The negative equivalent conductivity excess together with the positive activation energy excess indicate that the electrical transport is more hindered in mixtures than in the pure components. The nitrate anion is easily polarizable[21] and when inserted between cations of different radii will experience a net, permanent, electrical field. The resulting anion polarization increases the attraction between the nitrate and the smaller cation. These conditions will result in a higher resistance for the smaller cation to move relatively to the nearest nitrate; or, in other words, the mobility of the small cation relative to the nitrate will be reduced. Internal mobility[22] measurements in this system could be of interest just from this point of view.

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On the Growth of Ice in Aqueous Solutions Contained in Capillaries

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The growth rate of ice in supercooled water and in dilute aqueous solutions of various salts which dissociate in water into univalent ions was studied. The solutions contained in polyethylene tubes of small bore had concentrations between 10^{-6} and 10^{-1} moles liter^{-1} and were investigated at bath supercoolings between 1° and 15 °C. The growth rate of ice which in pure water was found to vary approximately with the square of the bath supercooling was affected in a systematic manner by the type and concentration of the salt in solution. At salt concentrations smaller than 5×10^{-2} moles liter^{-1} most salts did not affect the growth rate. However, the fluorides were found to increase the growth rate over and above the one in pure water. At concentrations larger than 5×10^{-2} moles liter^{-1} all the salts reduced the growth rate of ice below the one in pure water. By comparing solutions of salts with common anion it was found that at a particular bath supercooling and salt concentration the growth rate of ice was reduced most in lithium solutions and least in cesium and ammonium solutions. By comparing solutions of salts with common cation it was found that the growth rate of ice was reduced most in fluoride solutions and least in bromide solutions. It was concluded that in solutions with salt concentrations larger than 5×10^{-2} moles liter^{-1} the rate of dissipation of latent heat which controls the growth rate of ice is affected in a systematic manner by the freezing point lowering effects which result from pure mass transfer conditions prevailing at the ice-solution interface of a stagnant system. Some features of the observed growth rates are discussed in terms of the effect of dissolved salts on the growth forms of ice in aqueous solutions.

The problem of determining the growth rates and the growth forms of ice in water and aqueous solutions has occupied the interest of many scientists since the end of the 19th century[1–21]. Although the main importance of this problem lies in the realm of physical chemistry, recent studies in the

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field of low temperature biology stimulated additional interest and opened another aspect of this problem [22, 23]. Since it is well accepted now in cryobiology that the main assault on the living system at low temperatures occurs during the phase change, the rate of crystallization is of profound importance in the fate of the living system. Some recent comparisons between the efficacy and efficiency of processes used to desalinate ocean water have shown that freezing offers one of the lowest energy routes to desalination [24]. Large scale freezing processes, however, are beset with practical difficulties which center upon the growth and handling of the ice grains. A basic reason for these difficulties is the "platy" morphology of the ice crystals growing from water and aqueous solutions. An understanding of the growth rates and growth forms of ice crystals in water and aqueous solutions is of great relevance for overcoming these difficulties. Recent studies in cloud and precipitation physics have shown that a thorough knowledge on the growth rate and growth modes of ice crystals in supercooled water is also of fundamental importance to an understanding of the glaciation processes taking place in atmospheric clouds [25]. A survey of the mentioned literature shows that the information available on the rate of ice-crystal growth in aqueous solutions is very limited and that a systematic study of this problem for a wide range of supercoolings, salt concentrations and salt types is lacking. We have therefore undertaken such a systematic study.

Experimental Procedure

The growth rate of ice in supercooled water and various aqueous solutions was measured at bath supercoolings between 1° and 15 °C. The water used was purified by distillation and deionization according to the method described by PRUPPACHER [26]. From this water aqueous solutions were made by dissolving reagent grade salts in it and filtering the solutions through Millipore filters of 0.1 micron pore size. Solutions of concentrations 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1} moles liter^{-1} were prepared from the following substances: HF, NaF, KF, CsF, NH_4F, LiCl, NaCl, KCl, CsCl, NH_4Cl, LiBr, NaBr, KBr, CsBr, NH_4Br, and KI.

The water or aqueous solutions were filled into polyethylene tubes of 1.2 mm internal and 1.6 mm external diameter, suspended horizontally and submerged in a continuously stirred cold bath of low viscous silicone oil. The test section of the tube was 60 cm long. The water or aqueous solutions in the tubes could be supercooled by 18 °C before they froze spontaneously. After temperature equilibrium was reached between a particular solution in the tube and the oil bath freezing in the tube was initiated by touching one tube end sticking out of the bath with a piece of dry ice at a point about 20 cm away from the test section. The growth velocity of ice was measured by means of a stopwatch and by means of a motion picture technique which allowed to observe the growth of the ice crystals between crossed polaroids and to film it in color with a Bolex motion picture camera which was operated at 64 frames per second. The accuracy of the measurements was 0.5%, 1.3%, and 5.3% at the bath supercooling of 5°, 10°, and 15 °C respectively.

Results

In Fig. 1 the variation of the growth rate of ice in supercooled water with bath supercooling is shown. It is seen from this figure that at supercoolings between 0° and 10 °C the growth rate increased progressively with supercooling. At bath supercoolings between 10° and 12 °C a discontinuity in the variation of the growth rate was observed. In this temperature interval the values for

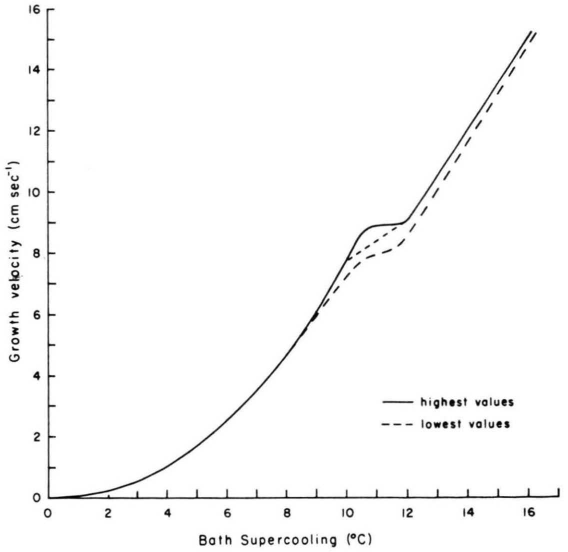

Fig. 1. Variation of the growth velocity of ice in pure water contained in polyethylene tubes with bath supercooling.

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the growth rate scattered considerably and were practically independent of the bath supercooling. At bath supercoolings larger than 12 °C the growth rate increased again with increasing supercooling but less rapidly than at supercoolings between 0° and 10 °C.

In Fig. 2 the variation of the growth rate of ice in water is plotted as a function of bath supercooling on logarithmic scale and compared with the results of Persidsky and Richards [16], Tammann and Büchner [10], and Kost [13]. It is seen from this graph that our observations agree with the observations made by Kost and can be fitted to a growth law of the type $V = A \times (\Delta T)_b{}^B$, with $A = 0.053$ and $B = 2.14$. Furthermore, it is seen from this graph that the temperature interval within which the growth rate discontinuity was observed agrees quite well with that determined by Tammann and Büchner and by Persidsky and Richards.

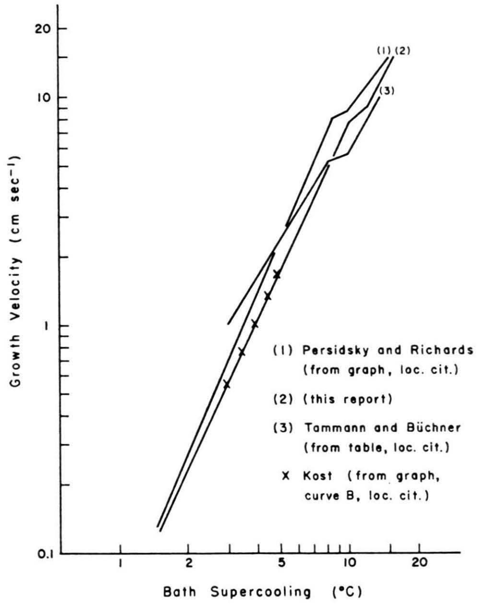

Fig. 2. Variation of the growth velocity of ice in pure water contained in tubes with bath supercooling according to different workers.

In Fig. 3 the variation of the growth rate of ice in various 0.1 molar aqueous chloride solutions is presented as a function of the bath supercooling. It is seen from this figure that the growth rate of ice in these solutions was significantly reduced below the growth rate of ice in pure water at supercoolings larger than about 2 °C. Fig. 3 demonstrates further that also in aqueous solutions a discontinuity in the variation of the growth rate of ice was observed which, however, compared to pure water, occurred at slightly smaller supercoolings. Similar results were obtained for 0.1 molar fluoride and 0.1 molar bromide solutions. The results of all these measurements are summarized in Fig. 4 and 5. It is seen from Fig. 4 that in solutions of salts with a common anion the growth rate was depressed most in lithium solutions and least in ammonium and cesium solutions. From Fig. 5 it is seen that in solutions of salts with a common cation the growth rate tended to be slightly larger in bromide solutions than in chloride and fluoride solutions.

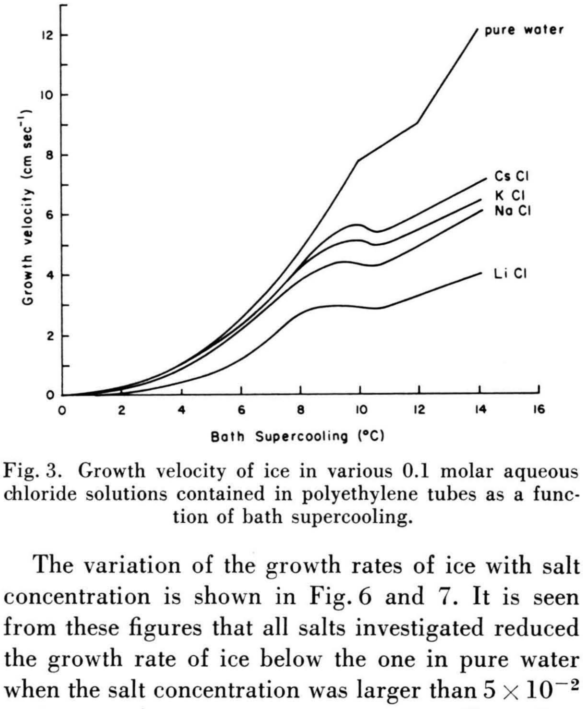

Fig. 3. Growth velocity of ice in various 0.1 molar aqueous chloride solutions contained in polyethylene tubes as a function of bath supercooling.

The variation of the growth rates of ice with salt concentration is shown in Fig. 6 and 7. It is seen from these figures that all salts investigated reduced the growth rate of ice below the one in pure water when the salt concentration was larger than 5×10^{-2} moles liter^{-1}. At concentrations smaller than 5×10^{-2} moles liter^{-1} some salts such as CsBr, CsCl, NH_4F, KBr, LiCl did not affect the growth rate at all (Fig. 6) while others such as NH_4OH and particularly KF, CsF, NaF increased the growth rate over and above the one in pure water (Fig. 7). Fig. 7 shows in particular that the enhancement of the growth rate of ice in solution over and above the one in pure water is confined to a certain concentration interval, is a maximum at about 10^{-2} moles liter^{-1} and is more pronounced at larger than at smaller supercoolings.

The growth modes of ice in supercooled water and aqueous solutions contained in capillary tubes

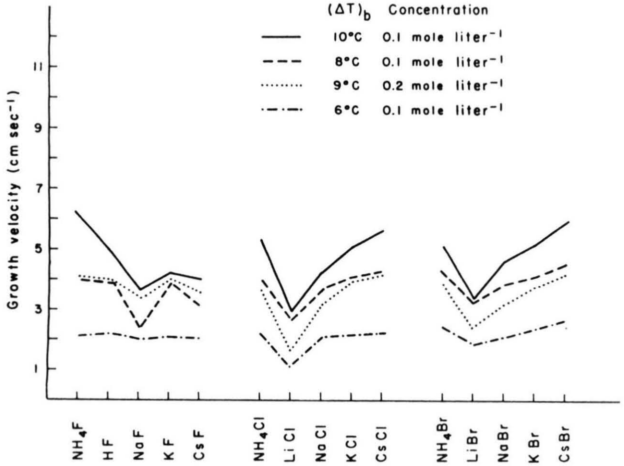

Fig. 4. Growth velocity of ice in 0.1 and 0.2 molar aqueous solutions of various salts with common anion at different bath supercoolings $(\Delta T)_b$.

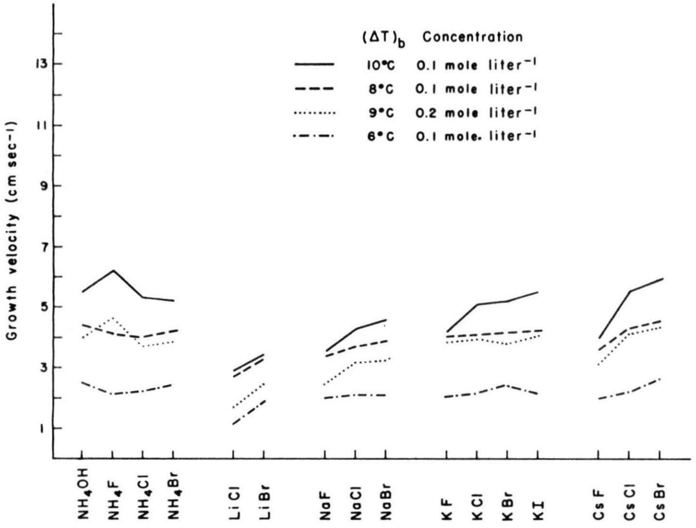

Fig. 5. Growth velocity of ice in 0.1 and 0.2 molar aqueous solutions of various salts with common cation at different bath supercoolings $(\Delta T)_b$.

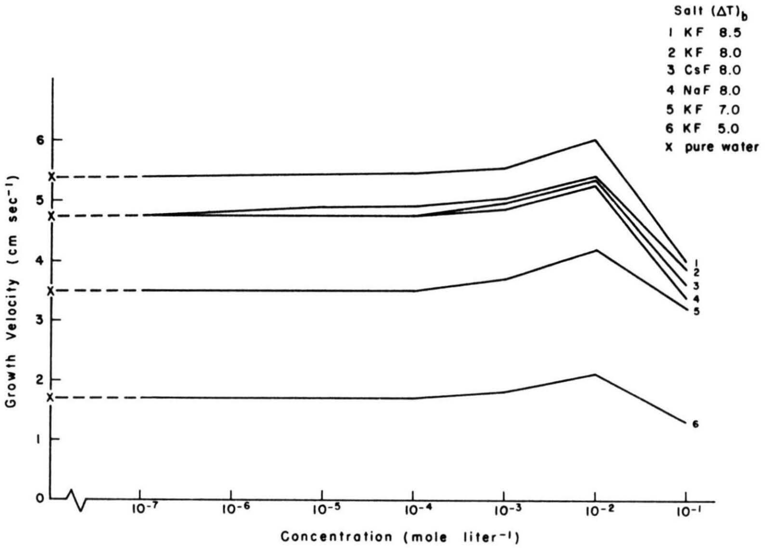

Fig. 7. Variation of the growth velocity of ice in various aqueous fluoride solutions with salt concentration.

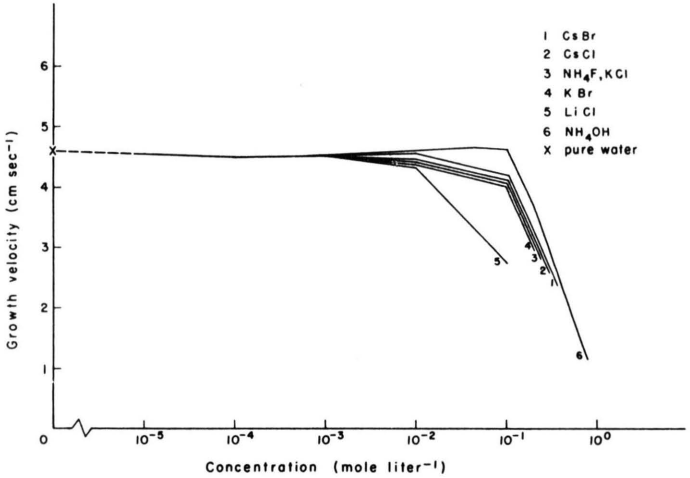

Fig. 6. Variation of the growth velocity of ice in various aqueous solutions with salt concentration. Bath supercooling: 8 °C.

were determined from an analysis of our motion picture records. This analysis, discussed in detail by PRUPPACHER[27], showed that at supercoolings between 1° and 4 °C a few individual ice dendrites were formed in the water or solution which grew along the tube axis. At supercoolings larger than 4 °C an increasingly larger number of dendrites formed, whose growth direction was inclined to the tube axis such that the dendrites hit the tube wall from which they proceeded growing in a new direction. As result of this behavior the ice crystals grew in a zig-zag fashion through the tube. The growth modes were considerably more complicated for growth of ice crystals in aqueous solutions. In this case the dendrites were thinner and their direction of growth deviated from the tube axis already at small supercoolings. Depending on the type of salt dissolved in water and depending on the concentration and supercooling growth often proceeded in a helical fashion.

Discussion and Conclusions

The conclusions which can be drawn from our results are summarized below.

1. At bath supercoolings between 0° and 20 °C, the growth rate of ice cannot be described by one single functional dependence of V on $(\Delta T)_b$. A sharp discontinuity in the variation of the growth rate at bath supercoolings between 9° and 12 °C separates two growth regimes: a regime at bath supercoolings smaller than 9 °C, within which the growth rate varies approximately with the square of the bath supercooling; and a regime at bath supercoolings larger than 12 °C, within which the growth rate varies approximately linearly with the bath supercooling. Our observations suggest that the discontinuity in the variation of the growth rate at bath supercoolings between 9° and 12 °C is due to the variation of the growth mode of ice in water. Our observations and those made by HALLET[25] showed that at supercoolings between 0° and about 8 °C the growth mode of ice in supercooled water varies in a systematic manner with supercooling. At supercoolings larger than about 8 °C the growth mode does not change any further. At these supercoolings an assembly of a larger number of dendrites is formed who thermally interact with each other. Due to the fact that the growth rate of ice crystals is primilarly controlled by the dissipation of latent heat from the tip of the growing dendrites it may be conceivable to assume that the growth rate of an ice crystal assembly is smaller and follows a different growth law than the growth rate of individual dendrites which do not thermally interact with each other.

2. An inspection of Fig. 6 shows that in dilute aqueous solutions the growth rate of ice is approximately the same as that in pure water. As the concentration of the solute in the bulk increases, the growth rate of ice in most solutions is reduced progressively below the one in pure water. It could be argued that this reduction of the growth rate is due to the fact that the thermal diffusivity has a smaller value in solutions than in pure water. Values for the thermal conductivity and for the density and specific heat of solutions (standard handbooks) show, however, that at solute bulk concentrations up to 10^{-1} moles liter^{-1} the effect of solutes on the thermal diffusivity is practically negligible and cannot explain the observed strong reductions of the growth rate of ice. The reductions of the growth rate can, however, be understood if one considers that the concentration of solute at the growing ice interface deviates from the concentration in the bulk. This is due to the fact that at the ice solution interface most of the solute is rejected due to its very low solubility in ice. Consequently, as the solute concentration at the interface increases, the local equilibrium freezing temperature is lowered and the interface supercooling, which is the driving force for growth is reduced. A comparison between Figs. 4, 5, and 8 shows that at bulk concentrations larger than 5×10^{-2} moles liter^{-1} the reduction of the growth rate of ice in solutions below the one in pure water reflects in a systematic manner the freezing point lowering effects which are associated in a stagnant system with insufficient transport of solute by diffusion away from the growing interface.

The behavior of solutes which are ionized in solution can be understood on the basis of their hydrating and water-structure breaking action. This action of the solute ions is due to their electric field in which water molecules are oriented and due to their misfit into the water structure. In solutions of large, structure breaking anions such as Cl^-, Br^- or I^-, or in solutions of large structure breaking cations such as Cs^+, the difference in hydrating action between

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[27] H. R. PRUPPACHER, J. Glaciology, in print.

the strongly hydrating Li^+, and the weakly hydrating Cs^+, and between the strongly hydrating F^- and the weakly hydrating Br^- shows up clearly in the equilibrium freezing point depression which is larger for LiCl and LiBr solutions than for CsCl and CsBr solutions, and larger for CsF than for CsBr solutions. A comparison between the equilibrium freezing point depression (Fig. 8) and the growth rates of ice in solutions (Figs. 4, 5) demonstrates the close and systematic relationship between these quantities. The comparison shows that the growth rate of ice is stronger reduced in a solution of large equilibrium freezing point depression than in one of small equilibrium freezing point depression. In NH_4Cl and NH_4Br solutions the growth rates of ice are approximately the same. Neither the growth rate of ice nor the equilibrium freezing point depression shows any significant tendency in potassium solutions. In solutions of salts with a common, strongly hydrating cation such as Li^+ and Na^+ or a strongly hydrating anion such as F^-, the hydrating action of the ion becomes more pronounced the more the water structure is broken by the component ion. Therefore, the equilibrium freezing point depression is larger for LiI and LiBr than in LiCl bulk solutions, larger for NaI and NaBr than for NaF bulk solution, and larger in CsF than for NaF bulk solutions. Considering this variation of the freezing point depression one would expect that the growth rate of ice is stronger reduced in LiBr than in LiCl solution, stronger reduced in NaBr than in NaF solution and stronger reduced in CsF than in NaF solution. A comparison of Fig. 8 with Figs. 4 and 5 shows that such relationships are not observed for these solutions. The reason for this lies in the fact that the equilibrium freezing point depression at the ice-solutions interface depends also on the rate of increase of the solute concentration at the growing and therefore advancing ice-solution interface. The stronger the water-structure breaking action of one ion of the ion-pair in solutions is, the larger is the rate of diffusion of the ions away from the interface and consequently the smaller is the rate of increase of the solute concentration at the interface. Therefore the growth rate of ice is less reduced in LiBr than in LiCl solution, less reduced in NaBr than in NaF solution and less reduced in CsF than in NaF solution.

3. In solutions of certain salts, in particular in solutions of fluorides of concentrations between 10^{-4} and 5×10^{-2} moles liter^{-1}, the growth rate of ice was raised over and above the one in pure water. This result is completely unexpected in the light of our discussion given above. It confirms, however, an observation made more than 30 years ago in NaCl solutions by Tammann and Büchner[9] whose results, obtained with a much less precise experimental set up, have up to the present time always been doubted by scientists. The growth rate enhancement must be explained by a specific action of the solute at the interface other than the freezing point lowering action discussed above. It could be explained on the basis of an increased rate of heat dissipation from dendrites with branches whose radius of curvature at the tip is smaller in solution than in pure water. Indeed, we observed that even in solutions of small solute concentration width and thickness of

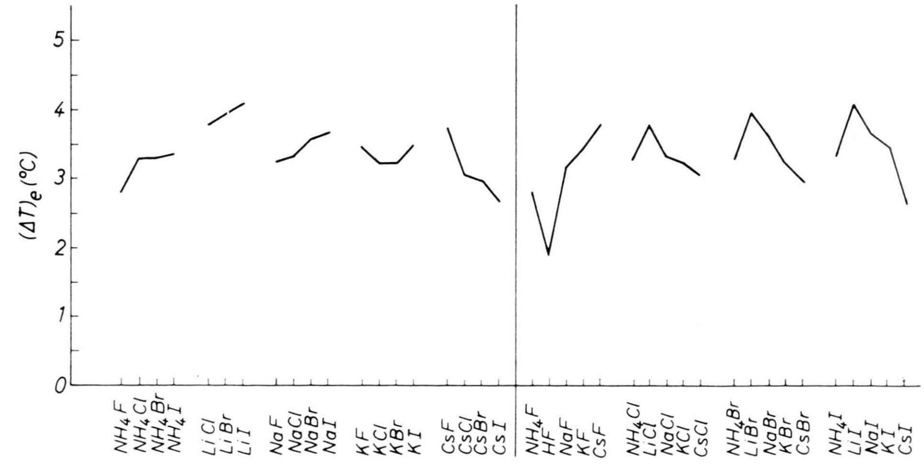

Fig. 8. Equilibrium freezing temperature depression of various 1 molar aqueous solutions.

individual dendrite branches were less in solutions than in pure water. The mechanism responsible for this effect is not understood. It may involve a specific adsorbtion of the solute ions on the growth spirals of screw dislocations emerging on the crystal faces such that the incorporation of water molecules are hindered everywhere safe at the growing tip of the ice dendrite.

Acknowledgment

I am much indebted to Professor M. Neiburger for his continued encouragement and his interest in the research presented in this paper. I also want to acknowledge the very fruitful discussions I had with Professor C. T. O'Konski, Department of Chemistry, University of California at Berkeley.

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Meßverfahren zur Bestimmung der Kristallitverkippung in dünnen Aufdampfschichten

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In the present paper a method is described, which permits the measurement of the crystal misorientation in thin films by means of electron diffraction. In some special cases it was possible to make use of other techniques to determine the degree of misorientation and to compare the values obtained by the different methods. The result of this comparison is a consistency of the measuring values within the limits of about 10%.

Bei der Untersuchung von Epitaxie-Aufdampfschichten sollte im Gegensatz zu vielen bisher veröffentlichten Arbeiten versucht werden, den Orientierungsgrad der Schichten quantitativ zu erfassen, um den Einfluß der Aufdampfbedingungen auf die Güte der Orientierung möglichst genau zu verfolgen. Dabei konnte beispielsweise gezeigt werden, daß bei Spaltung der einkristallinen Unterlagen in polaren Dämpfen (z. B. H_2O) und nachfolgender Bedampfung der Spaltflächen, die Güte der Metallschicht-Orientierung eine oszillierende Funktion von Unterlagetemperatur und Aufdampfrate ist[1].

Die bisher angewandten Verfahren, wie z. B. die Beobachtung von Orientierungsänderungen [Übergang einer (111)- in eine (100)-Orientierung] oder die Festlegung der Übergänge vom reinen Ringdiagramm über ein gemischtes Ring-Punktdiagramm zum reinen Laue-Diagramm in den Elektroneninterferenzbildern (vgl.[2]) erwiesen sich als nicht besonders geeignet, zumal unter experimentellen Bedingungen, die zu reinen Punktdiagrammen führen, praktisch keine Änderungen im Interferenzbild bei Variation der Aufdampfparameter sichtbar sind. Wie sich zeigte, heißt das aber nicht, daß in diesem Bereich die Güte der Orientierung nicht mehr von den Herstellungsbedingungen der Schicht beeinflußt wird.

Zu Beginn der Untersuchungen stellte sich die Frage, welche Größe besonders geeignet ist, die Qualität der Schichtorientierung zu definieren. Bekanntlich bestehen Epitaxieschichten, von Sonderfällen abgesehen, aus mehr oder weniger verkippten, mosaikartig angeordneten Einzelkristalliten. Es liegt nahe, den Betrag der Kristallitverkippung als Maß für die Orientierungsgüte zu verwenden. Bei niedrigen Unterlagetemperaturen, die zu schlecht orientierten Schichten führen, kann man die azimutale Verwackelung um die Foliennormale den Beugungsbildern entnehmen und den Einfluß der Aufdampfparameter auf die Orientierung quantitativ verfolgen (vgl. z. B.[3]). Verwendet man höher aufgeheizte Kristalle als Unterlage, so wird der Betrag der azimutalen Verwackelung außerordentlich klein, so daß genaue Messungen nicht mehr durchführbar sind. Im Laufe der Untersuchungen zeigte sich aber, daß der Betrag der Kristallitverkippung um eine *in der Schichtebene* liegende Achse sehr empfindlich auf Änderungen der Aufdampfparameter reagiert und darüber hinaus wegen der größeren Beträge genau

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