densities going down to $-1{\cdot}4\,\text{e.A.}^{-2}$ in the diffraction ring immediately surrounding the bromide ion. The error in the determination of the shape of the cation was considerably greater than in the case of the chloride crystal, because the scattering from the cation was a smaller fraction of the total. Thus, the shapes of the contours around the cation are inconsistent with one another, but the contours around the bromide ion are practically circular. Since no direction of preferred orientation of the cation is shown, we may say that the cation behaves as a free rotator, within the limits of error of the measurements.

Preliminary determination of the structure of the iodide

The centrosymmetric point group of the iodide was established as D_{4h}–$4/mmm$ by Laue pictures taken along the a and c axes of an iodide crystal. In these pictures a few anomalies of intensity appeared, presumably because of the absorption of the longer wave-lengths, but almost all of the spots showed entirely normal symmetry. The unit-cell parameters for the iodide were found from a Weissenberg photograph of the zero layer with [110] as rotation axis, on which was superimposed a sodium chloride powder pattern. Under the assumption that the structure is analogous to those of the chloride and bromide, the observed parameters are

$$a=6{\cdot}931\pm0{\cdot}003;\quad c=7{\cdot}332\pm0{\cdot}003\ \text{A}.$$

Here we find that the expansion of the unit cell on replacing chloride ion by iodide ion takes place only in the plane of the a axes, just as on replacing chloride ion by bromide ion.

Since X-ray diffraction pictures of the iodide with Cu $K\alpha$ radiation had shown strong absorption effects, Weissenberg pictures were taken with Mo $K\alpha$ radiation. Zero- and first-layer pictures were taken with the a axis as rotation axis of an iodide crystal of dimensions $0{\cdot}2\times0{\cdot}2\times0{\cdot}1$ mm. The Mo $K\alpha$ spots on both layers showed symmetry C_{2l}, without any anomalies of intensity, thus corroborating the existence of a two-fold axis. An additional Weissenberg picture of the first layer, taken with a short range of oscillation and a long exposure, showed the presence of faint spots which were indexed 103 and $10\bar{3}$. The existence of these spots clearly ruled out the structure proposed by Hendricks. No $hk0$ spots with $h+k$ odd were observed, however. Therefore, we conclude that the structures of the iodide, chloride, and bromide are, in all probability, analogous.

Whereas the decline of the intensities was about the same for the chloride and the bromide, it was much faster for the iodide. The interpretation is apparently that the amplitude of thermal vibration was much greater in the iodide crystal.

Appreciation is expressed to the donors of the Minnesota Mining and Manufacturing Co. Fellowship in Chemistry for 1947–8 to M. V. King.

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The Low-Temperature Modification of *n*-Propylammonium Chloride*

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The room-temperature structure of n-propylammonium chloride, which shows rotation of the cations, goes over in a second-order transition into a low-temperature form with fixed positions of the cations. In this process, the crystal of the room-temperature form breaks up reversibly into many domains of the low-temperature form, the domains having differing orientations. The space group of the low-temperature form is C^3_{2h}–$C2/m$. The transition is produced by the fixing of the positions of the cations in the $(1\bar{1}0)$ planes of the room-temperature structure in a centrosymmetric arrangement, with the result that the angle between the a axes is contracted, and the c axis is tipped in the direction of the axis [110]. The amount of these distortions varies with the temperature. Approximate positions of the atoms in the low-temperature form are given.

Introduction

Since a study of the room-temperature structures of the n-propylammonium halides by the present authors (1950) had shown the probable existence of rotation of the n-propylammonium ion, the study of the behavior of this rotating group at lower temperatures was of interest. Since a transition at low temperatures to a crystal structure having long-range order in the orientations of the cations was expected, it was therefore of interest to find which orientations the cations take,

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for comparison with the room-temperature structure. If the transition is an order–disorder transition, then the low-temperature structure may be formed without disruption of the arrangement of cations and anions.

Preliminary experiments showed gradual arrests in the cooling curves of *n*-propylammonium chloride between −80 and −90° C. and of the iodide between −90 and −105° C. A sharper arrest was shown for the bromide at −116° C. A gradual arrest should be expected in a second-order transition involving an order–disorder change. Therefore, the chloride was chosen for study, as involving probably a second-order transition.

Apparatus and procedure

An apparatus was used in which the crystal, mounted on a Weissenberg goniometer, could be cooled to the desired temperature by a stream of cold gas. Dry nitrogen was bubbled through liquid nitrogen, and led through a vacuum-jacketed tube to a nozzle directed at the crystal. The temperature of the issuing gas was measured by means of a copper–constantan thermocouple situated in the gas stream as close as possible to the crystal. In order to avoid condensation of moisture on the crystal mount, a double shield made of cellulose acetate swept out with another stream of dry nitrogen was placed around the crystal. Openings were made in the shield for the X-ray pinhole and for the nozzle of the cooling apparatus. The diffraction photographs were taken by rotation or oscillation technique on flat film.

The simplicity of this technique was made possible by the fact that the crystals were stable at room temperature, and the circumstance that the transition was of the second order, such that it was not necessary to preserve the crystals continuously at low temperatures. It was possible to align the crystals at room temperature, cool the crystal to the desired temperature, and make the X-ray exposure, maintaining the temperature by adjusting the rate of flow of the cold gas. The thermocouple and the crystal were mounted in such a way as to minimize heat conduction. The limits of error in the average temperatures, given below, of the crystal were estimated to be as large as ±20° C.

Structure determination

Rotation photographs were taken with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ A.) of a chloride crystal of dimensions $1 \times 1 \times 0{\cdot}2$ mm. The crystal was mounted in a drop of P296 Beckosol, a drying alkyd varnish, on the side of a capillary filled with powdered sodium chloride; the resulting powder lines furnished a reference standard for the low-temperature patterns. Both room-temperature and low-temperature rotation photographs were taken about the *a*, *c* and [110] axes. In addition, room-temperature and low-temperature oscillation photographs were taken with 35° oscillations about the *c* axis.

A low-temperature rotation photograph taken about the *a* (6·220 A.) axis showed the splitting of certain spots into doublets. A rotation photograph taken with [110] as rotation axis at an average temperature of −130° C. showed also a splitting of each of the *n*-layer lines into two closely spaced layer lines with spacings indicating repeat distances of 9·06 and 8·58 A. in comparison with the room-temperature value of 8·80 A. These data indicate a contraction of the angle between the *a* axes from 90 to 87°. The presence of both sets of layer lines indicates that domains of differing orientations are present simultaneously in the crystal at low temperatures. This pattern is shown in Fig. 1, and the room-temperature pattern for comparison in Fig. 2. Another rotation photograph taken with [110] as the axis of rotation, but at an average temperature of −67° C., showed a slight splitting of the spots within the layer lines, but no visible separation of different sets of layer lines. Apparently, at this temperature, the transition had begun through a slight deformation of the unit cell in some of its dimensions, but the repeat distances along [110] and [$1\bar{1}0$] were still practically equal.

The rotation and oscillation photographs taken at low temperatures with the *c* axis as rotation axis showed many spots not lying on the layer lines of the room-temperature photographs. Fig. 3 is a rotation pattern taken at an average temperature of −130° C., and Fig. 4 is the corresponding room-temperature pattern for comparison. Since room-temperature photographs taken before and after the low-temperature photograph had identical appearances, the transition is apparently reversible, and the appearance of the low-temperature photographs cannot be ascribed to misalignment of the crystal as a whole. The detailed study of both the rotation and oscillation photographs taken at low temperatures about the *c* axis showed that each spot on the room-temperature photographs split into a constellation of spots on the low-temperature photographs. This splitting indicated that the crystal breaks up at low temperatures into domains having their *c* axes oriented in slightly different directions. It was found that each of the *hhl* spots formed a constellation of three spots, each of the *h*0*l* spots formed a constellation of two spots, and each of the other *hkl* spots formed a constellation of four spots. Apparent exceptions were observed, of course, in faint spots, for which some of the expected components were not observed, apparently because they were too faint. The arrangement and number of spots in the constellations indicated that the *c* axis in each domain is tipped by about 8° in the direction of the bisector of the 87° angle between the *a* axes, i.e. in the ($1\bar{1}0$) plane, the amount of tipping depending on the temperature. In this process, the repeat distance along *c* remains practically unaltered. A few extra components were also observed for the strongest of the *h*0*l* spots. These extra spots lay at the positions of 200, 400 and 201 on the layer lines of the room-tem-

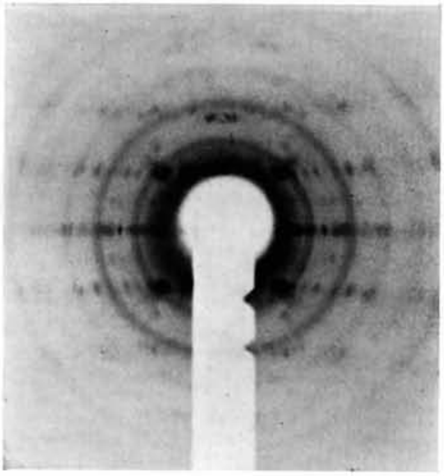

Fig. 1. Rotation photograph about [110] axis at $-130°$ C.

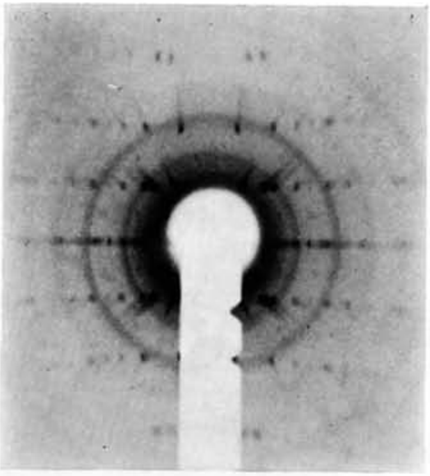

Fig. 2. Rotation photograph about [110] axis at room temperature.

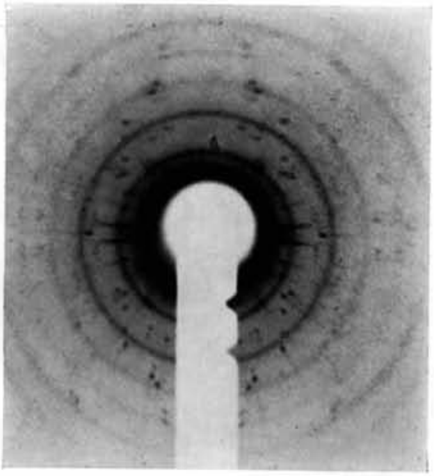

Fig. 3. Rotation photograph about c axis at $-130°$ C.

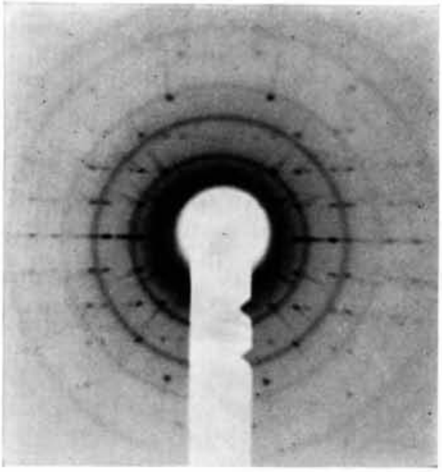

Fig. 4. Rotation photograph about c axis at room temperature.

perature picture, while the expected components, at least ten times stronger, lay at equal distances on either side of those layer lines. These extra components were ascribed to diffraction by material in the narrow regions between domains; this behavior is like that found by Kay (1948) for crystals of $BaTiO_3$ consisting of many domains. The unit cell of the low-temperature modification requires a symmetry no higher than monoclinic. Possible positions of the cation were studied in order to find what conclusions could be reached concerning the symmetry. The configurations assumed for the cation were the same as those assumed by the present authors in the study of the room-temperature structures of the *n*-propylammonium halides. These configurations were the familiar *trans* (zigzag) configuration, and the *gauche* configuration, derived from it by rotation of 120° about the central C–C bond. Of these, the *trans* configuration is more probable, since the *c* repeat distance of the unit cell will snugly accommodate the cations in this configuration, while much space is left to spare if the *gauche* configuration is assumed, such that a shortening of the *c* axis should be expected if the cations go over into the *gauche* configuration when the crystal is cooled below the transition range. The symmetry of the *trans* configuration is C_s. The *gauche* configuration has symmetry C_1, but a mixture of equal parts of the two enantiomorphous *gauche* forms has average symmetry C_s. Therefore, the cation was assumed to have a symmetry C_s, and to have greater dimensions in the symmetry plane than perpendicular to it, as suggested by models of the cation prepared from the Fisher–Hirschfelder–Taylor models. With these assumptions concerning the cations, the observed contraction of the angle between the *a* axes could be explained only under the assumption that the symmetry planes of the cations lay in the $(1\bar{1}0)$ planes. There are two possible arrangements of two cations in the unit cell lying in the $(1\bar{1}0)$ planes, one of the arrangements being centrosymmetric. However, only the centrosymmetric arrangement would give rise to the shearing force necessary to cause the observed tipping of the *c* axis in the $(1\bar{1}0)$ plane. On the basis of this argument the space group of the low-temperature modification of the chloride becomes uniquely C^3_{2h}–$C2/m$, with the parameters

$$a=9{\cdot}06\pm0{\cdot}08\text{ A.},\quad b=8{\cdot}58\pm0{\cdot}08\text{ A.},$$
$$c=7{\cdot}34\pm0{\cdot}10\text{ A.},\quad \beta=98\pm2^\circ.$$

The *a* axis of the monoclinic cell corresponds to [110] of the room-temperature unit cell, the *b* axis to $[1\bar{1}0]$ and the *c* axis to [001].

The spots having both *h* and *k* odd (indexed on the monoclinic cell) should depend entirely on the scattering from the cations, and hence their intensities should be very sensitive to the orientation of the cations. Structure-factor charts were prepared giving the trigonometric terms for atoms in positions (4*i*):

$$x,0,z;\quad \bar{x},0,\bar{z};\quad x+\tfrac12,\tfrac12,z;\quad \tfrac12-x,\tfrac12,\bar{z};$$

for the reflections 111, $11\bar{1}$, 112, $11\bar{2}$, 132, $13\bar{2}$, 312, $31\bar{2}$. By the use of these charts, values of the ratios

$$F_{111}:F_{11\bar{1}},\quad F_{112}:F_{11\bar{2}},\quad\text{and}\quad F_{132}:F_{13\bar{2}}:F_{312}:F_{31\bar{2}}$$

were estimated for various positions of the cations under the assumption that the scattering factor of CH_2 is 0·9 times that of CH_3 or NH_3^+ for the appropriate values of $\sin\theta/\lambda$. The positions tried for the cations had the same N–Cl distance, 3·18 A., as that given by Hughes & Lipscomb (1946) for methylammonium chloride, such that the N atoms were fixed in positions (4*i*), with $x=0{\cdot}26$, $z=0{\cdot}09$. A transparent template of the N and C atom positions of the cation in the *trans* configuration was laid on the structure-factor charts, and the positions of the atoms were varied by pivoting the template about the N atom and by inverting the template.

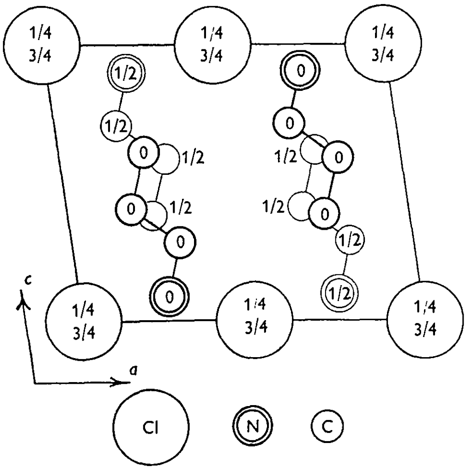

Fig. 5. Structure of the low-temperature modification projected along binary axis of the monoclinic cell.

The experimental ratios of the structure factors were:

$$|F_{111}|:|F_{11\bar{1}}|=0{\cdot}6;\quad |F_{112}|:|F_{11\bar{2}}|>2;$$
$$|F_{132}|:|F_{13\bar{2}}|:|F_{312}|:|F_{31\bar{2}}=1:<0{\cdot}6:2:<0{\cdot}6.$$

In order to get agreement of the calculated ratios with these data, it was necessary to assume the orientation shown in Fig. 5, with the line joining the N atom to the end C atom lying very nearly parallel to the *c* axis. The approximate positions of the C atoms were in (4*i*), with $x_1=0{\cdot}3$, $z_1=0{\cdot}3$; $x_2=0{\cdot}2$, $z_2=0{\cdot}4$; $x_3=0{\cdot}25$, $z_3=0{\cdot}6$. In Fig. 5 the origin has been transferred to $\frac34,0,0$ in order to give a clear drawing. The calculated ratios of structure factors with these positions of the atoms were:

$$F_{111}:F_{11\bar{1}}=-0{\cdot}5,\quad F_{112}:F_{11\bar{2}}=-4,$$
$$F_{132}:F_{13\bar{2}}:F_{312}:F_{31\bar{2}}=1:-0{\cdot}2:2:-0{\cdot}4.$$

Rotation of the template through 6° in either direction made the agreement appreciably worse. All attempted arrangements with the template inverted gave very poor agreement. The symmetry and the relation to the room-temperature structure required that the chloride ions should be in (4*e*):

$$\tfrac14,\tfrac14,0;\quad \tfrac14,\tfrac34,0;\quad \tfrac34,\tfrac14,0;\quad \tfrac34,\tfrac34,0.$$

A test of piezoelectricity in the chloride at the temperature of liquid nitrogen with an apparatus similar to that designed by Stokes (1947) was negative. However, no conclusion could be drawn, since either the piezoelectric effect might be too slight to detect, or the piezoelectric effects of many small domains might not be detectable in our apparatus. A chloride crystal remained dark when viewed between crossed polaroids along the *c* axis as the temperature was lowered through the transition interval. Since the low-temperature structure is definitely monoclinic, one may conclude either than the change in optical properties is slight, or that the domains are submicroscopic in size.

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Deficiencies in Order of Large Size in Fibrous Systems[†]

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A number of the fibrous proteins show small-angle diffraction of X-rays lacking evidence of the full complement of lattice translations characterizing normal crystalline order. Criteria for the judgment of the number of ordered dimensions from diffraction phenomena are particularly simple at small angles and are derived herein. These involve examination of diffraction shapes and the displacement of diffractions with tilting of the fibrous specimen from the normal perpendicular relationship to the incident beam.

Simple geometrical considerations suffice to show qualitatively the properties of the disk- or rod-like shapes characterizing diffracting arrays or nets in reciprocal space. These diffractors are usually conceived as of unlimited extension along ordered dimensions, but very thin transverse thereto. In practical cases the properties of the reciprocal-space disks and rods account for the diffraction broadening caused by reduction in particle dimensions along axes of order, or the sharpening effect of increased size along non-ordered directions—factors which complicate the simple criteria mentioned above. While disk or rod dimensions are normally independent of diffraction indices, this does not hold when the diffractors are internally distorted.

Introduction

Certain protein fibers which have been investigated by means of small-angle X-ray diffraction (Bear, 1944 *a*, *b*, 1945) and electron microscopy (Schmitt, Hall & Jakus, 1942; Hall, Jakus & Schmitt, 1945) showed evidence of periodic structure along only one (collagen) or two (paramyosin) fibril dimensions. These results gave rise to the question as to whether the remaining dimensions in each case did not, in fact, possess long-range order or whether the experimental evidence was deficient. The present paper considers the problem of obtaining definitive evidence for the number of dimensions possessing order, as independently as possible of a failure of intensity in the diffractions necessary for demonstration of order along a doubtful fibril direction.

Systems possessing one- and two-dimensional order are well known (cf. the linear arrays of halogen atoms described by West (1947) and the planar nets of carbon black discussed by Warren (1941) and by Biscoe & Warren (1942)). Indeed, Nowacki (1946) has attempted a rough classification, according to the number of axes of order, for substances yielding discontinuous small-angle diffraction. It has also been understood for some time that diffracting arrays and nets possess shape transforms resulting in disk- or rod-like distributions of intensity about each peak in reciprocal space (see Ewald, 1940). These concepts have not often been required, however, so that most accounts are concerned with the results of the application of the reciprocal lattice to three-dimensional crystals.

Reduction in the number of axes of order is not the only type of order-deficiency that may be encountered in fibrous systems. James (1948), in particular, noted some of these, emphasizing the importance of the diffraction aspects of thin linear arrays or limited imperfect aggregates of these in the study of fibers. Diffraction shapes are influenced by the degree of extension in space of both ordered and non-ordered

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