

327. Dehydration Nuclei on Crystals of Copper Sulphate Pentahydrate.

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THE shapes of the dehydration nuclei formed on nine faces of crystals of copper sulphate pentahydrate have been studied, and it is shown that dehydration occurs most rapidly along definite crystal planes. The 010 plane is the most important of these, and possible causes of the rapid dehydration along this plane are discussed in the light of the X-ray structure of the salt as determined by Beevers and Lipson.

THE shape of the nuclei formed on the (110) face of crystals of copper sulphate pentahydrate has been investigated previously (J., 1934, 1874). On this face the nuclei are star-shaped in the plane of the surface and possess an extension inward in the form of a flat disc which makes an angle of  $56^\circ$  to the surface. The longer arms of the star, from which the disc is suspended, are parallel to the  $c$  axis of the crystal, and the shorter arm makes an angle of approximately  $56^\circ$  to this axis. The production of a star-shaped figure is a matter of some interest, for it shows that dehydration occurs preferentially along certain directions in the crystal. In order to determine more precisely the planes along which rapid dehydration occurs, the shapes of the nuclei formed on nine different faces of the copper sulphate crystal have been examined, and the directions of growth measured with respect to certain crystal edges. An attempt has been made to correlate these directions with the mode of arrangement of the water molecules in the crystal (cf. Beevers and Lipson, *Proc. Roy. Soc.*, 1934, A, 146, 1570).

EXPERIMENTAL.

The apparatus was similar to that used in the earlier investigations. The crystals were prepared from a slightly supersaturated solution of Kahlbaum's copper sulphate in a dust-free atmosphere, the evaporation of the solution being brought about by the adsorption of water on solid sodium hydroxide placed at the bottom of the crystallisation chamber. The designation of the crystal faces is that due to Tutton ("Crystallography," 1911, p. 286). The  $p$ ,  $p'$ ,  $a$ , and  $b$  faces in the prism zone and the  $o$  and  $t$  faces were readily obtained of a suitable size for examination, but in order to obtain  $t'$ ,  $s'$ , and  $p''$  faces of a sufficient size, it was necessary to grow large crystals. These large crystals were then broken down to a suitable size for suspension in the apparatus. The rare  $c$  face could not be obtained. The nuclei were formed and grown in a hard vacuum, and the crystal then removed from the apparatus and mounted on the stage of a microscope. The photographs shown in the plate were then obtained.

*Nuclei.*—The upper row of the plate gives the photographs of those nuclei formed on the prism zone, and they are placed in the order in which the faces occur on rotating the crystal about the  $c$  axis, commencing with the  $p'$  face. The second row gives the nuclei appearing on the various end forms.

The nuclei formed on the prism zone all showed the most prominent direction of growth parallel to the  $c$  axis. A second and sometimes a third direction of growth also occurred, and these made angles with the  $c$  axis which varied from face to face. When two subsidiary directions of growth occurred, these were sometimes found on the same nucleus (see  $a$  and  $b$  on the plate) or occurred on different nuclei as on the  $a$  face. As will be seen from the photograph of nuclei on the  $p'$  face, the subsidiary directions of growth are sometimes absent. Thus there is an element of chance in the starting of growth in the subsidiary directions. The subsidiary horns on either side of the main directions of growth do not always spring from the same point along the  $c$  axis, and this makes it difficult to measure the angles with any certainty. There are, however, ribs passing down the middle of the horns and the intersection of these ribs is usually clearly visible. The angles given below are average values of the angles between the intersecting ribs. These give at the most the general direction of the rapid growth, for in certain cases there are wide fluctuations in the angles.

A striking feature of many nuclei is the formation of a halo which is due to growth along a plane into the interior of the crystal. This halo always grows towards the  $b$  face of the crystal, and its intersection with the surface gives the most prominent direction of growth on the surface. The angle the halo makes with the surface was measured only for the  $p$  face, and here the found angle of  $56^\circ$  is in agreement with the angle between the  $b$  and  $p$  faces, *viz.*,  $53^\circ 4'$  (Tutton, *op. cit.*, p. 288).

The angles between the main and the subsidiary directions of growth of the nuclei on the faces in the prism zone are given below, the angles being reckoned in an anticlockwise direction:

Face .....	$p'(1\bar{1}0)$	$p''(1\bar{2}0)$	$b(010)$	$p(110)$	$a(100)$
Angle .....	31° 30'	33°	51° 303°	56°	87° 28—52°

In the case of the  $a$  face there was an ill-defined direction of growth ranging between 28° and 52°. In all, twelve nuclei were measured on this face, and the angles varied uniformly between these limits. In the other cases, the variation in the angle was  $\pm 3^\circ$ , except for the  $p$  face, where the variation was smaller. The nuclei on the  $b$  face are exceptional in that they are lozenge-shaped and show no marked horns. The main direction is always parallel to the  $c$  axis.

The direction of the growth on the end faces was measured with respect to some crystal edge. The data are given below.

Face.	Zone.	Main direction of growth.	Subsidiary direction of growth.	Angle between directions of growth.	
				Exptl.	Calc.
$o, (\bar{1}11)$	$[pot]$	to $bo$ edge	to $ao$ edge	69°	67°
$t, (021)$	$[pot]$	to $bt$ edge	approx.    to $p't$ edge	72°	—
$t', (0\bar{2}1)$	$[at's']$	to $bs'$ edge	to $t's'$ edge *	69° 30'	70°
$s', (\bar{1}\bar{2}1)$	$[at's']$	to $bs'$ edge	to $t's'$ edge *	71°	68°

\* Shown as white lines on Plate I.

The main direction of growth on all the end faces is parallel to the edge between the face in question and the  $b$  face, *i.e.*, it lies in the  $b(010)$  plane. This is in accord with the fact that the main direction on the prism zone also lies in the 010 plane. The subsidiary direction of growth in the case of the  $o$ ,  $t'$ , and  $s'$  faces is parallel to the edge between the face in question and the  $a$  face, *i.e.*, it lies in the  $a(100)$  plane. The subsidiary direction on the  $t$  face is exceptional in that it does not lie in the 100 plane. It probably lies in the  $1\bar{1}0$  plane.

It will be noted that the prominent directions of growth lie in definite crystal planes. The 010 plane is particularly important, for it is the plane along which the haloes penetrate the crystal. Also the main directions of growth of all the nuclei are parallel to the  $c$  axis and hence lie in the 010 plane. The nuclei on the end faces,  $o$ ,  $t'$ , and  $s'$ , possess a subsidiary direction of growth lying in the 100 plane, but this is not so important as the 010 plane, since no halo is ever observed in it.

The subsidiary directions of growth on the faces of the prism zone,  $p'$ ,  $p''$ ,  $b$ ,  $p$ , and  $a$ , and on the  $t$  face are difficult to interpret, but even here certain regularities emerge. These directions only in one case lie in the 001 plane, growth in this plane being inhibited for some reason. Apart from this one exception (see  $a$  face below), there is a component along the  $c$  axis in the direction of growth, so that the subsidiary directions of growth take diagonal paths across the unit cell. The data are given below, the crystal directions being expressed in the usual nomenclature, and the experimental and the calculated angles are compared.

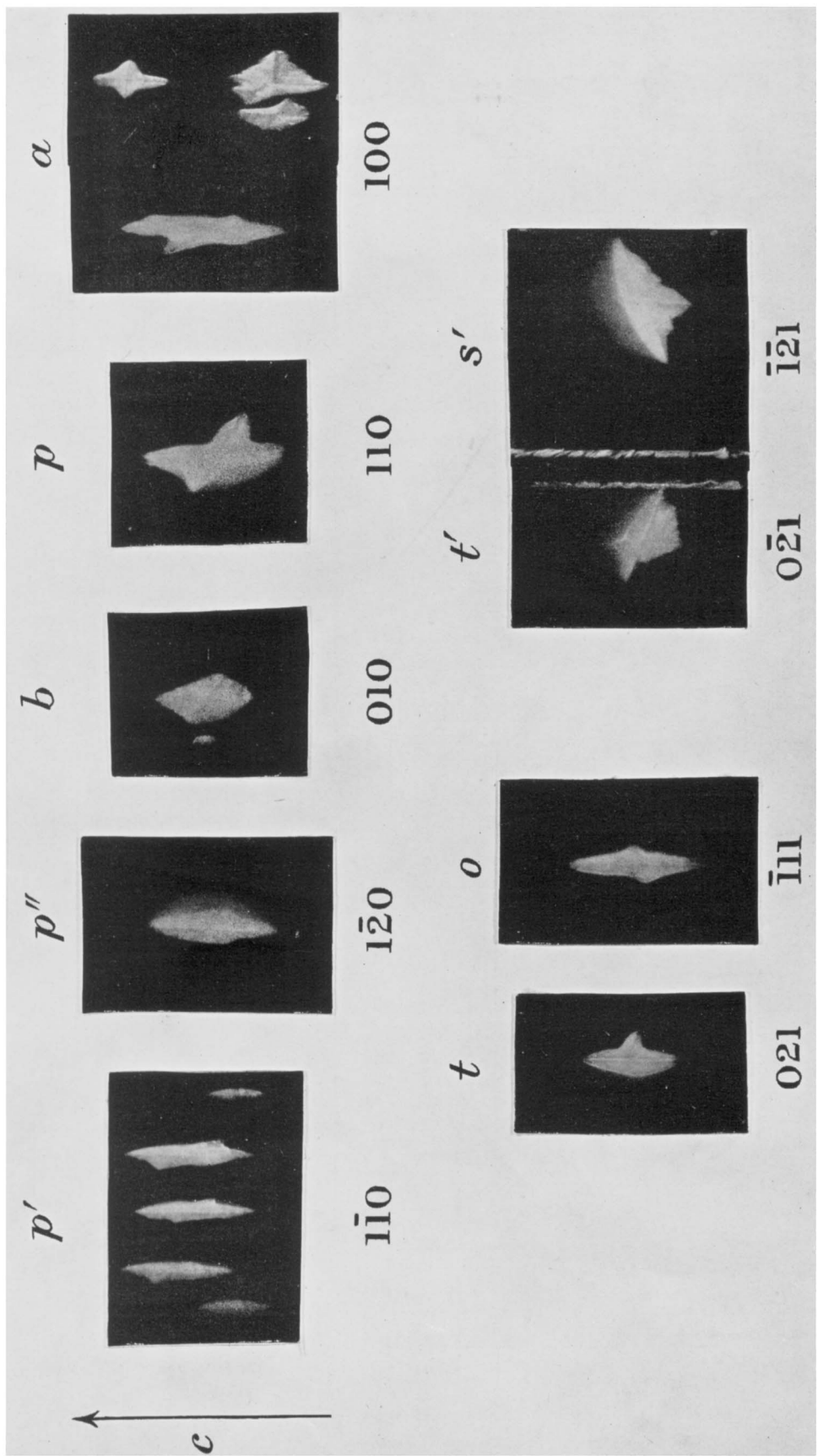
Face.	Angles of subsidiary growth with $c$ axis.	Crystal direction.	Calculated angle.
$p'(1\bar{1}0)$	31° 30'	$[\bar{1}14]$	26°
$p''(1\bar{2}0)$	33°	$[\bar{2}14]$	33°
$b(010)$	303°	$[\bar{1}01]$	305°
	51°	$[\bar{2}01]$	51°
$p(110)$	56°	$[\bar{1}11]$	54°
$a(100)$	87°	$[010]$	82°
	28—54°		

The crystal directions are given in zone axis symbols, and indicate the directions of growth starting from 0, 0, 0. The agreement between the calculated and the experimental values, except for the  $p'$  and  $a$  faces, is within experimental error. Growth along the  $a$  axis is never observed, and in only one case is there growth in the direction of the  $c$  axis.

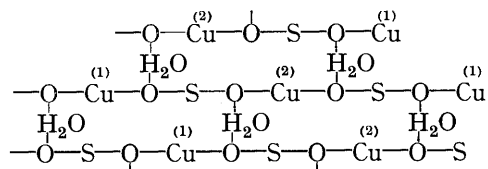
For the determination of the above crystal directions, use was made of a model of the X-ray structure as determined by Beevers and Lipson, and also of a wire model representing the crystal edges, as shown in Fig. 227 (Tutton, "Crystallography," 1922).

#### DISCUSSION.

The arrangement of the copper and sulphate ions and the water of crystallisation in the crystal has been determined by Beevers and Lipson (*loc. cit.*). The copper ions are arranged



in a face-centred pattern in the 001 plane and are each co-ordinated with four water molecules and two oxygen atoms from near-lying sulphate groups. If a direction parallel to the  $a$  axis be considered, it is seen that the copper ions are arranged in rows, and that the co-ordinated groups of alternate rows of copper ions have different configurations. Also, the members of alternate rows are differently placed with respect to the sulphate groups. The fifth water molecule is co-ordinated with two oxygens and two other water molecules, and is more firmly bound than the four water molecules co-ordinated to the copper ions. A conventional diagram which shows roughly how the atoms in the 001 plane are linked together is shown below. The three-dimensional diagram of the lattice structure can be seen in the paper of Beevers and Lipson (*loc. cit.*, Fig. 2). The horizontal rows consist of copper



(1 and 2) and sulphur atoms separated by oxygen atoms and run diagonally across the 001 plane in the form of a vertical zig-zag. The rows are bridged by the fifth water, and there is nothing to indicate that alternate coppers 1 and 2 are in any wise different from one another. The layer is, however, much distorted and crumpled by the valency angle requirements, and the crumpling causes alternate coppers to take up different configurations in the crystal. The layers in the 100 plane are held together in the direction of the  $c$  axis by the water molecules co-ordinated to the copper.

Dehydration can occur in three stages, giving the trihydrate, monohydrate, and anhydrous salt. Under the conditions of our experiments, *viz.*, nuclei formation in high vacuum, the dehydration proceeds rapidly to the monohydrate, and the existence of the trihydrate is only observed at temperatures above  $50^\circ$  (cf. Garner and Tanner, J., 1930, 47). Therefore we shall consider only the case of the direct dehydration from the pentahydrate to the monohydrate. This means the removal of the four water molecules co-ordinated to copper, which hold the layers together, and their removal must cause the collapse of the lattice in the direction of the  $c$  axis. The subsequent rearrangements of these layers are unknown, since the X-ray structure of the monohydrate has not been determined.

Since the water is liberated at an interface on one side of which is the pentahydrate lattice and on the other the collapsed lattice, it is clear that the direction of most rapid movement of the water molecules will depend to some extent on the structure of the collapsed lattice. If the layers in the 001 plane collapse in the direction of the  $c$  axis, then a possible consequence is that the escape of water along the 001 plane might be hindered. This would cause growth along this plane to be relatively slow. On the other hand, such a collapse might leave the avenues of escape for water molecules still open in the direction of the  $c$  axis. This would account for the dominant rate of growth along the  $c$  axis. It is clear that the structure of the collapsed lattice will play a dominant rôle in the dehydration phenomena, but until its nature has been made clear by X-ray analysis it is not worth while to discuss its possible contributions in any detail.

A study of the crystal model, however, shows that the greatest density of copper ions occurs in the 010 plane, and this is the plane in which the haloes lie. It is, therefore, probable that water molecules during dehydration pass from copper ion to copper ion along this plane until they reach the surface of the crystal. The activation energy required for this transference will depend on the arrangement of the copper ions and water molecules in the lattice, and will be expected to be smaller the closer the copper ions are to one another. There is little known about the change of activation energy with direction. An isolated observation by Bright, that the temperature coefficient of growth of the smaller horn on the  $\beta$  face is greater than that of the longer horn, is perhaps an indication that the activation energies are different in different directions.

On the  $b$  face, the distance between the copper ions along the  $c$  axis is 5.97 Å., whereas along the  $a$  axis it is 6.12 Å. Nuclear growth is slower along the  $a$  than the  $c$  axis, and this

is in agreement with the view that the distance apart of the copper ions plays a part in the transference of water. However, growth in a diagonal direction across the  $b$  face, where the copper distance is 7.2 Å., is greater than in the direction of the  $a$  axis. This shows that distance apart of the copper ions is not the only factor involved. Also on the  $p$  face, the most prominent direction of growth is along the  $c$  axis. Growth in the 001 plane, where the copper ion distance is 6.7 Å., is not specially marked, but there is a marked subsidiary direction of growth where the distance is 7.7 Å. Here, again, it is clear that there is some inhibition acting in the direction of the 001 plane. Similar considerations apply to the  $p'$  face. On the other hand, for the  $a$  face, where the 001 plane cuts the face along the  $b$  axis, growth does not appear to be inhibited in the 001 plane. The inhibition only applies to the  $a$  axis and directions lying between the  $a$  and the  $b$  axis. A special case of inhibition of growth occurs on the  $t$ ,  $t'$ , and  $s'$  end faces, where the growth of the halo and the resulting lattice changes inhibit the formation of a horn above it.

The process of dehydration is to a certain extent reversible, otherwise a steady dissociation pressure would not be obtained at constant temperature. Thus in considering the shape of the nuclei, the rate of return of the water molecules to the interface must be taken into account. Even in a high vacuum some of the molecules leaving the interface will diffuse backwards and thereby decrease the rate of dehydration. The rate of return will naturally depend on the magnitude and the sign of the curvature of the interface, which in some of the nuclei vary enormously. The high positive curvature at the tips of the horns of these nuclei will cause an increased rate of return of the water molecules to the interface. Consequently, the rate of dehydration will be reduced and thereby cause the tips of the horns to possess a rounded appearance.

It is therefore concluded that the shapes of the nuclei are controlled by three factors: (1) the activation energy for the removal of the water molecules, which will vary with direction; (2) the collapse of the lattice, which will hinder the escape of water in certain directions; and (3) the curvature of the interface, which affects the rate of return of water molecules to the interface.

Our thanks are due to Imperial Chemical Industries for a grant for the purchase of apparatus.

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[Received, May 27th, 1937.]

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