# Reports of the Academy of Sciences of the USSR

N. V. Gliki, A. A. Eliseev, and N. M. Marchenko

1960

SovietRxiv

## Abstract

## Full Text

Reports of the Academy of Sciences of the USSR
1960. Volume 135, No. 3

## CRYSTALLOGRAPHY

**N. V. Gliki, A. A. Eliseev, and N. M. Marchenko**

# FORMATION OF A SINGLE-CRYSTAL ICE GRANULE DURING THE FREEZING OF A SUPERCOOLED WATER DROP

*(Presented by Academician A. V. Shubnikov, 20 IV 1960)*

The freezing of a supercooled drop of water is the subject of many investigations. The influence of the size of the drop and of the rate of its cooling on the freezing temperature, the shape of the frozen drop, the rate and character of its freezing, the behavior of impurities dissolved in the water (salts, gases), the maximum permissible degree of supercooling of water in the droplet state, and, finally, the formation of nuclei of the ice phase in the presence, as well as in the absence, of foreign particles—such is a far from complete list of the questions being solved in the course of these investigations ($^{1-3}$).

Yet, despite the great variety of problems posed, the wide range of sizes of the drops studied (from several microns to two centimeters), and the differences in the apparatus used, in these works devoted to the investigation of the crystallization process of the melt, so well-known a method of crystallography as observation in transmitted light between crossed nicols has not found wide application, and no rigorous crystallographic description is given of the ice granules that form.

Crystallographic data on the internal structure of an ice granule can serve as a criterion of the correctness of our ideas about the mechanism of its formation, while observation in polarized light can facilitate the study of the kinetics of the process.

Therefore, in experimentally studying the conditions for the freezing of supercooled drops of water containing suspensions of various chemical compounds, we used polarized light and paid close attention to the morphology of the ice granules that formed.

Crystals of ordinary ice belong to the hexagonal system and therefore are optically uniaxial. Their optical indicatrix is an elongated ellipsoid of revolution; $n_e$—1.3105, $n_o$—1.3091. Since the birefringence of ice $n_e - n_o = 0.0014$ is very small, in polarized light it is expedient to examine only ice grains of sufficient thickness: a grain 417 $\mu$ thick will have indigo interference color, 397 $\mu$—dark red, 347 $\mu$—red-orange, etc. Accordingly, the experiments were carried out with drops several tenths of a millimeter in diameter; with the aid of a syringe the drop was suspended on a thin glass thread and introduced into a chamber cooled to a specified temperature.

The experiments showed that the freezing of a supercooled drop of water can be ($^2$) of two kinds. In some cases the granules are opaque; they contain many very small air bubbles. Such granules form under strong supercooling, when the air dissolved in the water is vigorously released from the drop, but owing to the high rate of crystallization the bubbles are captured by the solid phase and remain in it as inclusions. In other cases the granules prove to be transparent, almost devoid of air bubbles. They form at a lower rate, so that the bubbles of released air have time to leave the surface of the drop and are not captured by the advancing layer of ice. In the first case the moment of the phase transi-

of the process is always easy to notice, since, when a liquid drop is illuminated by transmitted light, its central part glows brightly, whereas when an opaque granule forms, the drop darkens instantaneously. In the second case, the appearance of the solid phase does not change the illumination of the drop, and the freezing of the drop can often be judged only from a slight change in its shape and from the cessation of small vibrations.

The use of polarized light makes it possible to register the appearance of the solid phase in both cases. If a liquid drop between crossed polaroids differs hardly at all from the surrounding dark background (the drop is illuminated only at the periphery, at the points of contact with the glass thread), then the frozen drop stands out against the dark background by its interference coloration. The color and brightness of the coloration are determined by the crystallographic orientation and the thickness of the ice phase that forms. Even during rapid freezing of a drop, one can notice small changes in the coloration of individual regions, making it possible to judge the duration of the freezing process of the drop. The variegation of the coloration of the granule thus obtained (Fig. 1a) indicates its granular structure, while the non-simultaneous extinction of individual grains when the granule is rotated indicates the diversity of the crystallographic orientations of the grains composing the granule.

In a number of cases, especially when the frozen drop is transparent, the character of its interference coloration differs substantially from that of a polycrystalline granule. Gradual changes in its coloration indicate the absence of grains and correspond to a gradual change in the optical thickness of the rounded granule. With a certain rotation of the granule about the vertical axis, simultaneous extinction of all its parts is observed. Such extinction confirms the absence in the granule of grains with different crystallographic orientations. The formation of a single-crystal granule (Fig. 1b, c) during freezing of a supercooled drop is an unexpected fact, indicating that, under certain conditions, crystallization of the volume of a small drop proceeds in a strictly definite manner, facilitating

Figure 1

Figure 1: Figure 1

the formation of a single crystal*.

Numerous experiments show that, at a given temperature, the probability of formation of a single-crystal granule increases as the size of the drop decreases. An increase in the freezing temperature of the drop promotes a decrease in the degree of polycrystallinity of a granule of a given size. Careful examination of dozens of single-crystal ice granules showed that the optical axes in them are usually oriented arbitrarily. At elevated temperatures, when a single-crystal granule is formed upon freezing of a drop exceeding one millimeter, a tendency toward a horizontal arrangement of the optical axis is observed. In this case, by viewing the granule along the direction of the optical axis, one can observe a blurred cross—the usual conoscopic interference figure characteristic of uniaxial crystals viewed in convergent light. In the present case, the role of the converging lens is played by the ice granule itself, whose shape is close to spherical or, more precisely, is an ellipsoid of revolution.

In all cases in which a single-crystal ice granule is formed, one can observe a transformation of the shape of the drop. The granules that form usually differ somewhat from one another in their degree of elongation. In this case the geometrical axis of the granule coincides in direction with its optical axis, i.e., it is the crystallographic axis $C$.

The ellipsoidal shape of the granule is fairly stable. If the granule is gradually evaporated, it diminishes with time in such a way that (within a certain interval of undersaturation) the degree of elongation of the ellipsoid is preserved. In this case the quantity of substance evaporating per unit time from the surface—of the ellipsoid, varies uniformly from point to point. In the direction of the major axis the evaporation rate is maximal, and in the direction of the minor axis it is minimal. The ratio of these rates is such that, at any given moment of time, any linear dimension of the ellipsoid changes by one and the same percentage. As the size of the granule decreases, this percentage increases somewhat, since the evaporation rate of the granule as a whole rises. The increase in the evaporation rate of the granule during the experiment is such that the linear dimensions of the ellipsoid (in particular, in the directions of its principal axes)

**Fig. 1.** **a** —polycrystalline ice granule; **b-d** —single-crystal ice granules; **b** — transparent, **c** —opaque, **d** — “banded” ; **e-f** —an ice granule consisting of an intergrowth of two single crystals: **e** —the nicols are crossed and rotated so that one component of the intergrowth is in the extinction position, **f** —both halves of the granule are in the illumination position.

* As A. V. Shubnikov informed us, when a melt of NaCl is sprayed, single-crystal granules of sodium chloride are sometimes formed.

Fig. 2

Figure 2: Fig. 2

decrease in proportion to the square root of time. In Fig. 2 curves are given for the dependence of the corresponding quantities on time. Data referring to the direction along the major axis of the ellipsoid are denoted by dark points, and those referring to the direction along the minor axis of the ellipsoid by light points.

**Fig. 2**

With a slight increase in the undersaturation, the character of evaporation of the granule changes substantially: the evaporation rate increases, its variation along the surface of the ellipsoid becomes very small, and the ellipsoid begins to elongate. A loss of stability of the ellipsoid shape during evaporation is also observed in the case where the undersaturation is appreciably reduced. Under such conditions, however, the shape of the ellipsoid changes toward an increase of its sphericity, since, simultaneously with the decrease in the overall evaporation rate, its variation along the surface of the ellipsoid increases appreciably.

For an additional check of the correctness of our conclusion concerning the position of the $C$ axis in the granule, we carried out a series of experiments that made it possible to determine the crystallographic orientation of the single-crystal ice granule by a purely morphological method. Near the granule, at the place of the presumed emergence of the $C$ axis, a supercooled water drop was placed. As in our first experiments ($^4$), this drop served as a source of moisture and made it possible for ice to grow on the surface of the ice granule located nearby. With time, numerous ice crystallites begin to develop on the surface of the granule; their basal planes are strictly parallel to one another and perpendicular to the direction of the geometrical axis of the granule. This universal identical orientation of the ice crystallites fully confirms the crystallographic homogeneity of the structure of the granule and the strict coincidence of its major axis with the crystallographic $C$ axis.

Sometimes, during freezing of a supercooled drop, an extremely thin threadlike protuberance appears at one of the ends of the forming single-crystal ice granule, its axis coinciding in direction with

major axis of the ellipsoid. In this case, with increasing humidity of the air, the development of a new crystallite takes place at the very tip of the protuberance. The crystallite grows in the form of a plate whose plane is strictly perpendicular to the axis of the protuberance, so that the $C$ axis of the crystallite is directed along the major axis of the ellipsoid. This result is especially significant if one takes into account that in this case the direction of the $C$ axis of the crystallite, characterized by the lowest growth rate, coincides with the direction of the maximum gradient of vapor concentration. This is possible only under the condition of strict crystallographic homogeneity of the substrate. Otherwise, owing to geometrical selection, a crystallite of such orientation develops on the substrate that the directions perpendicular to the crystallite's $C$ axis (4), characterized by considerably higher growth rates, coincide with the direction of the maximum gradient.

Lines are often visible on the surface of the granule, running parallel to one another over the entire extent from one "pole" of the granule to the other (Fig. 1 *e*). These "parallels" reflect the peculiar layered structure of the granule and are planes parallel to the glide planes of ice (0001), marked by numerous microscopic air bubbles. Sometimes the granule splits spontaneously along one of these planes.

In addition to single-crystal granules, we have also encountered granules that are intergrowths of two single crystals. Such granules are characterized by the non-simultaneous extinction of the two halves and by the presence of a serrated seam (Fig. 1 *d*). Examination in crossed nicols shows that the optical axes of the components of the intergrowth form an angle of $\sim 120°$; the magnitude of the mutual deviation of the axes can also be judged from the angle formed by the "parallels" in the two halves of the granule (Fig. 1 *e*).

The single-crystal ice granules we have found represent the simplest forms of a crystallized melt. Further study of their morphology, clarification of the conditions of formation, and direct observation of their formation should help to elucidate the growth mechanism of such forms and to refine those determining (elementary) growth processes whose various combinations create the complex process of crystallization of a supercooled melt.

Institute of Crystallography
Academy of Sciences of the USSR

Received
11 IV 1960

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*Note: Figure translations are in progress. See original paper for figures.*

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