

Supersaturation and Time Dependence of Ice Nucleation from the Vapor on Single Crystal Substrates

B. J. ANDERSON¹ AND J. HALLETT

Laboratory of Atmospheric Physics, Desert Research Institute, Reno, Nev. 89507

(Manuscript received 6 October 1975, in revised form 20 January 1976)

ABSTRACT

Nucleation of individual ice crystals on large (3.0 mm) cleaved crystals of solution-grown silver iodide and covellite is investigated by microscopy. The environmental vapor pressure is controlled by saturating two air streams by passage through ice labyrinths at different temperatures and mixing them in known proportion. This enables the vapor pressure to be changed over a period of about 10 s.

Ice crystals do not usually appear immediately when a supersaturation is imposed. Nucleation, defined as the appearance of crystals of 1 μm radius, is delayed between zero and 70 s near water saturation and between 20 and 400 s at a few percent ice supersaturation, the longer times occurring at higher temperature. This time decreases only marginally when the crystal is exposed to a period of higher supersaturation which ends a few seconds prior to the time crystals would appear at this higher value. The number of crystals per unit area increases with ice supersaturation at a given temperature; for CuS at -16°C , it increases by a factor of 3 between 3% and water saturation. Number concentrations on silver iodide are comparable, but increase with time when the surface is exposed to light. The absolute crystal concentration varies over the substrate surface. Large areas fail to nucleate at all; some areas give high concentrations, 500 mm^{-2} . Crystals form at specific nucleation sites. Each requires a different critical ice supersaturation for nucleation which remains unchanged in sequential tests. This property disappears for AgI after exposure to light; then nucleation sites do not repeat. Nucleation events per unit area are fewer than on particulates which are inferred to contain a proportionately greater surface concentration of nucleation sites.

Results are applied to crystal nucleation in the atmosphere and the characterization of ice nuclei in laboratory instruments.

1. Introduction

The initiation of the ice phase by particulates in the atmosphere is a problem of great complexity which has yielded only slowly to scientific investigation. Some of this complexity arises from difficulties which are intrinsic in working with small particles. For example, accurate counting and sizing of particles often proves difficult and tedious as does identification of their chemical composition, crystal structure and surface topography. Problems arise in delineating the history of nucleating particles, especially with respect to the humidities and temperatures to which they have been exposed. The experiments reported here were designed to avoid these problems by studying ice nucleation at well-defined sites on freshly cleaved basal surfaces of large (1–3 mm diameter) crystals in an environment in which temperature and humidity could be controlled in a systematic way. Silver iodide was chosen for this study because of its obvious importance in the field of weather modification. The mineral covellite was chosen because, like

silver iodide, it nucleates ice at relatively warm temperatures and forms epitaxial deposits of thin crystals on its basal surface (Bryant *et al.*, 1959). The way in which nucleation on a large substrate differs from that on a small particle becomes evident from the results of this study. The physical process of nucleation at a specific site on a large substrate surface simulates nucleation on an aerosol particle insofar as the dimension of the critical embryo is comparable with topographic features. Step heights present on the substrate surface are comparable with re-entrant irregularities of the same dimension as the particle which are often formed during aerosol formation and coagulation.

The work described here was concerned with the criteria for nucleation from the vapor without the appearance of any liquid phase. The dependence upon supersaturation, considering both magnitude and length of exposure time, was the primary topic studied. The techniques used enabled the environmental conditions to be specified with a higher degree of precision than in earlier experiments and to be controlled to give a realistic simulation of conditions leading to

¹Present affiliation: Space Sciences Laboratory, Marshall Space Flight Center, Huntsville, Ala.

ice formation in the atmosphere. The aim was further understanding of the nucleation process and resolution of discrepancies resulting from insufficient specification of operating conditions in ice nuclei counters. These problems were effectively underlined by Langer (1973).

2. Previous studies

While it has long been recognized that there is a strong dependence of the nucleation ability of particulates on temperature, the dependence on time of exposure to a specified supersaturation has received far less attention. Vonnegut (1949) found that ice crystals continued to appear for as long as 50 min after nuclei were introduced into a mixing cloud chamber. He interpreted this in terms of the probability of a nucleation event by a particle in a drop, together with the time taken for the aerosol to be captured by supercooled cloud drops through Brownian motion, a process which has subsequently been investigated much more extensively (Sax and Goldsmith, 1972). Comparable observations of natural aerosol in mixing chambers were reported by Warner and Newnham (1958) who found the rate of appearance and fallout of crystals decreasing exponentially with a time constant of about 15 min. Warburton and Heffernan (1964) reported a similar result for AgI aerosol, but the time constants were shorter. These results were interpreted by Fletcher (1959) in terms of a time-dependent nucleation of a spectrum of nuclei, active over a range of temperatures. Edwards and Evans (1960), on the other hand, interpreted a similar variation in terms of the probability of a nucleus passing through a high supersaturation and a low temperature in the turbulent mixing which takes place in a cloud chamber. The freezing of droplets containing nuclei cooled at a constant rate, where the environmental conditions are concisely specified, has been interpreted as a time-dependent nucleation process (Bigg, 1953; Vali, 1971).

From a different discipline, Elliot (1974) examined the nucleation of gold on mica in ultra high vacuum. An initial high nucleation rate on preferred sites was followed by a period of minutes during which the number of nuclei increased linearly with time. Surprisingly, there appears very little information on the time dependence of nucleation in vacuum deposition.

Some influence of supersaturation on the nucleation performance of particulates has been appreciated for many years, particularly whether particles required water saturation for nucleation. Mason and van den Heuvel (1959) found that AgI particulates nucleated at sub-water saturation in an ice diffusion chamber, providing the temperature was less than -12°C and the ice supersaturation exceeded 12%. A similar result was obtained by Bryant *et al.* (1959) for nucleation on single crystalline substrates. Edwards and Evans (1960), on the other hand, found that although a few

percent of larger ($10\ \mu\text{m}$) AgI particles were active close to ice saturation between -5 and -15°C , most particles required a supersaturation with respect to water before nucleation occurred. This conclusion was supported by Mossop and Jayaweera (1969) who found that "pure" silver iodide required a water supersaturation of 1 to 5%, and even AgI containing NaI required 0.5%. More recently, Gagin (1972) found a significant supersaturation dependence on the concentration of natural ice nuclei. Crystal numbers increased by a factor of 10^2 as "nominal" supersaturation, calculated from the temperature drop of saturated air passing over a colder surface, increased from 10% to 200%. Huffman (1973) found that an increase of activation of both AgI particles and natural nuclei by 10^3 occurred as supersaturation increased to 30% over ice in the temperature range -12 to -20°C . Langer (1973) interpreted results of the 1971 International Ice Nucleus Workshop in terms of a dependence of nucleation on supersaturation. He attributed discrepancies in counter comparisons to differences in the supersaturation leading to a few initial nuclei removing vapor and preventing the nucleation of others.

Variability of nucleation by particles has been attributed, in addition to the statistical effects of the nucleation process itself, to the variability of "active" sites. These regions have higher nucleation activity by virtue of the presence of impurities or crystalline defects which give changed surface topography. This is evidenced by preferred nucleation at steps and surface scratches (Bryant *et al.*, 1959), increased activity of silver iodide after initial photolysis (Rowland *et al.*, 1964), and increased activity of crushed particles (Davis and Blair, 1969)

3. Experimental method

The covellite crystals used in this study were natural mineral samples from Silver Bow County, Montana. The silver iodide crystals were grown artificially in the laboratory by a modification of the method developed by Cochrane (1967). About 30 ml of 4N HI solution² saturated with AgI³ was placed in the bottom of a flask with a very long neck. A few milliliters of HI was added very slowly to form a buffer zone above the HI-AgI solution; the flask was then carefully filled with about 60 ml of de-ionized water. Convective mixing did not occur because of the high specific gravity of the acid solutions. The flask was stored in the dark in a thermostated bath for more than 8 weeks. During this period diffusion occurred which diluted the acid and supersaturated the solution. High-quality pyramidal crystals up to 4 mm across grew in the bottom of the flask.

² B+A reagent grade (Allied Chemical) without preservative.

³ Analyzed reagent ROC/RIC Chemical Corporation, Sun Valley, Calif.—AgI 99.95%; 0.005% Pb max; 0.001% nitrate.

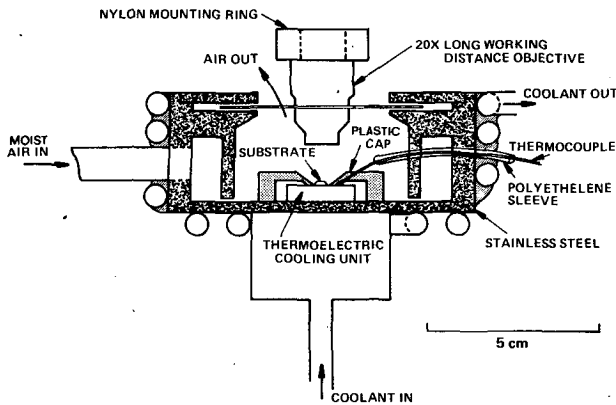


FIG. 1. The experimental chamber. Foam insulation covers sides and bottom.

The nucleation experiments were carried out in a small stainless steel chamber (Fig. 1). Cold alcohol was circulated through the external coils of the chamber. The temperature of the substrate crystal was maintained a few degrees cooler by the thermoelectric cooling unit upon which it rested. The chamber remained dry and ice free. The humidity was controlled by the airstream which flowed steadily at a rate of $33 \text{ cm}^3 \text{ s}^{-1}$ into the chamber from the annular space around the bottom. The airstream was regulated by the system illustrated in the flow diagram (Fig. 2). Air from a cylinder was split into two streams, one to each of the flowmeter-valve combinations. Thence it flowed to the chamber by one of several possible paths. Moisture was added by flow through one of the two ice labyrinths downstream of each flowmeter. The chamber was supplied with either dry air direct from the cylinder (dew point below -40°C), moist air from either ice labyrinth saturated at the given temperature, or a mixture of air from both labyrinths. As air left each labyrinth its temperature rose by some 10°C prior to mixing so that no supersaturation was produced. When air from both labyrinths was mixed, the relative flow rates determined the mixing ratio. The temperature of each ice labyrinth was uniform and constant to within $\pm 0.1^\circ\text{C}$. Under typi-

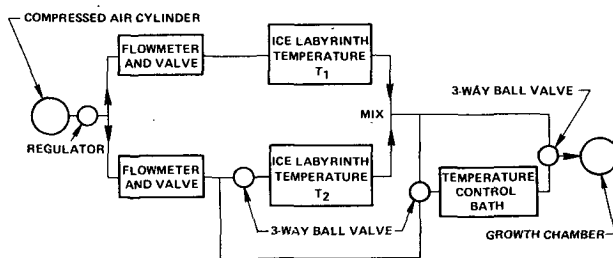


FIG. 2. Air flow diagram. This system enables either dry air direct from the cylinder, or moist air from either or both ice labyrinths, to be fed into the experimental chamber at controlled rates.

cal experimental conditions, one labyrinth was set $1-4^\circ\text{C}$ warmer than the other.

First, air from only the coldest labyrinth was fed into the chamber and the substrate temperature was adjusted to the frost point by determining that ice crystals on the substrate neither grew nor evaporated. Care was taken to select only crystals with thickness greater than $0.5 \mu\text{m}$ for this measurement since crystals thinner than $0.2 \mu\text{m}$ [as determined by thin film interference colors (Hallett, 1961)] were occasionally stressed and evaporated at slight ice supersaturation. The thermocouple next to the substrate crystal did not indicate the substrate surface temperature with sufficient accuracy for the determination of the excess vapor density because of the large temperature gradient in this area. It was used only to monitor the temperature so that it did not drift after it had been set at the frost point of the air from the cooler labyrinth. The temperature was held constant at that point for the duration of the experiment. Ice was grown when air from both ice labyrinths was mixed in the appropriate proportions to give a supersaturation; it was evaporated by allowing dry air from the cylinder to flow through the chamber.

This system had two distinct advantages. First, it allowed the excess vapor density (or supersaturation) to be accurately determined. For $T = -8^\circ\text{C}$ the uncertainty in the excess vapor density was $\pm 0.032 \text{ g m}^{-3}$ or better; for $T = -19^\circ\text{C}$ it was $\pm 0.016 \text{ g m}^{-3}$ or better. This represented an uncertainty in the saturation ratio of $\pm 1.5\%$ or better over the entire operating range. Second, the vapor density in the chamber reached steady state in a short time, $10 \pm 4 \text{ s}$ after the controls were reset. This number was obtained empirically by measuring the change in growth rate of a step on an ice surface when the excess vapor density was changed (Fig. 3). This arrangement enabled crystals to be repeatedly nucleated, grown and evaporated on the same surface.

Ice crystals were examined by a metallurgical microscope with vertical illumination, the objective pro-

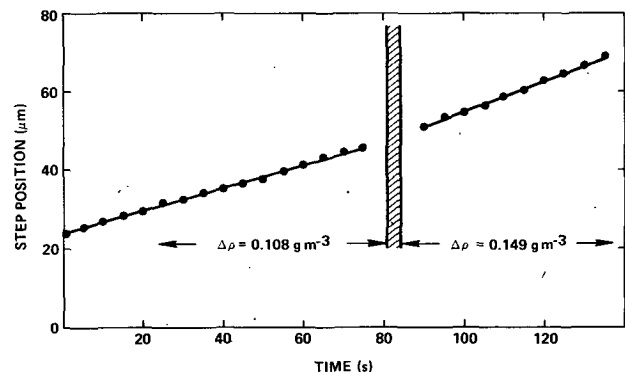


FIG. 3. Position of a step on an ice surface as a function of time. When the excess vapor density was changed the growth rate assumed a new, constant value within 10 s . $T = -15.1^\circ\text{C}$.

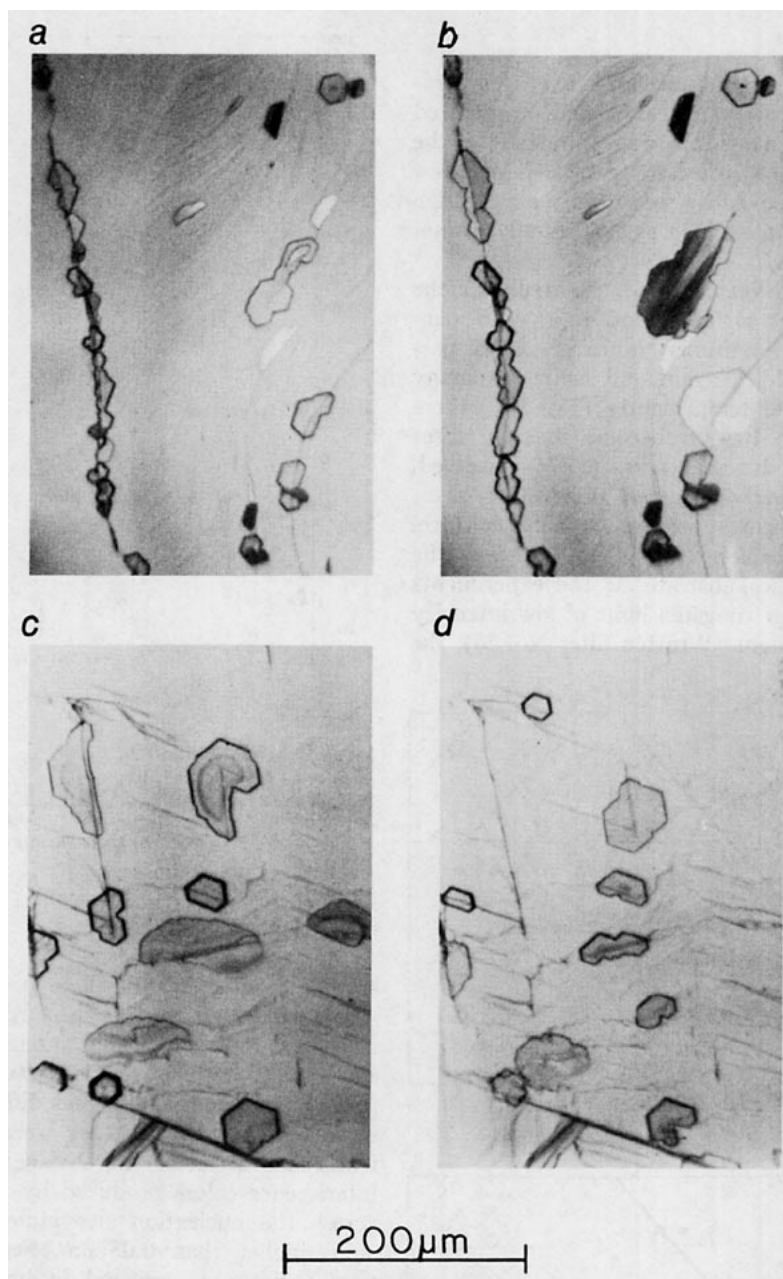


FIG. 4. Ice crystals on covellite (a,b) and silver iodide (c,d) at $T = -15.9^{\circ}\text{C}$ and $\Delta\rho = 0.11 \text{ g m}^{-3}$. Ice nucleates repeatedly at the same locations on CuS but on AgI many sites fail and new sites appear when the light intensity is high ($>2 \text{ W m}^{-2}$).

truding into the top of the chamber. A $10\times$ objective with an 8 mm working distance or a $20\times$ objective with a 13 mm working distance were used with a $10\times$ wide field eyepiece. Experiments were recorded on Ektachrome 7242-B film with a 16 mm movie camera and lapse drive at 96 frames per minute. This system allowed ice crystals to be detected before they reached $2 \mu\text{m}$ diameter and their subsequent growth to be studied.

4. Results

Experiments were carried out at temperatures between -5 and -24°C on both silver iodide and covellite substrates. Sorption nucleation of crystals (there was no visible condensation) occurred at supersaturations of more than a few percent with respect to ice on both substrates.

a. Repeated nucleation

The substrate was maintained at a fixed temperature while crystals were nucleated and evaporated consecutively. After moist air was admitted to the chamber, crystals were grown for a period of a few minutes and then removed by passing dry air through the chamber for about 4 min. Crystals usually evaporated in less than 30 s.

On covellite nucleation occurred repeatedly at the same locations on the surface (Figs. 4a,b) with identical environmental conditions; in each case a particular site nucleated ice again and again, as many as 20 times. At higher temperatures ($\sim -5^\circ\text{C}$) there was a tendency for sites to become inactive after about 10 cycles. As Bryant *et al.* (1959) observed, nucleation sites generally occurred along steps or at other identifiable features on the covellite surface. On silver iodide the behavior was complicated by the photosensitivity of the substrate. If the experiments were carried out under tungsten light of low intensity ($\lesssim 2 \text{ W m}^{-2}$) or red light (Wratten filter No. 25), the

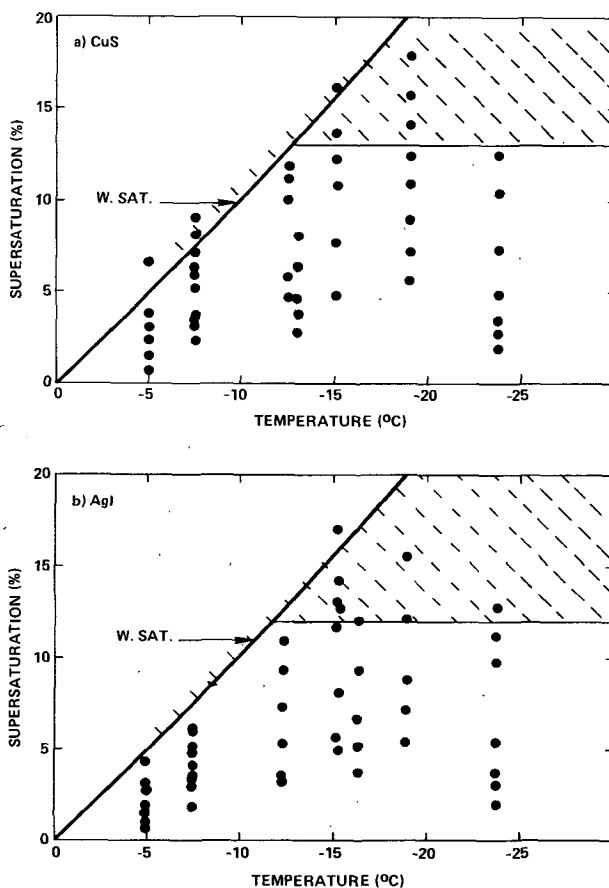


FIG. 5. Temperatures and supersaturations at which ice nucleates on covellite (top) and silver iodide (bottom). Each point represents one experiment. Shaded area is where ice was reported by Bryant *et al.* (1959). The tests on AgI were made under white light from a tungsten source ($> 2 \text{ W m}^{-2}$).

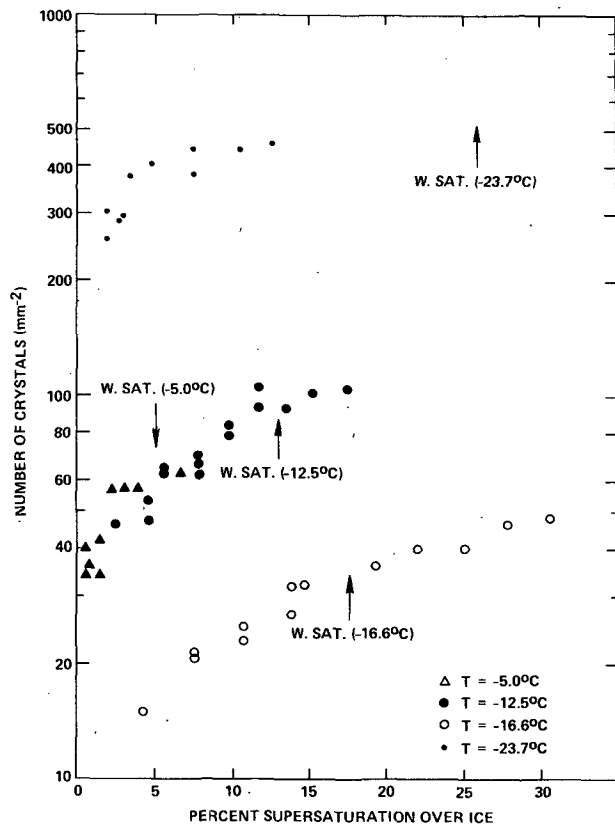


FIG. 6. Number of ice crystals nucleated on covellite as a function of supersaturation. Each data set represents a different covellite surface.

substrate behaved much like covellite. Nucleation at steps and other surface features predominated and sites repeated. If the light intensity was increased to about 5 W m^{-2} , nucleation sites were activated by photolytic action. These sites differed from the former in several ways. First they were located on smooth, featureless areas of the surface; examination of the interference colors produced by thin crystals growing across the nucleation site indicated the absence of steps higher than $0.05 \mu\text{m}$. Second, the nucleation sites sometimes appeared in linear patterns on the surface; neither individual sites nor linear patterns repeated. Figs. 4c and 4d illustrate a case in which the light intensity is near the threshold value. New nucleation sites are formed but some also repeat.

b. Supersaturation dependence

Former studies by Bryant *et al.* (1959) had shown that water saturation was required for nucleation on CuS between -5 and -13°C , and between -4 and -12°C on AgI. A critical supersaturation of 13% and 12% respectively was required at lower temperatures. The present results show that significant nucleation did occur at lower supersaturation (Fig. 5); in fact, at ice supersaturation as low as 2%. The

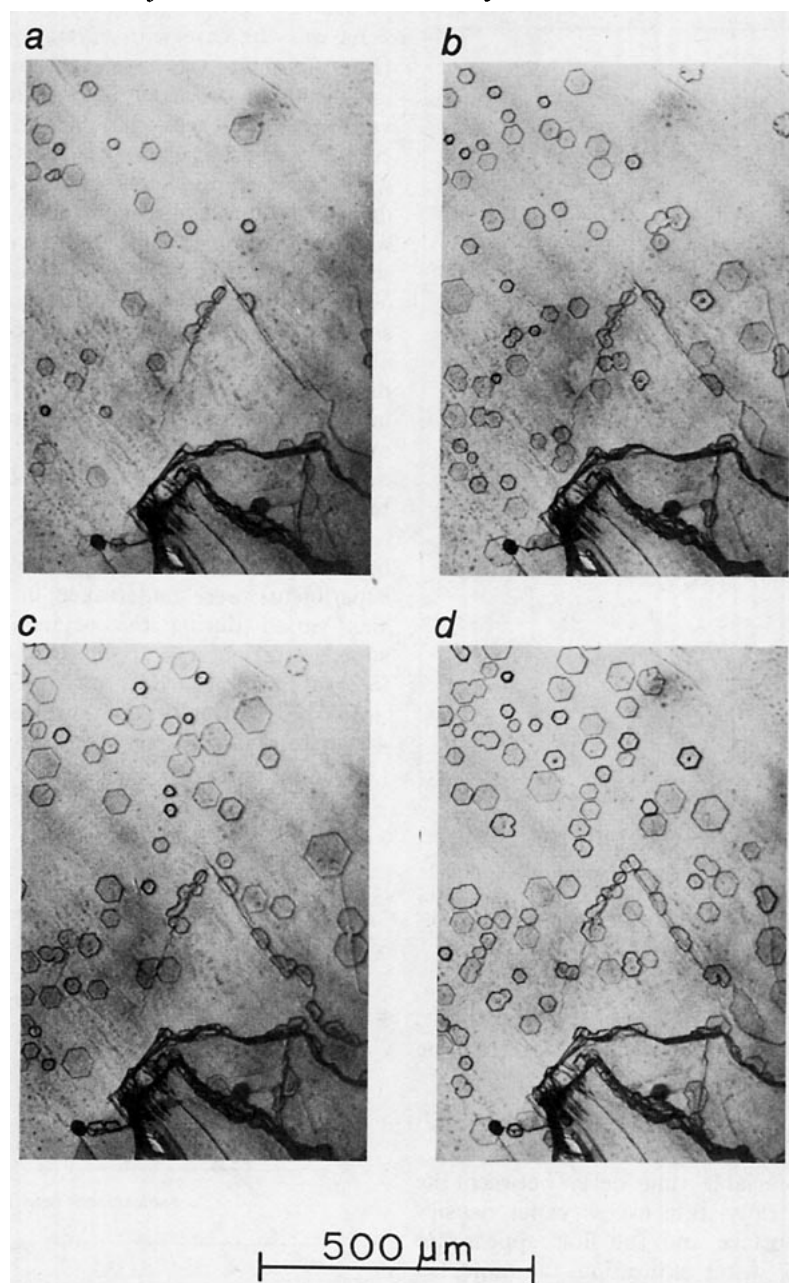


FIG. 7. Ice crystals nucleated on a silver iodide surface at -14.6°C . The excess vapor density is (a) 0.063 g m^{-3} , (b) 0.115 g m^{-3} , (c) 0.148 g m^{-3} , (d) 0.179 g m^{-3} . The number of crystals increases with increasing excess vapor density. Light intensity is about 2 W m^{-2} .

number of crystals nucleated on a given area of substrate increased with ice supersaturation. Fig. 6 demonstrates this dependence for covellite substrates at different temperatures. Several features of this graph are important. These curves were obtained with specific crystal faces. The detailed structure of each surface depends on the cleavage so that some crystals had more steps than others. The absolute number of crystals was greater when more steps were apparent on the surface, although this relationship was difficult

to quantify. The curves given therefore reflect a property of the surface with specific nucleation sites in addition to the influence of temperature and vapor density. Crystal numbers always increased with supersaturation, within the range of slopes of Fig. 6. A corresponding result was also obtained on AgI substrates. However, for this substance the continued production of nucleation sites by photolytic action also influenced the number of crystals obtained. Figs. 7 and 8 illustrate that the crystal numbers increase with super-

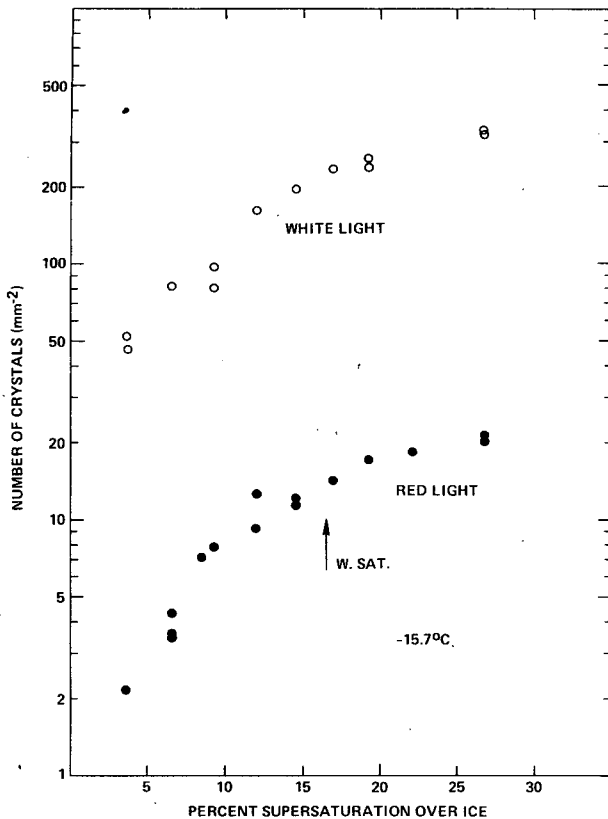


FIG. 8. Number of ice crystals nucleated on silver iodide as a function of supersaturation at $T = -15.7^{\circ}\text{C}$. Both data sets were taken on the same surface. The production of additional nucleation sites by photolytic action is evident.

saturation both under white light and red light, although the total number of active sites may be significantly greater under white light.

c. Nucleation time lag

There was an appreciable time delay between the establishment of a steady-state excess vapor density over the substrate surface and the first appearance of ice crystals. Near water saturation the time lag ranged from zero to 70 s; at a few percent ice supersaturation the range was 20 to 400 s, the longer times occurring at higher temperatures (Fig. 9). These figures show the time until the appearance of the first crystal in the field of view ($300\ \mu\text{m} \times 400\ \mu\text{m}$).

After the first crystal appeared the rest soon followed. On covellite 95% of the crystals appeared within 25 s of the first crystal (Fig. 10). Usually silver iodide substrates behaved in an identical manner, especially at higher supersaturation where a large number of crystals were nucleated. In cases with low crystal concentrations nucleation continued for several minutes on silver iodide surfaces, since white light from the illuminator continually produced active sites.

As was the case with crystal surface concentration (Fig. 6) there was a significant variability in the magnitude of the absolute time dependence and in its variation with excess vapor density (the slope of the curve). For example, in Fig. 9a the data at -14.7°C were taken on the same surface on three consecutive days and show a spread of delay times which is well within experimental error. However, when results from several cleaved surfaces are compared there is a spread of data which is outside the expected errors of measurement (Fig. 11). The evidence suggests that this also is due to variability in topography caused by differences in cleavage. In spite of the large variability in Fig. 11, Fig. 9 does demonstrate that there is an overall trend of time lag, which becomes longer with decrease of excess vapor density and at higher temperatures.

In order to investigate further those aspects of the nucleation mechanism responsible for the time lag, experiments were undertaken in which the humidity was varied during the drying interval before the supersaturation was applied and during the time lag interval itself. Consider an experiment conducted at -15.6°C . Normally the substrate was exposed for 4 min to dry air direct from the cylinder, frost point

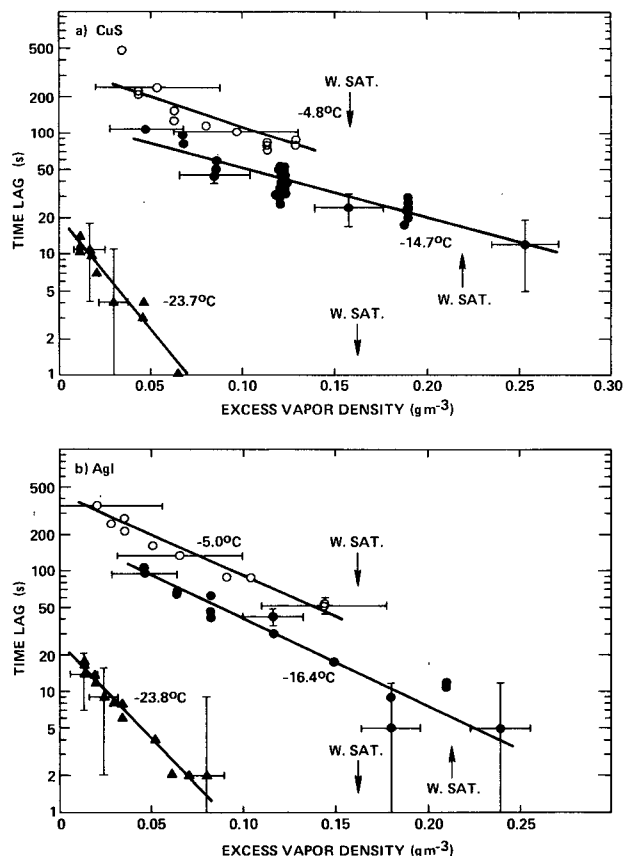


FIG. 9. Time lag for ice nucleation on covellite (a) and silver iodide (b) surfaces.

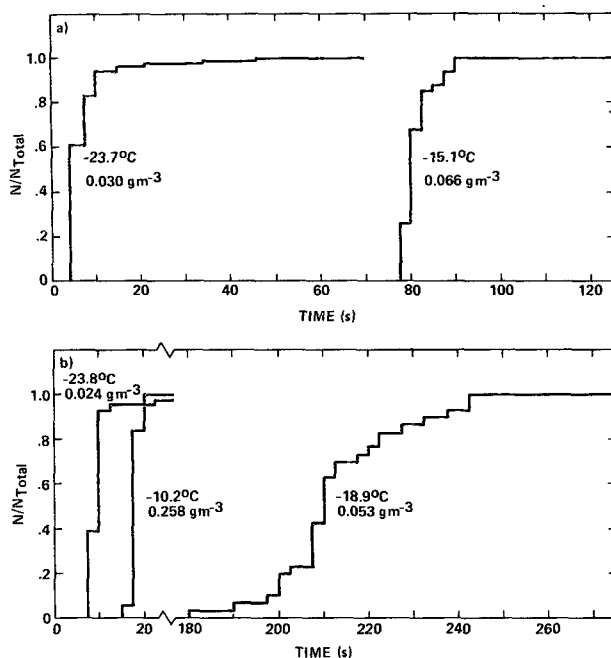


FIG. 10. The appearance of ice crystals as a function of time on covellite (a) and silver iodide (b) substrates. The -18.9°C curve has been shifted 150 s to the left.

below -40°C . When the frost point of the drying air was raised to -30°C the time lag was reduced by about 17%; when it was raised to -26°C the time lag was reduced by 38%. Thus the time lag was sensitive to low levels of humidity applied for relatively long periods of time. However, it was not sensitive to the application of a high transient humidity, as illustrated in Fig. 12. The substrate was dried in the normal fashion. When the system was brought from undersaturation directly to a given value of excess vapor density (illustrated by the solid curves) ice occurred at the points marked A. This was the measured time lag. The contribution resulting from the system time constant is included in the illustration. However, when a high excess vapor density was initially applied and then reduced 7–10 s before ice was expected (dashed curve, Fig. 12) ice failed to appear until the point marked B. B was so close to A, the normal value for the time lag at the final excess vapor density, that it was not always possible to separate the two within experimental error. If the vapor density was not reduced quite soon enough (dotted line) ice would occur at C. The number density of crystals nucleated at B corresponded to the number expected at the final excess vapor density value; at C it was some intermediate value.

All crystals which appeared within a selected field of view were counted in this study, irrespective of their growth characteristics. Most crystals grew in both *c* and *a* crystallographic directions, but, as in the earlier study, some crystals of thickness $\lesssim 0.1 \mu\text{m}$

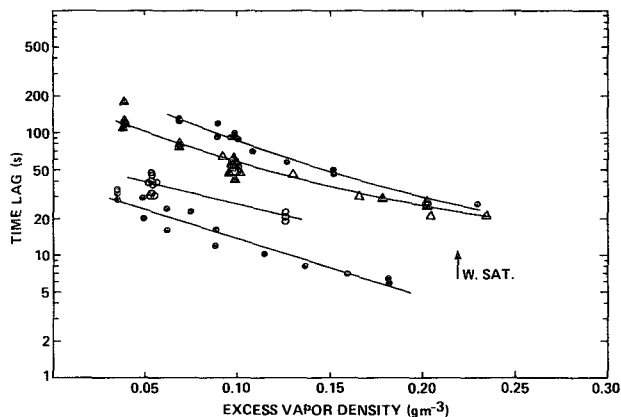


FIG. 11. Variability of the time lag on different covellite surfaces. In each case the temperature was -10°C . The time lag is measured to within ± 7 s; the excess vapor density to within $\pm 0.027 \text{ g m}^{-3}$.

grew only laterally. More of these crystals appeared at lower temperatures—10% at -10°C , 30% at -20°C .

5. Discussion

a. Time lag

The time lag of nucleation reported here differs drastically from that reported by earlier workers in that a definite time lapses before any nucleation begins; in earlier cases nucleation rate decreased continuously from an initial high value. A critical assessment of earlier cold box studies shows that the physical mechanism of nucleation—deposition, freezing or contact—was in no case defined, with probably all three mechanisms operative. Our experiments were concerned only with deposition nucleation insofar as there was undersaturation with respect to water in most tests, and even with water supersaturation visi-

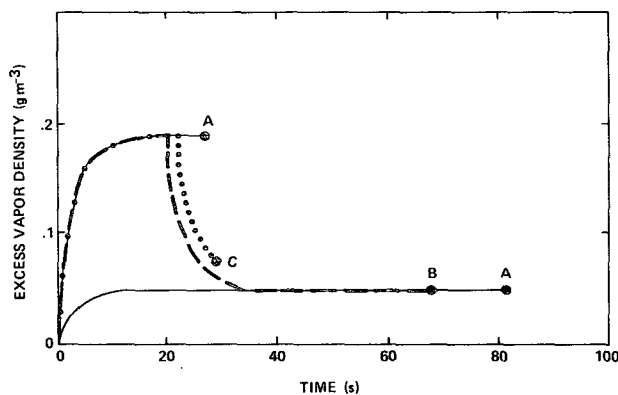


FIG. 12. The effect of a transient high supersaturation on the time lag. If the excess vapor density follows the solid curves ice appears at the points marked A. If a larger excess vapor density is applied briefly (dotted and dashed curves) and is then reduced, ice appears at B or C.

ble drops did not occur. It follows that neither earlier measurement of time lag in cold boxes nor of freezing drops is directly comparable to these experiments.

The nucleation curve (Fig. 12) shows that once nucleation begins, crystals appear quickly, the rate falling with time until nucleation either ceases (CuS) or continues at a very low rate by photolytic activation (AgI). The falloff after initial nucleation can be interpreted in terms of nucleation probability and a spectrum of active sites as earlier studies have shown, together with the reduction of supersaturation by growing crystals which may extend some 5 to 10 diameters away.

The initial delay period, not previously reported, requires another explanation. We consider four mechanisms:

- 1) Time for the surface to reach thermal equilibrium as adsorption latent heat is released. This sometimes gives delays in BET type experiments when powders are suspended in isolated containers (Deitz and Carpenter, 1961). In the present case, the adsorbing crystal is 1.0 mm thick. Assuming a 5-layer adsorption, and a crystal thermal diffusivity of $\kappa = 0.02 \text{ cm}^2 \text{ s}^{-1}$ ($0.02 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$), the time constant for heat diffusion is $x^2/4\kappa \approx 0.05 \text{ s}$ (Carslaw and Jaeger, 1959). The temperature rise, assuming the latent heat of water vapor to be 2500 J g^{-1} , is $\sim 10^{-2} \text{ }^\circ\text{C}$.

- 2) Sometimes the surface crystal lattice is favorably modified by the diffusion of water vapor molecules into the volume of a crystal, leading to a change in its surface lattice configuration. If we suppose that a layer 10 molecular layers ($0.002 \text{ }\mu\text{m}$) deep absorbs vapor and assume a diffusion coefficient of $10^{-11} \text{ cm}^2 \text{ s}^{-1}$ ($10^{-15} \text{ m}^2 \text{ s}^{-1}$), we obtain a time constant $x^2/4D \approx 10^{-3} \text{ s}$.

- 3) Time to achieve equilibrium of embryos in the vapor estimated to lie between 10^{-5} to 10^{-7} s (Mason, 1971).

- 4) The time to grow from a critical embryo size to a visible size ($r = 1 \text{ }\mu\text{m}$). This calculation has been performed for growth entirely in the vapor by a method similar to the approach of Fukuta and Walter (1970) but applicable to very small ice crystals.

Relationships were derived for an isolated spherical ice crystal in air and were employed to yield an order of magnitude estimate of the growth time of a hemispherical crystal on a surface by eliminating the temperature accommodation term from the solution and using the thermal conductivity of the substrate in place of the thermal conductivity of air. Migration of molecules adsorbed on the surface was neglected in this approximation. It was found that the time required for a crystal to grow from critical radius plus $3 \times 10^{-4} \text{ }\mu\text{m}$ to $r = 1 \text{ }\mu\text{m}$ is of the order of tens of seconds if it is assumed that the condensation coefficient β is of order 0.001. Even if β is of order 0.1, the time required for this growth is about one second.

Of these four mechanisms, only the growth from critical embryo size offers a possible explanation. However, the conclusions to be drawn from the initial application of a transient high supersaturation are in conflict with this concept. The transient should lead to an increase in growth rate and a shortening of the time constant, in contrast to observation. This observation suggests that the establishment of an equilibrium distribution of embryos on the surface may be a more lengthy process than in the vapor. Further studies are evidently required to solve these questions of molecular kinetics.

b. Supersaturation dependence

The results from covellite and silver iodide under red light show conclusively that, at one temperature, each nucleation site requires a different ice supersaturation for activation. The value of the supersaturation remains unchanged for successive growth and evaporation cycles. This suggests that each site has a topographical characteristic which determines its behavior. This is consistent with the preferred nucleation at steps or some geometrical irregularity on covellite and on AgI under red light. On AgI under tungsten illumination the lack of reproducibility of nucleation sites suggests that the surface has a dynamic structure with surface sites being created and destroyed over a period of minutes by ionic processes within the lattice. The absence of any relation between step height and critical supersaturation for nucleation suggests that the step shape (straight or kinked) or presence of a crystal defect is the controlling consideration. Such a conclusion merits further study of the sites by more refined techniques. However, it can be concluded that the supersaturation dependence of crystal surface concentration is linked to the surface geometry of the crystal and the probability of a given geometrical configuration.

It is of interest that steps are present on the crystal surface with heights which are of the same magnitude as the diameter of particles important in the nucleation process. On covellite steps of height greater than about $0.1 \text{ }\mu\text{m}$ are required to nucleate preferentially; AgI particles of diameter $> 0.05 \text{ }\mu\text{m}$ are found to be necessary for nucleation from the vapor (Gerber *et al.*, 1970). Particles of diameter $0.5\text{--}0.05 \text{ }\mu\text{m}$ have a surface area $\sim 10^{-6}$ to 10^{-8} mm^2 . Every particle active as an ice nucleus therefore corresponds to $10^6\text{--}10^8$ active sites per square millimeter. A comparison with Fig. 6 shows that these numbers are far in excess of the numbers of sites measured on large single crystals for both CuS and AgI. There are large areas of these crystals which are inactive and the observed nucleation sites are indeed quite distinct from the general surface. Even at temperatures near those where particulates are 100% active (about -15°C) there are still significant areas which fail to

nucleate crystals even when mutual competition of neighboring crystals is taken into account.

We may make the hypothesis that results obtained on active sites on large crystal substrates are a characteristic of the nucleation process in general and can be extended to aerosol particles, lacking a soluble component. The enhanced activity of aerosol particles may be attributed to a greater area concentration of nucleation sites. This extension appears realistic when the formation mechanism of solid aerosol particles is considered. Mechanical generation will certainly give rise to defects as particles are fractured; particle coagulation after generation will give rise to re-entrant angles at the contact point. While Gerber *et al.* (1970) found, under the electron microscope, that most AgI particles were single hexagonal or column crystals, the active particles were substantially larger ($0.08 \mu\text{m}$) than the mean size of all particles ($0.02 \mu\text{m}$) and may well have consisted of multiple particles of this kind.

In conclusion, whether or not a particle is capable of nucleation at a specific temperature and supersaturation depends on the probability of having a specific site. This, in turn, depends on its generation history.

6. Application : Deposition nucleation by particulates

We here examine the implications of extending the results to particulates important in the atmosphere. The conclusions are necessarily limited to those particles which do not contain a soluble coat.

Application to nuclei counters points to some specific problems. First, if nuclei are to be detected at subwater saturation, the exposure time must be at least that of Fig. 9 depending on ice supersaturation. This suggests that some mixing and expansion chambers working at subwater saturation for test times less than 1–2 min were probably failing to count particles which would have been active at longer times. Millipore filter techniques at subwater saturation usually expose for 10–20 min and thus avoid this problem. Second, the activity of each particle at a given temperature is dependent on ice supersaturation. Hence, to obtain accurate counts a system must maintain a given temperature, produce a given ice supersaturation quickly, and maintain it for a period of minutes for nucleation and growth to visible size, which at low instrument magnification might require at least 15 min. The occurrence of short transient high supersaturation may not influence nucleation, although the extensions of the transient beyond the time lags of Fig. 9 certainly could give unrepresentatively high values. Transients leading to water condensation are excluded from this analysis. The processing techniques already developed for Millipore filters could fulfill this criterion. The supersaturation over a filter could be increased in steps as Huffman (1973) carried out for AgI, with sufficient

time to permit nucleation and growth, remembering the limitation that growing crystals compete for available vapor (Huffman and Vali, 1973).

For tests to simulate deposition nucleation by particles in a water cloud, time lags are less than 10 s at lower temperatures and only present problems for a rapid expansion chamber. At higher temperatures, however, even at water saturation the time constant is ~ 50 s which could lead to problems in continuous flow systems like the NCAR counter where the residence time is about this period. Supersaturation well in excess of water saturation, which leads to the high nucleation rates reported by Gagin (1972), was not examined in this study since vapor depletion would occur too quickly by droplet and crystal growth at other places in the chamber. The data of Fig. 6 do give points for supersaturations in excess of water saturation up to about 10%; no droplets were nucleated on the surface. These supersaturations are still well below those studied by Gagin.

The relative importance of production of ice particles by deposition, contact nucleation and drop freezing under differing atmospheric conditions is still far from understood. Situations do exist, however, in which water saturation is never reached, yet ice supersaturation can be attained so that only deposition nucleation is possible providing the particles do not contain a soluble component (Bigg and Meade, 1971). This could occur on a widespread scale in a frontal system or on a much smaller scale in a shallow lee wave or in precumulus convection. A lag time of minutes would indicate that such short-period lee waves and short-lived convective elements might be less likely to produce ice than frontal systems or longer period events.

7. Conclusion

By careful control of environmental conditions for nucleation, it has been shown that single crystals of AgI and CuS contain preferred sites for nucleation from the vapor. At a given temperature, each site requires a critical supersaturation, which must be applied for a critical time before crystals become visible. The number of sites increases with ice supersaturation. The lag in crystal nucleation is consistent with the time required for growth from a critical embryo, although there is some suggestion that the time for establishment of a distribution of embryos on the surface may be important. The dependence of site density or supersaturation is interpreted in terms of the local geometry of the surface. The nucleation activity of large single crystals is $\sim 10^3 \text{ mm}^{-2}$, well below $0.3 \times 10^8 \text{ mm}^{-2}$ for a $0.1 \mu\text{m}$ particle. It is inferred that active particles must contain a greater number of active sites produced during the generation process.

In the atmosphere, deposition nucleation may under some circumstances compete numerically with nucleation by particles embedded in or contacting supercooled drops. Nucleation of ice in this way may be important under those conditions which just fail to give water saturation. Laboratory tests for the nucleation of these particles must be carefully controlled to give sufficient time for crystals to appear and prevent any transient high supersaturation which would give spurious high counts.

Acknowledgments. This work was supported by a grant from the National Science Foundation, Atmospheric Sciences Section, Washington, D. C. This work fulfilled in part requirement for a higher degree (B.J.A.) in the Physics Department, University of Nevada, Reno.

REFERENCES

- Bigg, E. K., 1953: The supercooling of water. *Proc. Phys. Soc.*, **B66**, 688-694.
- , and R. T. Meade, 1971: High level stratocumulus clouds. *Weather*, **26**, 55-57.
- Bryant, G. W., J. Hallett and B. J. Mason, 1959: The epitaxial growth of ice on single crystalline substances. *Phys. Chem. Solids*, **12**, 189-195.
- Carslaw, H. S., and J. C. Jaeger, 1959: *Conduction of Heat in Solids*, 2nd ed. Oxford University Press, p. 62.
- Cochrane, G., 1967: Preparation of single crystals of hexagonal silver iodide. *Brit. J. Appl. Phys.*, **18**, 687-688.
- Davis, D. L., and D. N. Blair, 1969: Role of substrate strain in ice nucleation. *J. Geophys. Res.*, **74**, 4571-4580.
- Deitz, V. R., and J. G. Carpenter, 1961: The rate of adsorption at low surface coverage. *Advances in Chemistry*, Vol. 33, Amer. Chem. Soc., 146-159.
- Edwards, G. R., and L. F. Evans, 1960: Ice nucleation by silver iodide I. Freezing vs supersaturation. *J. Meteor.*, **17**, 627-634.
- Elliot, A. B., 1974: Nucleation kinetics for Au deposited onto mica substrates. *Surface Sci.*, **44**, 337-359.
- Fletcher, N. H., 1959: On ice crystal production by aerosol particles. *J. Meteor.*, **16**, 173-180.
- Fukuta, N., and L. A. Walter, 1970: Kinetics of hydrometeor growth from a vapor-spherical model. *J. Atmos. Sci.*, **27**, 1160-1172.
- Gagin, A., 1972: The effect of supersaturation on the ice crystal production by natural aerosols. *J. Rech. Atmos.*, **6**, 175-185.
- Gerber, H. E., P. A. Allee, U. Katz, C. I. Davis and L. O. Grant, 1970: Some size distribution measurements of AgI nuclei with an aerosol spectrometer. *J. Atmos. Sci.*, **27**, 1060-1067.
- Hallett, J., 1961: The growth of ice crystals on freshly cleaved covellite surfaces. *Phil. Mag.*, **6**, 1073-1087.
- Huffman, P. J., 1973: Supersaturation spectra of AgI and natural ice nuclei. *J. Appl. Meteor.*, **12**, 1080-1082.
- , and G. Vali, 1973: The effect of vapor depletion on ice nucleus measurements with membrane filters. *J. Appl. Meteor.*, **12**, 1018-1024.
- Langer, G., 1973: Analysis of the results from the 2nd International Ice Nucleus Workshop with emphasis on expansion chambers, NCAR counters and membrane filters. *J. Appl. Meteor.*, **12**, 991-999.
- Mason, B. J., 1971: *The Physics of Clouds*, 2nd ed. Clarendon Press, 11-12.
- , and A. P. van den Heuvel, 1959: The properties and behavior of some artificial ice nuclei. *Proc. Phys. Soc.*, **74**, 744-755.
- Mossop, S., and K. O. L. F. Jayaweera, 1969: AgI-Natural aerosols and ice nuclei. *J. Appl. Meteor.*, **8**, 241-248.
- Rowland, S. C., R. G. Layton and D. R. Smith, 1964: Photolytic activation of silver iodide in the nucleation of ice. *J. Atmos. Sci.*, **21**, 698-700.
- Sax, R., and P. Goldsmith, 1972: Nucleation of water drops by Brownian contact with AgI and other aerosols. *Quart. J. Roy. Meteor. Soc.*, **98**, 60-72.
- Vali, G., 1971: Qualitative evaluation of experimental results on the heterogeneous freezing of supercooled liquids. *J. Atmos. Sci.*, **28**, 402-409.
- Vonnegut, B., 1949: Nucleation of supercooled water by silver iodide smokes. *Chem. Rev.*, **44**, 277-289.
- Warburton, J. A., and K. J. Heffernan, 1964: Time lag in ice crystal nucleation by silver iodide. *J. Appl. Meteor.*, **3**, 788-791.
- Warner, J., and B. D. Newnham, 1958: Time lag in ice crystal nucleation in the atmosphere. *Bull. Obs. Puy de Dome*, No. 1, 1-10.