Acta Cryst. (1960). **13**, 495

Studies on the Behaviour of Growth Steps on Sucrose Crystals

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(*Received* 10 *September* 1959 *and in revised form* 10 *November* 1959)

Experimental observations of growth steps on sucrose crystals are described, together with their behaviour under controlled conditions. The paper is divided into four sections.

1. A method is given by which crystal-growth processes can be studied on selected areas of sucrose crystals. When a sucrose solution in contact with silicone grease is used for crystal growth, the crystals can be removed from solution with the growth features preserved. A drop of the same solution placed on the crystal does not spread, and if the solution is supersaturated growth steps on the surface grow out to the boundary of the drop leaving a smooth area. Growth in this area can continue if the termination of a screw dislocation is located within it or by a two-dimensional nucleation process. The method can be used either to grow crystals from selected dislocations or to study two-dimensional nucleation.

2. We have previously shown that large growth steps are visible on sucrose crystals which have been nucleated and grown in the presence of dextrose. Further experiments are described showing that when such crystals are transferred to pure sucrose solution there is no alteration in the step height or change in step pattern. The rate of step movement remains as before.

When another impurity (raffinose) is added to a pure solution in which crystals are growing normally the growth steps stop moving even though the solution is supersaturated. On replacing this solution by pure sucrose solution, the growth steps resume their normal rate of movement.

3. Complex step patterns are common on growing sucrose crystals and these patterns sometimes show a continuous change in detail. This change has been studied and shown to arise close to the growth centre. Under the conditions appertaining in these experiments, mechanisms which have been advanced in the literature for the production and stability of large growth steps do not appear to operate.

4. Further information on the growth process for sucrose crystals has been obtained by measurements of the temperature coefficient of the rate of step advance for the range 24·5 °C. to 35·3 °C. From these measurements an activation energy of 16·7 cal. per mole for the process was calculated. This value indicates that the rate controlling step is not diffusion in the solution. Measurements at 50 °C. and 70 °C. suggest that this conclusion may also be valid at these temperatures.

Introduction

Study of the processes of sucrose crystallization may be divided into two parts—nucleation, including formation of dislocations, and the movement of growth steps on the crystal faces. Observations of the second of these processes under controlled experimental conditions are described here.

1. Movement of steps on selected areas of crystal surfaces

Introductory

The techniques required for the observation of growth steps on sucrose crystals have been described in previous articles (Albon & Dunning, 1957, 1959). These techniques enable most crystals to be grown for long periods without changes in the dislocations present: this is shown by the unchanged pattern of the growth steps. Solutions of known supersaturation were used and were stored above saturation temperature, drawn through a filter and pumped through a cooling and thermostat system before passing over the crystals.

Experimental

Several methods were developed (Albon & Dunning, 1959) for removing the solution without destroying growth features. We have found recently that when silicone grease is used for lubricating joints in the circulating system the crystals after removal of the solution are no longer wetted by the solution when drops are placed on the surface. When the microscope cell was emptied the crystal faces were left with growth features preserved and free of solution. Fig. 1(*a*), (*b*) illustrate the surface structures found on crystals treated in this way. The presence of traces of silicones did not affect the crystal surface permanently since, when sucrose solution was again pumped through the cell, growth was resumed without any detectable change.

Instead of removing the solution completely, in some cases drops were left on the otherwise dry crystal surface. When the area covered by the drop was free from dislocations, the steps grew until they reached the boundary of the drop, and growth then ceased, the area beneath the drop being without steps. When the crystals were totally immersed again, growth began and eventually the smoothed portions of the face moved to the crystal edge leaving no permanent feature. This experiment provided a striking direct observation of the hypothesis that steps on an ideal crystal surface would grow out and that in the absence of a screw dislocation, growth is imperceptible at low supersaturations. There was no evidence that growth on these smooth regions by a two-dimensional nucleation process was significant at a supersaturation of 0·01.

Crystal surfaces were examined for dominated dislocations (which are otherwise easily missed when using growth features to locate them), by covering with solution all the surface except the dominant growth centre.

The surfaces produced by covering with solution those parts of a crystal face which are dislocation-free are presumably molecularly smooth. Areas of up to 4 sq.mm. were found on sucrose crystals. Such smooth surfaces are suitable for experiments on two-dimensional nucleation processes, overgrowths and adsorption.

However, if growth is limited to a selected dislocation by the same method crystals containing known dislocations can be grown. These have advantages over the use of whiskers for study of the properties of dislocations. Presumably dislocations could also be selected by first etching the crystal and then growing from the etch pits.

Discussion

The growth of sucrose crystals has been studied previously by the authors using the same methods as in this investigation except that the lubricants present did not affect the wetting of the crystals by the solution. For many earlier experiments no lubricant was used. The use of silicone does not affect the rate of step movement at a given supersaturation or produce any change in the step pattern or step height, as observed in the earlier experiments. The only effect upon the growing crystals detected has been upon the wetting of the crystal surfaces.

From experiments similar to those described the rate of two-dimensional nucleation of molecular layers on a crystal surface could be measured. Any growth steps on that part of the crystal surface under the drop of solution move until they reach the boundary of the drop, leaving a smooth surface at the same level as the top of the highest step covered. Except between the points where the circumference of the drop cuts the highest step the growth steps accumulate to form a cliff.

Further growth will result in an increase in height of the area under the drop which will be visible along that part of the boundary where the growth steps have not accumulated. Measurement of the height of the step formed and the time elapsed will give the rate of two-dimensional nucleation. Growth will also result if the droplet covers a dislocation of Burgers vector so small that the steps emitted are invisible. This can also be measured and readily distinguished from two-dimensional nucleation by kinetic considerations. The observations made so far indicate the absence of dislocations and an extremely low rate of two-dimensional nucleation at a supersaturation of 0·01.

Support for the conclusions reached in section 3 of this paper is given by observation of crystals on which smooth areas are produced and which are then completely immersed in supersaturated solution. The areas move to the crystal edge without any change being visible in the adjacent step pattern. This indicates that the steps visible are not formed by the bunching of monomolecular steps travelling at a different rate, a mechanism proposed by Frank (1958) and Cabrera & Vermilyea (1958).

2. The effect of impurities on growth steps

Introduction

It has been reported earlier (Albon & Dunning, 1957, 1959) that the addition of dextrose ($C_6H_{12}O_6$) to pure (99·99%) sucrose solution results in a striking increase in the number of dislocations of multiple Burgers vector. Further, it was shown (Albon & Dunning, 1958) that the addition of dextrose from 0·2% up to a concentration of 1% was without effect markedly on the rate of advance of growth steps. Addition of fructose ($C_6H_{12}O_6$) was without effect on the strength of dislocations in crystals grown from the solution.

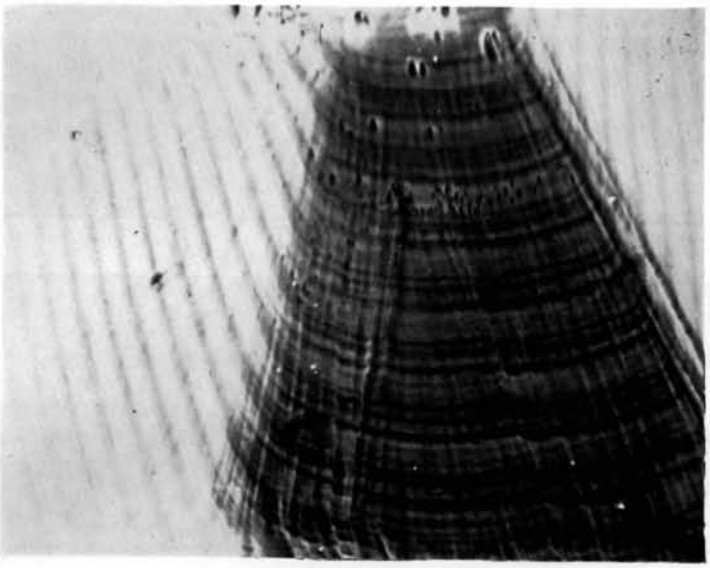
Experimental (1)

Sucrose crystals were nucleated and grown in the presence of 0·2% dextrose and at a supersaturation of 0·01, and step systems on the crystals were observed. The solution was then replaced completely with a pure sucrose solution of the same supersaturation. The growth steps did not alter but continued to grow, moving at the same rate as before. During growth for two days in pure sucrose solution, no change in the step pattern which could be ascribed to the decrease of the dextrose concentration was observable.

Discussion

If the large steps are due to a bunching of small steps as a result of the dynamic adsorption of impurities and if dextrose is in this case the active impurity, then the drastic reduction in the concentration of dextrose does not bring about a resolution of the large steps into smaller ones. On the other hand, if, as is probably the case, the large steps are due to dislocations of large vector, it seems that the stabilisation of these dislocations is not dependent on the impurity (dextrose) concentration.

(*a*)



(*b*)

Fig. 1. (*a*), (*b*). Step systems on sucrose crystals removed from solution: 100 faces. Aluminium coated, × 180, phase contrast.

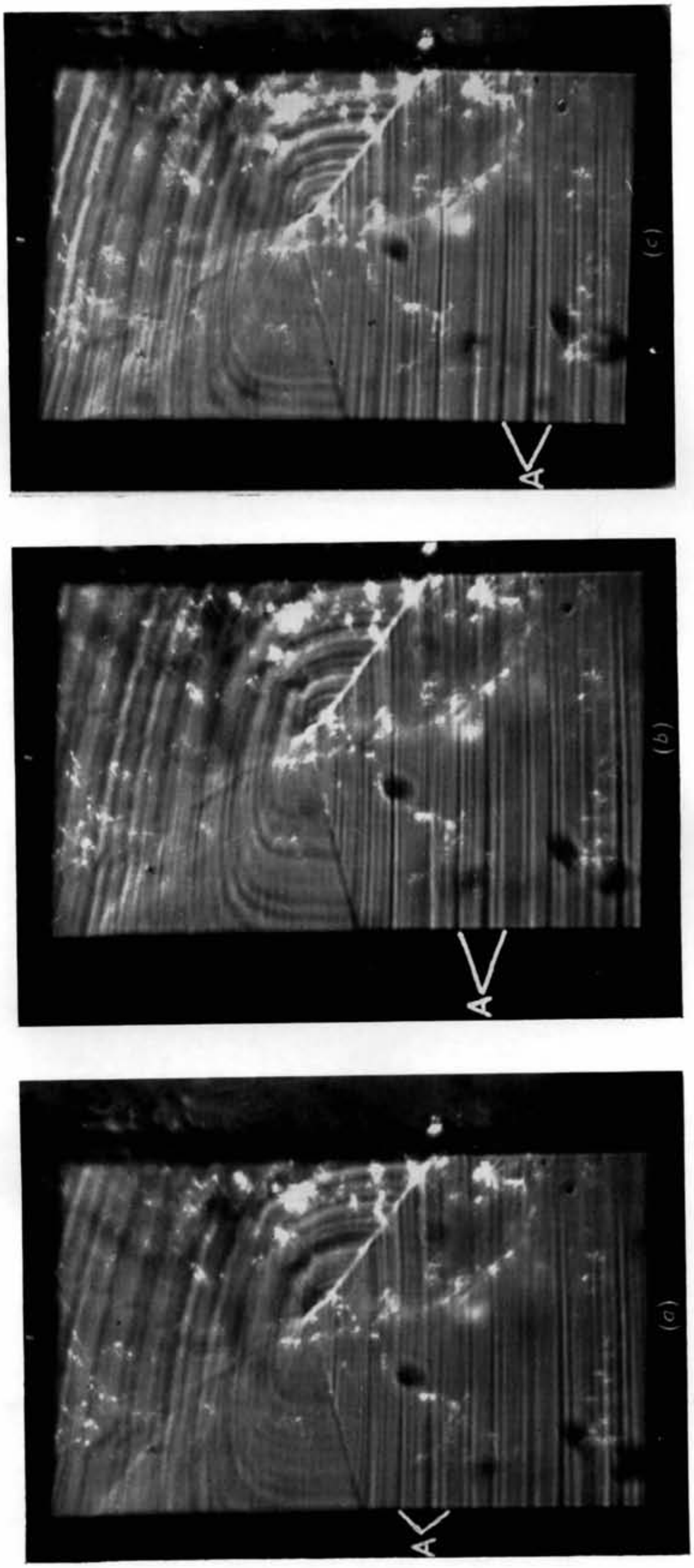


Fig. 2. (*a*), (*b*), (*c*). Growing sucrose crystal photographed at 10 min. intervals: (100) face. ×295.

Experimental (2)

A crystal on which a step system was visible was used and was grown in pure sucrose solution of supersaturation 0·01. Raffinose ($C_{12}H_{22}O_{11}$) was then added as a strong solution until present in a concentration of 4%, the sucrose supersaturation being unchanged. The growth steps ceased moving and the step pattern remained without alteration. Even when the temperature was reduced by 5 °C. and the supersaturation correspondingly increased, the steps did not advance during an observation period of 5 hr. When the raffinose solution was completely replaced by pure sucrose solution, normal growth of the crystal was resumed and no evidence of any resulting changes in the crystal was apparent. Other experiments indicated that unidentified compounds present in relatively impure sucrose solutions produced a similar effect.

Discussion

When present in high concentration, raffinose is adsorbed reversibly on to the growth steps and stops growth. Hungerford & Nees (1934) studied the effect of raffinose in diminishing the overall rates of growth of single sucrose crystals and our experiment just described elucidates the mechanism.

The experiment demonstrates that the suggestion, frequently made in the literature, that adsorption of impurities on to steps could modify rates of crystal growth, is sometimes correct. However, not all impurities produce this effect. The method described can be used to investigate this process and also makes it possible, by addition of suitable impurities, to 'freeze' growth features for later examination.

3. The formation of large steps during crystal growth

We thank Mr D. G. Mead for carrying out the experiments reported in this section.

Introduction

Much experimental work has been reported (for example, Forty, 1952, and Verma, 1953) which confirms the theoretical prediction that crystal growth proceeds by the movement of steps across the crystal faces and that these steps exist as a result of the presence of screw dislocations in the crystals. Although it was thought that the steps would be monomolecular, most observations were of steps of multimolecular height. Our studies of the growth of sucrose crystals have shown that growth nearly always proceeds by the movement of steps which are between 10 and 500 molecules in height. Also, all types of dislocations occur, but groups containing a number of co-operating dislocations usually dominate growth.

Experimental

Study of the surface of a sucrose crystal growing at supersaturation 0·014 revealed several significant features. Photographs were taken of the growth features at 5 min. intervals and some of these are reproduced here (Figs. 2(*a*), (*b*), (*c*) show the crystals whilst growing, the photographs were taken at 10 min. intervals, all ×295). The step pattern consists of groups of steps of varying heights (visibility being proportional to height), similar systems of steps being common. In this case the pattern changes slightly at almost every revolution of the growth spiral. This change occurs near to the centre where a line shown most clearly in Fig. 2(*c*) marks the points of emergence of a dislocation group. As the ends of the steps pass along this line of dislocations, there is an interchange of centres, and there may also be changes in the dislocations. The total Burgers vector of the dislocation group and, therefore, the total height of the steps emitted per revolution cannot change unless either a dislocation moves away from, or a dislocation of opposite sign joins, the group.

Changes in step pattern as described in this section are relatively infrequent. A simple system has been observed in which a pattern consisting of two small and one large step was emitted. These steps terminated at a short line around which the steps rotated, and no change in the pattern occurred during growth.

Further evidence of the behaviour of growth steps can be obtained from these photographs. Once a group of steps forms, it moves outward to the crystal edge without any change. This can be seen by following the group marked *A* on the photographs.

Discussion

These observations indicate that the complex systems of large steps found on sucrose crystals arise because of the existence of corresponding groups of dislocations. Although the height of corresponding steps changes as the crystal grows, this change occurs at the centre of the growth hill. In this case there is no evidence to support the adsorption theories of the bunching of steps discussed by Frank (1958) and Cabrera & Vermilyea (1958).

Whilst the general behaviour of growing sucrose crystals is described by the dislocation theory, it is clear that more complex processes occur which require further study.

4. The mechanism of step movement in the growth of sucrose crystals

Introduction

Previous observations (Albon & Dunning, 1957, 1958, 1959) had shown that the growth of sucrose crystals at temperatures between 15 and 30 °C. proceeds by a movement of steps which originate from screw dislocations. These observations have now been extended up to 70 °C. without observation of any significant change in the mechanism.

The detailed mechanism of growth may involve a number of successive stages. For example, the sucrose molecule may first be transferred from the solution to an adsorbed state on the crystal surface. It may then migrate over the surface to a step and finally it may be incorporated into a kink on the step. The relative importance of each process in determining rates of crystal growth is not clear, although there is some evidence that, for the complicated sucrose molecule, incorporation into a kink is a slow process. To investigate this, the influence of temperature on the rate of step advance has been determined; for temperatures between 25 and 35 °C. the following method was used.

Experimental

A 70·43% by weight sucrose solution containing 0·2% of dextrose was prepared and used to fill a microscope cell at 35 °C. Crystals formed in the cell and sucrose solution was circulated over them. After observing the rate of advance of the steps on a suitable crystal, the circulating solution was diluted by adding a small amount of water and the rate of advance at this lower supersaturation was again measured at the same temperature. The temperature was then reduced until the supersaturation was increased to a suitable extent and the rate again measured; the solution was again diluted to reduce the supersaturation. In this way, by dilution alternating with cooling, the temperature-supersaturation variables were traversed. The results for the [010] direction on the (100) face for one crystal are given in Table 1.

Table 1. *Effect of temperature on the rate of advance* (cm./min. × 10^4) *in the* [010] *direction of steps on the* (100) *face of a sucrose crystal*

Temperature	Supersaturation	Rate
35·3 °C.	0·0139	7·5
35·5	0·0065	3·4
33·1	0·0121	5·1
33·0	0·0059	3·2
30·3	0·0125	4·7
30·5	0·0039	2·4
27·0	0·0153	3·3
27·5	0·0028	1·7
24·0	0·0111	2·2
24·5	0·0055	1·5

From these rates, the rate at 0·0125 supersaturation was then interpolated for each temperature. The logarithm of the rates at 0·0125 supersaturation was plotted against the reciprocals of the absolute temperature (Fig. 3). Also plotted on Fig. 3 are the results of measurements made of rates of step movement at 50 and 70 °C.; these are also for the [010] direction on the (100) face at 0·0125 supersaturation but were determined on different crystals at each temperature.

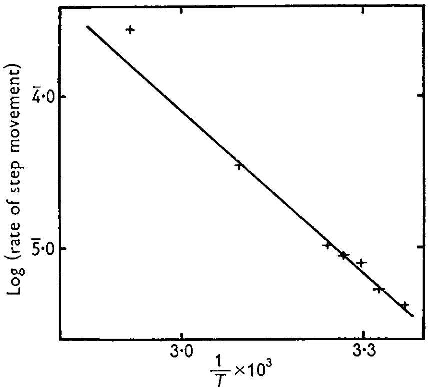


Fig. 3. Graph showing effect of temperature on rate of step movement.

Conclusions

From Fig. 3 an activation energy of 16·70 cal./mol. was calculated. This is much higher than the activation energy for the diffusion of sucrose in solution (8·7 cal./mol., English & Dole, 1950), which indicates that diffusion in solution is not the rate-controlling process. Since the rates at the higher temperatures, although requiring confirmation, together with those at the lower temperatures, lie close to a single straight line, it seems that the nature of the slow stage remains unaltered over this range of temperatures. The shape of the growth terraces suffered no change on raising the temperature, which suggests that the relative importance of the various factors involved has also remained unchanged.

We thank Mr W. M. North and the Directors of Tate and Lyle Limited for their support and interest.

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