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Some observations on growth and etching of crystals with the diamond or zincblende structure.

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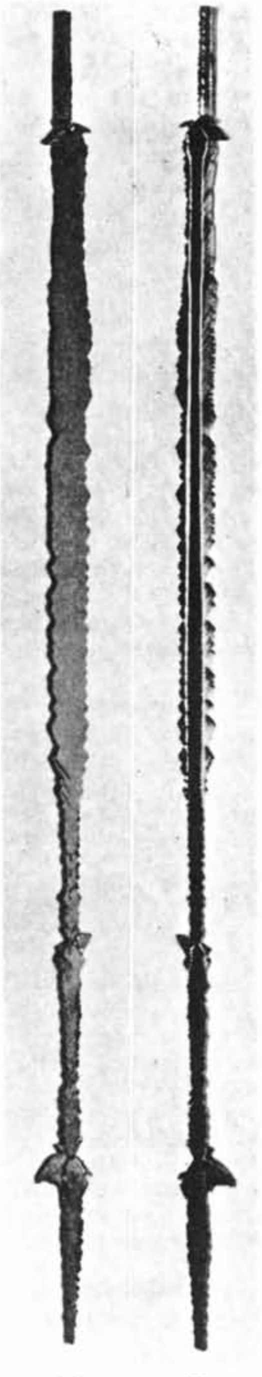
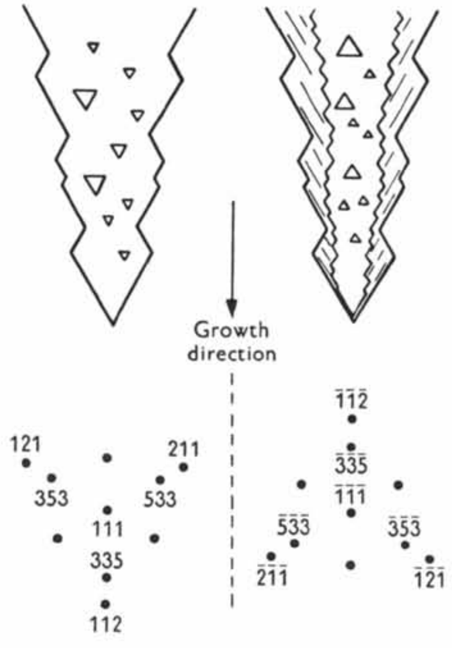


(*a*) (*b*)

Fig. 1. Germanium single crystal. (*a*) Better developed face (111); (*b*) less well developed face $(\bar{1}\bar{1}\bar{1})$. Scale: four-fifths full size.

A technique has recently been developed for preparing dendritic plates of germanium and other solids with the diamond or zincblende structure, in the form of long, thin lamellae of fairly uniform width (Billig, 1955). These plates are perfectly monocrystalline and often display large faces of high perfection. Owing to their polar nature, the two opposite faces of any dendrite are not crystallographically identical and display characteristic differences. Laue reflexion photographs from the two main faces always display threefold symmetry and correspond to {111}, the planes of highest atomic packing. The patterns obtained from two opposite faces are rotated by 180°, corresponding to (111) and $(\bar{1}\bar{1}\bar{1})$ (Fig. 2). As shown in Fig. 1, one face is usually somewhat wider and displays a higher degree of perfection than the other. From Laue photographs taken on a number of dendrites mounted with their original growth direction pointing downwards, the wider and more perfect face* was always found to give the pattern oriented in one and the same direction, i.e. (112) and certain other reflexions below the central spot, whilst the less perfect one gave the opposite pattern. The general growth direction of the dendrite has been identified as $[\bar{1}\bar{1}2]$ in every case.



(*a*) (*b*)

Fig. 2. Orientation of etch pits and of back-reflexion Laue photograph, (*a*) on better developed face (111), (*b*) on $(\bar{1}\bar{1}\bar{1})$.

A further characteristic difference of the two faces is revealed on etching. Under the action of a suitable

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* This will be defined as the (111) face of the crystal.

etchant, for instance $AgNO_3$, the etch pits tend to form a hollow tetrahedron, bounded by the four $\{111\}$ planes; so that on a (111) face the pits take the form of an equilateral triangle, the sides of which are arranged along the three $\langle 1\bar{1}0\rangle$ directions. On the more perfect face, (111), each pit has one corner pointing towards the $[\bar{1}\bar{1}2]$ direction, i.e. towards the growing tip of the dendrite, whilst on the other face, $(\bar{1}\bar{1}\bar{1})$, the pits point away from the tip, towards $[11\bar{2}]$ (see Fig. 2).

Both these phenomena, i.e. the difference in perfection of the two opposite faces and the different orientation of etch pits on them, can be understood by considering in detail how individual atomic layers are laid down on top of an underlying (111) crystal face (Billig, 1955). The edge of such a growing layer is formed by a zigzag chain of atoms arranged along the $[1\bar{1}0]$ direction in the (111) plane. Consideration of a three-dimensional structure model reveals that an atom arriving at this step from the melt will find two bonds available for interlocking only if the step faces in one direction, but not in the other. Sideways extension of the half plane, i.e. crystal growth by the deposition of new chains, can thus take place readily only in one direction, but not in the opposite one. These favourable growth directions are $[\bar{1}\bar{1}2]$ for the (111) face, and $[11\bar{2}]$ for the $(\bar{1}\bar{1}\bar{1})$ face. Conversely, removal of a chain on etching proceeds more readily from a step facing the other way.

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The space group and unit-cell dimensions of ammonium, potassium and rubidium glucuronate.

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In one technic employed by us in attempting to determine the structure of the glucuronate ion by X-ray diffraction methods, a pair of isomorphous salts of glucuronic acid was required. It was hoped that such might be found among the ammonium, potassium and rubidium salts of this acid. Ehrlich & Rehorst (1929) have reported that the potassium salt crystallizes with one and one-half molecules of water and that the ammonium salt crystallizes in the anhydrous form. No information on the rubidium salt could be found.

Although pure glucuronic acid is not readily available, glucuronolactone may be obtained in pure form by recrystallization of the commercial compound†. In aqueous solution it undergoes delactonization to a limited degree to form an equilibrium mixture with glucuronic acid. The salts were prepared by dissolving a weighed quantity of glucuronolactone in distilled water and adding gradually the equivalent amount of the respective bicarbonate. The bicarbonates were used instead of the hydroxides because of the instability of the glucuronates in solutions of high pH value. Even when the bicarbonates were used the solutions darkened considerably and required decolorization with carbon. The solutions were concentrated at room temperature under reduced pressure, then exposed in a desiccator to an atmosphere of ethyl alcohol vapor. Small crystals separated as the alcohol slowly diffused into the solutions.

Crystals of the ammonium and potassium salts were quite stable in air, but the rubidium salt lost water of hydration rapidly and for the X-ray studies required a protective coating of oil.

Weissenberg photographs taken about the crystallographic axes showed that all three salts crystallize in the orthorhombic system. The only systematic extinctions found among the reflections in each instance were the odd orders of $(h00)$, $(0k0)$ and $(00l)$, which identifies the space groups as D_2^4–$P2_12_12_1$. The densities were determined by the flotation method, using an adjusted mixture of carbon tetrachloride and 1,2 dibromo-ethane. The unit-cell dimensions listed in Table 1 were determined from measurements of the Weissenberg photographs, which were taken with nickel-filtered Cu $K\alpha$ radiation.

Table 1. *Crystallographic data*

	Ammonium glucuronate	Potassium glucuronate	Rubidium glucuronate
a_0 (Å)	$5{\cdot}95\pm0{\cdot}01$	$5{\cdot}55\pm0{\cdot}01$	$5{\cdot}56\pm0{\cdot}01$
b_0 (Å)	$16{\cdot}25\pm0{\cdot}05$	$16{\cdot}52\pm0{\cdot}05$	$17{\cdot}08\pm0{\cdot}05$
c_0 (Å)	$10{\cdot}14\pm0{\cdot}05$	$11{\cdot}28\pm0{\cdot}05$	$11{\cdot}42\pm0{\cdot}05$
ϱ (g.cm.$^{-3}$)	1·524	1·718	1·908
M_1	225·0	267·6	310·7
M_2	229·19	268·26	314·64
Z	3·92	3·99	3·96

The molecular weights of the three salts (M_1 in the table) calculated on the basis of a cell content of four molecules as required by the space group, is in good agreement with those required (M_2) for the monohydrate of the ammonium salt and the dihydrate of the potassium and rubidium salts. The value of Z, the cell content, was obtained from the observed density, cell dimensions and the molecular weights corresponding to these hydrates. A preliminary investigation of the electron distribution in the cell by Fourier methods has substantiated the di-hydration of the potassium and rubidium salts.

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