer produced by grinding should be removed. For maximum intensity the surface should again be worked very lightly. We have found that a crystal of lithium fluoride ground as a concentrating monochromator, etched and subsequently very lightly worked gives a uniform, intense monochromatic beam.

For other details relating to the use of concentrating monochromators, reference may be made to an earlier publication by Evans *et al.* (1948). It may be pointed out here that by reversing the directions of the beams, these monochromators may be used to provide very wide uniform X-ray beams.

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The Unit-cell Dimensions of Potassium Soaps

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Powder photographs have been prepared for a series of potassium soaps at 25 and 75° C. Three distinct crystalline phases are recognized; their transition temperatures are given and the unit-cell dimensions are determined for each existing phase of all the soaps.

Little previous work has been published on the crystallography of soaps, and most of this has been concerned with sodium soaps. Piper (1929) has published a paper giving only the long spacings for a series of potassium soaps, and more recently Vand, Lomer & Lang (1949) have published the complete crystal structure of potassium caprate. The lack of more detailed results on other soaps is largely due to the extreme difficulty of growing crystals suitable for single-crystal investigation, but recent work by Vand has shown how the unit-cell dimensions of crystals of low symmetry may be determined from powder photographs. The methods used are particularly valuable for the investigation of long-chain compounds such as soaps, fatty acids and hydrocarbons in general, since in these compounds one cell edge is much longer than the others and as such is easily recognized on a powder photograph. Part of the object of this and the succeeding paper is to show that powder photographs may be interpreted in more detail than has hitherto been the practice.

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Experimental

The soaps were prepared by neutralizing alcoholic solutions of fatty acids with alcoholic solutions of potassium hydroxide. The resulting solutions were evaporated to dryness over calcium chloride *in vacuo*. The soaps were then mounted between moisture-proof cellophane and photographed in the high-resolution X-ray powder camera recently described by Vand (1948*a*). Before commencing work with the soaps this camera was calibrated by the author, using the known spacings of quartz, rock salt, gypsum and calcite. For values of d/n over 5 kX. the long spacings of a series of silver soaps, the higher orders of which extend into the calibrated range, were used. The calibration showed that reciprocal spacings (n/d) could be measured to an accuracy of $\pm 0{\cdot}0007$ kX.$^{-1}$.

Results

The powder photographs of the soaps were measured and their d/n values obtained. Visual inspection of the photographs showed the striking similarity of the patterns of soaps of different chain length in the same phase, and immediately showed that there are three main phases. Soaps of chain length from 4 to 10 carbon atoms inclusive crystallize from alcohol in one phase (A), while those from 12 to 18 crystallize in a second (B). With the exception of potassium butyrate and caproate (4 and 6 carbon atoms respectively), all of the soaps transform on heating to a third distinct phase (C). Potassium butyrate and caproate show only very slight changes in pattern on heating, and these are due merely to thermal expansion. The change on heating in the pattern of potassium caprylate is also slight, but represents a true phase change. In all the other soaps the transition from the low-temperature phase (A or B) to the high-temperature phase (C) is quite definite and occurs at a fixed temperature. On cooling, all soaps revert to their original phase as crystallized from alcohol, with one exception. This is potassium laurate which crystallizes from alcohol in the B phase. This phase, on heating, transforms to the C phase, which in its turn transforms on cooling to the A phase. This phase, however, is not stable and reverts slowly over a period of months to the original B phase.

The transition temperatures were measured by taking a series of X-ray photographs at different temperatures. In the temperature-controlled specimen holder the edges of the sample in contact with the hot specimen holder were warmer than the central portions, so that over a small range of temperature, as recorded by the specimen-holder thermometer, a photograph of the mixed phases was obtained. The transition temperature could thus be estimated, probably with an accuracy of ± 3° C. A few of the transition points were checked by a microscopic method. The soaps were warmed on the microscope stage in an electrically heated chamber containing a thermocouple. The transition was manifested in one or more of three ways: A crystal, initially arranged in its extinction position, would suddenly become brightly illuminated with interference colours; or secondly, a few of the small crystals would execute sudden small jumps in the chamber; or finally, the transition might be detected only by the sudden appearance of minute cracks in some of the crystals. Frequently no change was observed on heating above the transition point, but whenever a change was observed it always occurred at a temperature in fair agreement with the X-ray value. The values of the transition temperatures (accurate to about ± 3° C.) are given in Table 1.

Table 1. *Transition temperatures*

Soap	Transition	Temperature (° C.)
Potassium caprylate	From A to C	55
Potassium caprate	From A to C	76
Potassium laurate	From B to C	54
Potassium laurate	From C to A (cooling)	54
Potassium myristate	From B to C	61
Potassium palmitrate	From B to C	68
Potassium stearate	From B to C	78

The long spacings of soaps in the same phase are a linear function of the number of carbon atoms in the chain

$$d_{001}=PN+Q, \tag{1}$$

where d_{001} is the long spacing, N the number of atoms in the chain and P and Q are constants. The observed values of the long spacing have a probable error of the order of 0·5 %; they are given, together with their values calculated from equation (1), in Tables 2–4.

Table 2. *Long spacings of A phase at* 25° C.

$P=2{\cdot}147\pm0{\cdot}024,\quad Q=5{\cdot}88\pm0{\cdot}20$

Soap	d_{001} (obs.) (kX.)	d_{001} (calc.) (kX.)	Difference
Potassium butyrate	14·39	14·46	−0·07
Potassium caproate	18·89	18·76	0·13
Potassium caprylate	22·95	23·05	−0·10
Potassium caprate	27·47	27·35	0·12
Potassium laurate	31·56	31·64	−0·08

Table 3. *Long spacings of B phase at* 25° C.

$P=2{\cdot}048\pm0{\cdot}018,\quad Q=5{\cdot}25\pm0{\cdot}28$

Soap	d_{001} (obs.) (kX.)	d_{001} (calc.) (kX.)	Difference
Potassium laurate	29·72	29·80	−0·08
Potassium myristate	33·98	33·90	0·08
Potassium palmitrate	38·10	38·00	0·10
Potassium stearate	41·99	42·09	−0·09

Table 4. *Long spacings of C phase at* 75° C.

$P=2{\cdot}148\pm0{\cdot}011,\quad Q=6{\cdot}56\pm0{\cdot}15$

Soap	d_{001} (obs.) (kX.)	d_{001} (calc.) (kX.)	Difference
Potassium caprylate	23·75	23·75	0·00
Potassium caprate	28·00	28·05	−0·05
Potassium laurate	32·21	32·34	−0·13
Potassium myristate	36·84	36·64	+0·20
Potassium palmitate	40·95	40·94	+0·01
Potassium stearate	45·22	45·23	−0·01

The long spacings of the *B* phase agree with those of Piper (1929). In all phases the deviations of the observed values from those calculated are less than the estimated probable error of measurement, and since the deviations are positive and negative quite independent of *N* there can be no question that the relationship is anything but linear.

From the knowledge of the long spacings and the densities of the soaps the photographs were indexed, using the first graphical method described by Vand (1948*b*). The unit cells were then calculated, also as described by Vand (1948*b*). The results are given in Table 5.

Vand & de Boer (1947) have shown theoretically that *S* may be expected to vary as *N* changes, and report having observed the expected effect in sodium and silver soaps. Although no variations were observed among the potassium soaps of the *A* phase, Vand & de Boer do report an increase in *S* with increasing *N* for potassium soaps in the *B* phase. This finding conflicts with the measurements made by the author which show no significant variation of the cross-section for any of the phases of the potassium soaps. It seems probable that the variation reported by Vand & de Boer is due to experimental error, the magnitude of which is not reported in their paper.

Table 5. *Cell dimensions of the potassium soaps*

Soap	Temp. (° C.)	Phase	*a* (kX.)	*b* (kX.)	*c* (kX.)	α (°)	β (°)	γ (°)	Density (g.cm.$^{-3}$) Calc.*	Density (g.cm.$^{-3}$) Obs.
KC_4	25	*A*	8·10	5·68	14·40	90	92	90	1·256	1·291
KC_6	25	*A*	7·98	5·73	18·90	90	91·9	90	1·177	1·185
KC_8	25	*A*	7·90	5·67	22·96	90	92·1	90	1·170	1·171
KC_{10}	25	*A*	8·06	5·67	27·52	90	93·5	90	1·105	1·125
KC_{10}†	25	*A*	8·09	5·63	28·81	90	108·0	90	1·112	—
KC_{12}	25	*A*	7·95	5·66	31·72	90	95·7	90	1·106	1·120
KC_{12}	25	*B*	4·13	5·59	29·98	97·4	92·0	94	1·149	1·139
KC_{14}	25	*B*	4·14	5·60	34·00	91·6	91·5	93	1·118	1·125
KC_{16}	25	*B*	4·16	5·60	38·19	92·7	91·3	93	1·096	1·117
KC_{18}	25	*B*	4·15	5·56	42·03	91·5	91·6	94	1·102	1·110
KC_4	75	*A*	8·09	5·70	14·50	90	92·2	90	1·245	1·289
KC_6	75	*A*	8·05	5·74	19·10	90	92·8	90	1·154	1·168
KC_8	75	*C*	8·07	5·72	23·76	90	91·7	90	1·097	1·108
KC_{10}	75	*C*	8·10	5·67	28·01	90	91·8	90	1·079	1·107
KC_{12}	75	*C*	8·06	5·66	32·30	90	94·2	90	1·071	1·068
KC_{14}	75	*C*	8·06	5·68	36·87	90	92·1	90	1·042	1·053
KC_{16}	75	*C*	8·03	5·70	40·95	90	90·1	90	1·038	1·050
KC_{18}	75	*C*	8·05	5·66	45·37	90	93·2	90	1·031	1·037

* Assuming four molecules/unit cell for *A* and *C* phases and two for the *B* phase.

† As determined from single-crystal photographs (Vand *et al.* 1949).

Discussion

Some authors have attempted to calculate the 'angle of tilt' of the molecules in the crystal from values of *P* (Tables 2–4). (The angle of tilt is the angle between the axis of the molecule and the base plane of the unit cell.) This calculation depends on knowing the distance between alternate carbon atoms in the molecule, and a value of 2·52 kX. is commonly used, calculated on the assumption of a C–C bond length of 1·54 kX. and a tetrahedral bond angle in the chain. There is, however, a considerable volume of evidence to suggest a greater value than 2·52 kX. (Brummage, 1947; Murison, 1934; Vand *et al.* 1949), and it is believed that the distance 2·61 kX. obtained by single-crystal measurement by Vand *et al.* is the most reliable. The calculation of the angle of tilt also assumes that the angle is constant in all the soaps in the same phase, and there is no evidence to show that this is true. However, even an approximate value for the angle is a great help in single-crystal analysis. Table 6 gives such values, based on a distance of 2·61 kX. between alternate carbon atoms.

From the values of the long spacings, the densities and the angle of tilt, it is possible to calculate the cross-sectional area (*S*) of the soap molecules (Table 6).

The cell dimensions have a probable error of ±0·02 kX.; it is thus clear that, with the possible exception of the butyrate, all the soaps in the same phase have the same short cell dimension. The average difference between the observed and calculated values of the reciprocal spacings n/d is 0·0007 kX.$^{-1}$, which corresponds to an error of 0·1 mm. in measuring the radii of the haloes on the film. This is equal to the estimated error of radius measurement, so that it seems certain that the photographs are correctly indexed and that the unit cells have been determined as accurately as the experimental observations permit. The apparent discrepancy between the cell dimensions of potassium caprate as determined by powder photograph and single-crystal measurements is due merely to a different choice of the monoclinic angle; the value of $c \sin \beta$ is 27·40 kX. for both cells.

Table 6. *Angles of tilt*

Phase	Angle of tilt	Cross-section of molecule (kX.^{2})
A	55° 30′	18·47 ± 0·13
B	53°	18·09 ± 0·11
C	55° 30′	18·84 ± 0·09

A series of photographs showed that the cell dimensions of potassium caproate varied continuously with temperature and no sudden change in the diffraction pattern was observed. The change in the cell dimensions is thus a measure of the coefficient of expansion of the crystal.

The only cell dimension to increase significantly was a, the coefficient of expansion parallel to this axis being $1{\cdot}75\times10^{-4}$ per °C. It is interesting that the direction of maximum expansion is normal to the plane of the molecule; this is the direction one would predict if the thermal energy supplied in heating were equally divided among vibrations about three mutually perpendicular axes, since the moment of inertia of the molecule about its long axis is very much smaller than that about the other two. The amplitude of the vibrations about this axis would thus be much larger than those about the other two, and this would tend to produce the maximum expansion in a direction normal to the plane of the molecules.

It is known from single-crystal measurement that the A phase of potassium caprate crystallizes in the space group $P2_1/a$. As the photographs of all other members of the A phase, with the exception of the butyrate, could be completely indexed without introducing indices $h0l$ with h odd, or $0k0$ with k odd, it seems certain that all these soaps also crystallize in the space group $P2_1/a$. In the butyrate, however, the 010 reflexion was observed, so that this soap must be in a different space group. Moreover, the observed and calculated densities do not agree so well as for the other soaps, and it must be realized that the photograph may be incorrectly indexed, although much patient work failed to produce a better agreement. The soaps in the B phase are triclinic, $P1$ or $P\bar{1}$. The photographs of soaps in the C phase were all indexed without the introduction of the indices $10l$ and 010. This slight evidence suggests $P2_1/a$ as the most probable space group for this phase as well.

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The Application of Booth's Method of Steepest Descents to the Determination of the Structure of Potassium Caproate

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The crystal structure of potassium caproate has been determined from powder photographs alone by the application of the method of steepest descents. The use of the method is discussed, and the means of overcoming some of its limitations is indicated.

The unit cell and probable space group of potassium caproate have been determined in the preceding paper, which has shown the possibility of indexing powder photographs of such organic compounds of low crystal symmetry. The present paper attempts to go a stage further and to determine the complete crystal structure of such a compound from its powder photograph. The chief limitation to this is that only an incomplete set of structure factors can be obtained, since the reflexions from some planes overlap each other, and many weak reflexions, which would easily be recorded on single-crystal photographs, are lost in the high background of the powder photograph. Fourier-series methods for the refinement of atomic parameters are thus not feasible, but the method of 'steepest descents' (Booth, 1947) may be used since this does not require a complete set of structure factors. In this method a quantity R is defined which measures the discrepancy between the observed and calculated structure factors. From the differentials of R with respect to each of the atomic parameters it is possible to compute the required changes in each parameter in order that R may be diminished as rapidly as possible. The definition of R,

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