

## GENERAL DISCUSSION

THE final session of the Symposium took the form of a general discussion under the chairmanship of Dr J. W. Glen.

J. W. GLEN: This final session of the Symposium is a general discussion. It is, therefore, an opportunity to discuss matters on the Physics and Chemistry of Ice. They may be matters which were cut off in the middle of a good discussion, or they may be things which people wished they had asked immediately after a paper, or which on more mature, scientific reflection they think they would like to ask. I hope there will also be a chance for a discussion which looks back over where we have got to in improving our understanding of the physics and chemistry of ice, which takes stock of the advances made in the last five years, and which then looks forward in an attempt to see on what it might be worthwhile focusing our attention in the future.

We have in this meeting people with very varied backgrounds of experience and knowledge of different theories and techniques, and it may well be that suggestions from one group can indicate a useful line for another. There are not so many people working on ice that we can afford to work in isolation and keep good ideas to ourselves just in case we have a chance to use them in the future. I am sure that most research groups are relatively small and it is through a meeting like this that we realize that we are part of a larger group looking at this very interesting substance in breadth.

As time proceeds, I may suggest that we move to a different topic so that we do not spend all of our time in one particular area, but I hope to give an adequate time to anything which people want seriously to discuss. Having said that, is anyone wishing to start and raise some questions?

N. W. RILEY: A large number of people (I have found, in conversation) feel that a lot of very interesting information was put over by Dr Rice but, as he said, the spread of our ability is such that we cannot appreciate just what he has done. Perhaps if he could explain further in written answer to this (as he is not here), or maybe Dr Whalley could explain to us what Dr Rice seems to be seeing. In other words, what are the salient differences between the amorphous solid and the ice Ih?

GLEN: Dr Whalley, could you give your views? I think Dr Rice said, correct me if I am wrong, that he did *not* have evidence for a large fraction of broken bonds.

E. WHALLEY: That's right! He thought he had but he changed his mind subsequently; he published a statement which he has now withdrawn.

GLEN: By an appreciable number he means per cents, I think.

WHALLEY: 10 or 12%.

GLEN: That is to say, each water molecule is connected, by and large, to that sort of accuracy to four other water molecules by hydrogen bonds.

WHALLEY: As far as one can tell. These hydrogen bonds are a little longer, but not very much longer, than in ice Ih. From the neutron diffraction and X-ray diffraction, the angles are appreciably different, almost certainly. There is a great deal of distortion in the bond angles not much distortion in the bond lengths. The bond angles are a little bit broader, but there is a slight spread in the bond lengths, apparently, in the infrared spectrum for example. But there is a big spread in the bond angles.

GLEN: Do we know anything about density?

WHALLEY: There are supposedly two kinds of amorphous ice according to Rice. There have been a number of others reported.

GLEN: For example, as Dr Johari has pointed out, this is all different from glassy ice.

WHALLEY: Rice claims to have made two kinds of ice. One is high density which as far as I know he has made only once and which he has not been able to reproduce. Then there is the ordinary amorphous ice with which we are all readily familiar. He has, of course, made this many times.

GLEN: The density of that?

WHALLEY: Not much different from ice Ih.

GLEN: Although, of course, if it were more like the liquid, one might expect it to be more dense.

WHALLEY: I could not speak with authority. Maybe some per cent, I do not know.

GLEN: Rice also suggested, did he not, that this high-density form, which he got when he happened to try a single copper crystal substrate, might bear some relation to the structure of a high-pressure phase of ice. It occurs to me that it might be a good idea to try depositing amorphous ice on substrates of the kind which L. F. Evans (1967) used when he found that you could nucleate the high-pressure phases of ice outside their range of stability using these things. I don't know whether this is a suggestion of some interest. I mentioned this to Dr Rice last night and he seemed to think it might be worth thinking about.

RILEY: If you could clarify a point for me here. The temperature at which I thought Dr Rice was looking at ice Ih seemed to me to be in that part of the phase diagram where we would be looking at ice Ic.

GLEN: Well, ice Ic is not at present thought to be stable anywhere; it is in that region where, if we had had a high-pressure phase and it had transformed, it might have got to ice Ic.

RILEY: So, despite the temperature, he was definitely looking at ice Ih.

WHALLEY: If he devitrified or crystallized his amorphous ice by just heating it, then almost certainly it would go to ice Ic, but the measurements on "amorphous ice" are all on the amorphous phase; whether they relate to the hexagonal or cubic phase is hard to tell. Essentially all the properties you use are identical for hexagonal and cubic, or very nearly identical, if not exactly the same.

In amorphous ice there are probably available, one does not know, rings other than six-membered rings; there are only six-membered rings in crystalline ice Ih. The problem is, there may well be five-membered rings, and rings with four, seven, or eight members, as occur in other high-pressure phases, but nobody really knows.

GLEN: Not only high-pressure phases, but low-pressure phases if one counts the clathrates which have five-membered rings.

J. E. BERTIE: I would like to comment on the densities. The low-density form has a density of  $0.93 \text{ g/cm}^3$  and the high-density form has a value of  $1.19 \text{ g/cm}^3$ . I am absolutely certain that Rice would agree that the speculation that the high-density form might be a distorted ice-II structure is simply based on the fact that its density is comparable with that of ice II.

I think the important things to keep in mind with amorphous ice are the experimental facts. With ice Ih you have high peaks in the X-ray radial distribution function at the

neighbour distances; a strong peak at the nearest neighbours at 2.75 Å, another well-defined peak at the next nearest neighbour, and so on. In amorphous ice, the nearest-neighbour peak, at 2.76 Å, seems to be just as sharp as that for ice Ih, suggesting that the range of nearest-neighbour distances is very similar to that of ice Ih. But the second nearest-neighbour peak is much broader and when you get out to third and higher nearest neighbours the peaks tend to get very broad and lost. So, it is very much a picture of short-range order, at least in the radius of the atoms around a given atom. As you get out beyond second neighbours, things get very fuzzy and I think it is true to say that we have no knowledge of what happens.

GLEN: Of course, one of the troubles is that as soon as something is known not to be stable, there are inherently an infinity of possibilities for what it might be. There is one stable form; there is an infinity of non-stable forms. So that the fact is that Rice has two different amorphous ices and that Johari has pointed out that neither of them fit with what one might expect for ice cooled to a glass.

Let us not forget that solutions, aqueous solutions, can be frozen into glasses, even, I think relatively dilute solutions of some of those things containing freezing suppressants such as are used by cryobiologists (the low-temperature microscopy people in biology). You can get glassy ice in that way, although it has got impurities in it, and presumably this might have quite different properties again. I imagine Dr Johari would expect it would; perhaps he knows it does?

G. P. JOHARI: I expect that it would.

There is one more difference between hexagonal ice and amorphous ice, and that is in the thermodynamics energy functions, heat capacity, entropy, and enthalpy of ice. It seems also evident that when vitreous ice or amorphous solid water (the low-density form) is heated to 134 K its heat capacity rises by about the same amount by which the heat capacity of hexagonal ice rises at 273 K when ice is melting. So, the amount of energy taken at the melting point is about the same as the amount of energy taken when vitreous ice is brought into the molten form before crystallizing into cubic ice. This, of course, creates problems of reconciling the entropy of vitreous ice with the entropy of fusion of hexagonal ice.

GLEN: Do you know if anyone has done work on glassy aqueous solutions?

JOHARI: Yes. Professor C. A. Angel at the University of Purdue at Lafayette has been studying the glass transformations of aqueous solutions of zinc chloride, potassium nitrate, and glycerol. We have ourselves studied mixtures of glucose and glycol in water. They all show a glass transition in their differential thermal analysis curves.

GLEN: Do we know if any work similar to that of Rice has been carried out on these materials?

JOHARI: The spectroscopy has not been done, but there are certain doubts whether the structure of water when acting as a solvent is the same as the structure which pure water would be expected to have if supercooled to the glass-transition temperature.

GLEN: Does that apply both to the salts and to those organic substances which appear to suppress freezing by condensing onto any potential freezing nuclei? One of the organics was reported as being in the bodies of Antarctic fish which survive at temperatures at which one would expect them to freeze—which is Nature having done the job already. Such materials are well known to the biological electron microscopists because they put them into their samples deliberately so that cells will not suffer dendritic damage when cooled, but instead the water goes glassy. (I was invited to give a paper to a low-temperature biological microscopy conference earlier this year and I discovered that this is what they think of as being the important part of ice physics.)

M. R. BLOCH: Has the viscosity of glassy ice been measured as the temperature changes?

JOHARI: As far as I know it has not. The viscosity of water has been measured down to  $-20^{\circ}\text{C}$  in the supercooled state, however.

GLEN: One suspects that the glassy ice, like the amorphous ice, might be very rigid, very hard to deform. Interestingly, the electron microscopists have to cut sections of this material with a microtome so they might know something about this.

BERTIE: I would like to make a semantic point about vitreous ice: What do we call what? Rice called his material "amorphous solid water", I have always called it "vitreous ice", and synonymous with that "glassy ice". These are the terms, it seems to me, we generally use for the non-crystalline form obtained when one condenses from the vapour. What, then, do we call the hypothetical phase we get when we supercool water to the point where it reaches the glass transition?

GLEN: I hope you would not call something glassy which had not passed through a glass transition.

JOHARI: I agree with Dr Glen. Unless a material has undergone a glass transformation it should not be called a glass. There are at least five names which have frequently been used in the literature to describe the vitreous or non-crystalline forms of water and certain terms are in danger of being contradictory. Take "vitreous ice" as an example. One implies that "ice" is crystalline, so to use the term "vitreous ice" is equivalent to saying a "vitreous crystalline material"!

I have had a suggestion made to me by an editor who crossed out the phrase "amorphous solid water" and replaced it with "vitreous ice" arguing that the name of the substance is derived by its usage—this was a British editor so I suppose that this must be right!

GLEN: I find it difficult to counter that argument, but I must say that it sounds a very strange ruling. It is important that we try to develop a consistent usage.

R. W. WHITWORTH: I would like to extend this discussion of the nomenclature of amorphous or non-crystalline ice. We have been talking up to now about things which are rigid. There is, of course, another transition from ordinary crystalline ice to things in which molecules can move more easily, ultimately, of course, to liquid water. But what about intermediate states? I think that one might draw attention to the boundary layer between crystalline ice and liquid water. How do the molecules behave in that layer, and, if one can get a region of such material as, perhaps, at a dislocation core, what ought it to be called?

GLEN: I do not see an army of hands going up to answer this question. I suspect therefore that anyone who writes on this subject must be very careful to explain how they are using the terms—that is the best message we can give at the moment.

J. L. KASSNER: I would like to speculate upon the molecular processes that Dr Whitworth's question is seeking to examine. I would suggest that the liquid state has a structure which is clathrate-like with five-membered rings. This structure could propagate almost indefinitely but not have any crystallographic order. It would be full of cracks and crevices where most of the bond breaking and making is probably taking place.

We have carried out some modelling on a model similar to this if you have some way of "freezing-out" the intermolecular vibrations and allowing the clathrate to grow to some maximum extent. It is possible for this structure to take in a great deal of strain energy without making the transition to ice. In fact, for perhaps 120 molecules in the structure, we had seven or eight bond energies contained in the strain energy incorporated in the bonds. One can envisage the ice transition as taking place when a bond breaks. The shock involved

in this breaking could produce a chain reaction in which a number of bonds are broken, the unit cell forms, and the transition takes place.

Now, in the glassy states which we are talking about, the states can be maintained providing that one has a way for removing the vibrational energy or the energy that is tied up in the internal degrees of freedom. On the other hand, if the transition is made from a glassy to a real ice state, then you will expect very much the transition that you have from the liquid to be solid.

GLEN: Except, of course, that at those temperatures it goes, experimentally, to the Ic form instead of Ih.

N. K. SINHA: On behalf of glass physicists, I think I should make one comment. Twenty or thirty years back we used to define a "glass transition temperature" in the case of ordinary (silica) glasses. Now general experiments by different authors have shown that nothing alters at this "transition"—it depends on the experimentalist concerned. So now we tend not to refer to a "transformation" but rather a "so-called transformation".

GLEN: Is this merely a question of time scale? I remember Marcus Reiner referring to the "Deborah number" in this context. Old Testament scholars will see the connection.\*

SINHA: Yes, it was just a question of time.

J. HALLETT: I think we have to be a little bit careful here and think about the so-called glass transition in terms of a real experiment. One way of doing this is to measure a crystallization velocity over the whole range of supercooling. In the case of water one can measure this crystallization velocity down to about  $-20^{\circ}\text{C}$  or a little further if one is more careful. The velocity increases dramatically as the temperature falls, reaching *c.* 1 m/s at the largest supercooling reached. But with the glass solutions, such as sodium thiosulphate or sodium acetate, the changing velocity can be measured very well as a function of temperature. At first, as the temperature falls, the crystallization velocity increases roughly as the square of the supercooling, then there is a broad range of temperature through which the velocity is constant (about 20 or 30 deg). The velocity then drops dramatically to a low value. This happens, typically, at about  $-60^{\circ}\text{C}$ .

On the other hand, one can do another kind of experiment in which one forms a glass from the liquid by rapid cooling to a low temperature. If, as it warms up, no crystallization is observed, it is evident that all nucleation processes are suppressed in the time scale of the experiment. In addition one can put crystals into the liquid at various temperatures and see if they grow. I think that these techniques can give us experimental handles on the physical processes which are occurring, either through growth or nucleation, because the viscosity, which really goes into both, is a macroscopic parameter and influences each of them in a slightly different way.

S. A. RICE [written contribution]: I apologize to my fellow conferees that the commitment to another engagement made it necessary for me to leave the meeting early so that I could not participate in the final session. I am grateful to the Editors for the opportunity to add this comment.

I am pleased that despite the short time available for the presentation of my paper and the large amount of data presented, the several commentators seem to have apprehended very well what I was trying to say. Almost all of the questions raised in the final session are answered by data tabulated or discussed in the paper, so these will in large part be resolved when the printed text is available to everyone. For that reason I will only make the following very few remarks:

\* Judges v. 5. Literal translation of the Hebrew: The mountains flowed before the LORD, as given by Authorized Version, marginal reading.

I do not believe that there is any significant number of broken hydrogen bonds in low-density amorphous solid water, and that the destruction of long-range order comes about via the existence of a distribution of O—O—O angles about the tetrahedral values  $109.5^\circ$ . It is very difficult for me to quantify the level at which broken hydrogen bonds can be excluded. It is my opinion that it is significantly less than the 10 or 12% mentioned by Dr Whalley, probably by at least an order of magnitude.

The interpretation of the structure of low-density amorphous solid water which I have put forward is strongly grounded in an analogy with the relationship between amorphous and crystalline silicon, as is explained in the text of my paper. As to the high-density form of  $\text{H}_2\text{O}(\text{as})$ , Dr Whalley is correct in that we have observed this material only in X-ray diffraction, and only once. Unfortunately, the data analysis followed dismantling of the setup, and we have not yet gotten back to diffraction studies. I hope to do that soon. The suggestion that high-density  $\text{H}_2\text{O}(\text{as})$  is related to one of the higher crystalline ices in a fashion similar to that described for low-density  $\text{H}_2\text{O}(\text{as})$  and ice I is, as Professor Bertie remarks, intended to be suggestive. Aside from the logic of parallel construction and the similarity in density with ice II and ice III, there are not now data available to support this conjecture. As remarked by Dr Glen I do believe that use of different substrates (other than oriented single crystal Cu) for deposition of  $\text{H}_2\text{O}(\text{as})$  is a very good suggestion and I hope to undertake such experiments in the near future.

Finally, a word on the relationship between liquid water and low-density  $\text{H}_2\text{O}(\text{as})$ . I believe that the possibility that these are closely related remains plausible despite the arguments advanced by Dr Johari. As mentioned in a comment elsewhere in this Symposium, we have observed that thin films of low-density  $\text{H}_2\text{O}(\text{as})$  remain stable long enough at 160 K to enable recording of an infrared spectrum. I suggest that if very rapid heat-capacity measurements are made, the heat capacity of  $\text{H}_2\text{O}(\text{as})$  will be found to be very close to that of ice I up to 160 K. Possibly, if measurements could be made on a millisecond time scale, even higher temperatures could be reached. If these conjectures are correct, the objection by Dr Johari concerning the entropy anomaly and the consequent inferred behaviour of the heat capacity of amorphous solid water *vis-à-vis* that of ice I will be removed. Professor Austin Angell and I plan to make measurements of the heat capacity of very thin films of amorphous solid water in the very near future to test this idea.

**GLEN:** I think we have had quite a good discussion on this particular topic and perhaps we might move on to something rather different. I have asked two people to think around topics that they might suggest to us and I will ask the first of these, Dr Bilgram, if he has anything he could suggest to us as of interest in the areas in which he operates.

**J. H. BILGRAM:** One area is that of the dielectric properties of ice, in particular the mobility of point defects. From the experiments it turns out that Bjerrum defects and ion states (whatever we think about the nature of ion states) have the same mobility at  $0^\circ\text{C}$ . Traditionally it is assumed that a water molecule has to rotate for the movement of a Bjerrum defect, whereas a quantum-mechanical tunnelling process is involved in the ion movement. In the light of the experimental data now available I find it very hard to believe that picture. Perhaps we should begin discussing this topic.

**M. HUBMANN:** Formerly, the number of ions in ice was estimated to be very low and so a very efficient process had to be invented for their movement. In so far as we are sure that the number of ions is large, we no longer need such an explanation; we can introduce a hopping process for the ions too. There is, however, another point of view; it may be that a great many of the ions are captured by some traps (whatever the nature of these traps may be)—we may not have as many mobile ions as we derive from the dopant concentration. If we have

fewer mobile protons than we imagine then we appear to see a higher mobility. I do not think that, at the moment, any conclusions can be drawn definitely.

GLEN: Yes, we have heard on one or two occasions during this past week about the possibility that ionic defects may couple rather strongly with Bjerrum L-defects. Dr Bilgram suggested that himself; it came out as one of the models which we could not distinguish as either better or worse in the paper which Camplin, Paren and I presented. It was suggested, though nothing more, by the orientation which water molecules adopted when approaching an ion in Plummer's paper. I think we must ask the question: if this is happening on a large scale, how does it affect the picture? If, of course, it happened at one temperature range and not at another, then we ought to see one transition that I suspect we have not seen (though perhaps we have seen it and failed to identify it). If, on the other hand, the association is pretty general through the temperature region, then there are probably two or three possibilities: the ions might be the mobile element, those few remaining ones as Dr Hubmann suggests, or the ion-Bjerrum defect pairs may be the mobile element which is what Dr Bilgram suggests, or the ions may be moving without the L-defects and the attraction between them may not be as big as we thought.

Someone should try to sort out which suggestion is correct.

HUBMANN: There are other defects which can act in the same way. I am reminded of the vested vacancies proposed by Kopp in earlier times, I think we should keep them in mind especially when we think of the large number of vacancies which are present, as has been shown by Eldrup (1976) and reported by Mogensen and Eldrup in this Symposium.

GLEN: Of course, the thing which we naturally think of as going to vested vacancies is the D-defect rather than the ions or the L-defect. Perhaps they all do; perhaps Mogensen and Eldrup have enough vacancies for everybody.

J. G. PAREN: This question about the relative mobilities of defects is a tricky one and I can only offer one piece of help. Camplin, Glen, and I (Camplin and others, 1978) have tried hard to analyse the data which we have on HF-doped ice. We are happy to give anyone access to this data because we are not sure what the way ahead should be. The experiments have been done, but no one is now suggesting vital, new dielectric experiments. If we cannot suggest new experiments all we can do is produce new data on different dopants such as HCl (of which we have heard quite a lot at this conference) and try to get one uniform analysis based on present ideas. Such an analysis should presumably be done by one laboratory or group who could take all the data on all dopants.

We often compare the dielectric behaviour of ices with different types of impurity in them—many impurities have been chosen, not just HF or  $\text{NH}_3$ . Yet, if one looks at the form of the data, it always looks similar; what the dopants are does not seem to matter, the end result turns out to be the same. I think it is time that all these data were put together and analysed afresh. Then perhaps we would find what is moving; what the mobilities are. But until that is done, I think we are in the dark.

GLEN: Do we need to put these data together with those on vacancies?

PAREN: Yes, without any doubt at all.

GLEN: Is that a feasible thing to try?

M. ELDRUP: I think that you can get some information about the vacancy formation energies from the migrating vacancies of our experiments, but if you have to include all the interactions between vacancies and the well-known defects, then it becomes a tall order to expect all these parameters from one set of experiments.

JOHARI: How sure is one that, by doping or contaminating ice with HF or some other material, one is obtaining a homogeneous mixture and that one is substituting oxygen by HF? Is there any evidence that this is so?

I am aware of two papers that seem to suggest that contaminated ice is actually heterogeneous, is actually in an energy state which is higher than that of pure ice, and is tending to become purer and purer by losing its doping material towards the surface. Nakamura and Jones (1973) published some figures in which they examined the concentration of some dopant material as a function of the radius of a cylindrical ice specimen and as a function of time. They found that the radial distribution was such that there was a minimum in concentration at the centre of the cylindrical axis, this minimum decreased with time.

There is other evidence, if I remember correctly, from the Munich group which showed also that contaminated ice tends to lose its contaminant with time by moving the impurity towards the surface. Now this raises an important point: doped ice is a metastable material, if it were stable then there would be no concentration gradient within it and the concentration gradient could not change with time.

If you are dealing with HF-doped ice at different times you would anticipate that the dielectric properties of such a material would change because the concentration distribution changes.

KASSNER: There is an experimental problem in all ice physics of which we need to be aware. De-ionized water may not be best for specimen preparation because it contains impurities which are organic in nature. These organic impurities may scavenge ionic impurities as time goes on. A more elaborate purifying technique may be needed. Although these organics might not have a direct influence on the conductivity immediately after preparation, they may make their way to the surface as some surface-active organics do, and they may scavenge the ionic dopant which has been added to the specimen before or after freezing.

C. JACCARD: We have discussed the isolated ion and the ion bound to a D-defect. But there is a third possibility, especially in a crystal in which the Bjerrum defects are in the majority. This third case is an ion with a diffuse cloud of D-defects in the shape of a Debye layer, it might have different properties from the other two models. It might look like a polaron (an electron coupled with a deformation of the lattice). It is quite different, of course, but it would bring some difference as regards the mobility for example.

Concerning the position of the  $F^-$  ion in the lattice, the hypothesis whether it is substitutionally or interstitially incorporated is still not established. Bilgram has done a lot of work on this incorporation of HF, but I think another experiment is needed. We are planning a channelling experiment in an attempt to see where the  $F^-$  ions are sitting, but there is another, better method—it uses the extended X-ray absorption fine structure and this can indicate the environment of specific isolated impurities, whether incorporated in either crystals or amorphous substances. I do not know whether anyone here can make such measurements, but this may be one experimental direction.

P. CAMP: Let us back off from the details of the defects and ask a question. Are we all in agreement (and I assume that we are) when one does not ask about the details of the conductivity process in ice? Are we not in fundamental agreement on the basic idea of the Jaccard theory of two processes in series which give rise to the conductivity and two processes in parallel which give rise to the dielectric constant? These two processes are related to the microscopic model over which we may haggle.

GLEN: Are we in agreement? Or do some people want either to say that the series-parallel process is in question or that the two processes are in question? For example, might it be four processes?



The vested vacancy might be there as well as the free electrical point defects giving another component to the same term. The basic structure would still be there but we would have more terms to play with or, if you like to put it another way, we have further things to find out before we understand.

BLOCH: I would like to ask whether the dielectric changes are such that one can see this by comparatively coarse optical methods. Comets are made almost entirely of ice according to Whipple (1951) and I think this theory is accepted. It is possible that the optical changes in ice are large enough to establish the nature of the ice in comets. This ice might be crystalline or glassy, it might contain doped ices as, according to the Whipple theory the ice of a comet contains methane, ethane, ammonia, mixed hydrides (both water and ammonia are hydrides), silicon hydrides, and probably also the hydrides of alkali metals. All these are stable at 10 K providing that they do not warm up. If they do then they begin to react with each other. In other words, it seems that a comet made of mixed hydrides is a store of chemical energy and hydrogen which can be liberated by a slight warming-up. Perhaps the methods of Raman spectra techniques, optical spectra investigations, even of X-ray spectra techniques (we have sufficient X-ray sources in space!) might give us the opportunity to look at the ice in a comet. Is this possible?

GLEN: I do not see a taker. It seems that you have made a daunting challenge. I suspect we have enough difficulty working out what ice does when we know what we have put into it and that we are a little chary of looking at ice that has the sort of composition you have described. Clearly it is a field we should bear in mind.

BILGRAM: I have a question about the out-diffusion of impurities. In HF- and  $\text{NH}_3$ -doped samples out-diffusion of the impurity under investigation can be observed. It is possible to prevent out-diffusion by applying a high vapour pressure of the impurity in question to the ice sample. Hubmann has done such experiments. Dr Gross has reported new results on HCl-doped samples and he did not observe any out-diffusion. Are there additional differences between HCl and other impurities? Does there exist an interpretation? How is HCl incorporated in the ice?

G. W. GROSS: Dr Bilgram's question brings me back to a statement made a while ago, that all impurities appear to behave more or less the same in ice, at least from the dielectric standpoint. That is not exactly true. There are differences but you have to look for them; they are subtle. I am not in a position to answer the question directly, but I can point out a few differences between HCl and HF. The spectra of the two in ice are remarkably similar; I mentioned that in my presentation. However, if you consider distribution coefficients as an expression of the way in which an impurity is incorporated into the solid, then indeed you have some drastic differences between HCl and HF. The distribution coefficient of hydrogen chloride is practically independent of concentration while, as Jaccard and Levi (1961) showed the distribution coefficient of HF is very strongly concentration dependent. Moreover, the distribution coefficient of hydrogen chloride in ice is typically an order of magnitude lower than that of HF (Gross and others, 1975[a], [b], 1977). This suggests that the structural relations of the chloride to the ice lattice are indeed different from those of the fluoride, and this is as far as I wish to go at this point. We do not know what this difference is, and perhaps the method Professor Jaccard pointed out using X-ray absorption fine structure, or even scanning electron microscopy, might be useful for investigating where these impurities actually go. I think we have arrived at the limit of what we can do with dielectric measurements. These, as is well known, are rather non-specific—this is true with regards to other dielectrics as well, not just ice. We use dielectric measurements because we have no better methods, and Dr Johari's point is well taken: we do not know where the impurities are in the ice lattice.

In discussing differences between specific impurities one problem arises, I think, from the fact that only HF has been studied systematically, and therefore we have no way of comparing or of seeing other effects. For instance, the common dopants (admittedly within a narrow concentration and temperature range) can be roughly classified in two categories which I have called, for lack of a better terminology, proton-increasing and proton-suppressing, respectively, implying that one group introduces extrinsic protons into the ice lattice while the other excludes or suppresses them. There is a drastic difference in the static conductivity between these two classes. But there are other, less obvious differences in the dielectric spectrum as well. For instance, if you make dielectric measurements on ice doped with ammonium bicarbonate, ammonium chloride, or ammonium hydroxide you can use stainless-steel guard electrodes. For the first two solutes you get Cole–Cole plots free of all space-charge effects. Moreover, the Cole–Cole plots subtend an arc of better than  $90^\circ$  at frequencies of 20 Hz or higher, down to temperatures as low as  $-100$  to  $-120^\circ\text{C}$  indicating that the Debye relaxation frequency is substantially increased compared to pure ice. For  $\text{NH}_4\text{OH}$  doping, on the other hand, the spectrum is more nearly like that of pure ice, and space-charge effects were present though minimal. Ammonium bicarbonate depresses the Debye relaxation time less than do HCl or HF at comparable concentrations and temperatures. The effect of  $\text{NH}_4\text{Cl}$  on the Debye relaxation time, on the other hand, appears similar to that of the two acids. Von Hippel and others (1974) doped ice with methyl alcohol which behaved like a proton-suppressing dopant, that is, it gave a spectrum very similar to that of pure ice but with a greatly reduced static conductivity. Another dopant of interest is  $\text{CO}_2$ . Years ago we did some measurements with this impurity; not realizing at the time its interest for glaciologists, we did not do a systematic study, however. In an impromptu presentation at the Ottawa symposium I briefly described the spectrum of ice containing a  $10^{-5}$  to  $10^{-4}$  molar concentration of carbon dioxide. The principal dispersion was identical with that of pure ice. The static conductivity was increased by an order of magnitude or so over that of pure ice, and it was only weakly or not dependent of temperature (exhibited a plateau) down to about  $-40$  to  $-50^\circ\text{C}$ , at which point it turned down in the fashion that we have seen from dilute ( $\leq 10^{-7}$  molar) HF ice (Camplin and Glen, 1973) and dilute HCl ice (Gross and others, 1978). Other differences between solutes were pointed out by Von Hippel and others (1974) and by Gross and others (1978).

A. HIGASHI: We are now working with many dopants for ice, not just HF or  $\text{NH}_3$  which introduce electrical defects, but other materials like HCl, NaCl and so on. I am never sure that all of these dopants are always in solid solution except at very low concentrations. Are there any phase diagrams for ice with other materials?

P. CAMP: I believe that Brill (1957, p. 28) has published the phase diagram with  $\text{NH}_4\text{F}$ .

G. NOLL: I would be glad if we clarify what Dr Gross has mentioned about the distribution of impurities in a crystal. Without casting any aspersions on the early measurements of Jaccard and Levi, I think that the art of growing crystals has advanced a good deal in the meantime. Bilgram has done work on the growth and segregation of impurities and I think we now know a little more about the distribution during growth and I think perhaps we can clarify any important differences regarding concentrations.

BILGRAM: It is possible to produce pure water by distillation but this is very difficult and also expensive. We prepare pure water by zone-refining. The total concentration of organic impurities in our samples is comparable to that obtained after distillation with  $\text{KMnO}_4$ . This has been measured by means of gas chromatography in the Electrochemisches Institut of the ETH.

BERTIE: A comment on this which might be relevant if the preparation of pure water is a problem: Brian Conway, who is an electrochemist, said some years ago that the Ottawa water could not be purified by any method except electrolysis followed by combustion of hydrogen and oxygen. They had a lot of organics in the water and all other attempts at purification failed. If water purity is a problem then you might think about electrolysing the water and then burning the hydrogen and oxygen to form water. Conway published this a few years ago (Conway and others, 1973).

GLEN: It sounds as though we are in for a period of drastically difficult specimen preparation.

RILEY: Taking Dr Bilgram's point before last, where he was asking what we know about different impurities, as someone on the mechanical rather than the electrical side, I do not think we have mechanical data in depth as do the dielectricians, but we certainly have data in width; that is, we have a wide range of dopants which have been tested. I am interested in whether doped single crystals of ice will creep faster or slower than pure material. Are they going to have accelerating or decelerating creep curves? Most dopants tested to date have shown an accelerating curve, but if the work which we reported here (Riley and others, 1978) is correct then NaCl as a dopant will produce a decelerating curve.

I am in a cleft stick here because Dr Jones has doped single crystals with HCl and produced accelerating creep curves; I put in NaCl and I think I see decelerating creep. These are not incompatible until we add Gross's observations which suggest that we get the Cl<sup>-</sup> going into the crystal but very little else. The rejection of the Na<sup>+</sup> seems to be very strong so, if just the Cl<sup>-</sup> is going in, Dr Jones and I cannot both be right.

GLEN: Unless your detailed internal structure is different.

RILEY: Is this telling us where dopants are going into the crystal?

GLEN: Is it worth asking Dr Jones how he made his doped crystals, was it the same method as we used?

S. J. JONES: I think essentially the same method, in glass tubes. I would add one comment: although you observe decelerating creep you are still getting very high strain-rates and so the ice may not in fact be that much harder.

GLEN: Did you test NaOH as a dopant?

JONES: Yes.

GLEN: We seem to be moving on to mechanical properties. I did ask Dr Goodman to think around where we have got to in this area.

D. J. GOODMAN: I would like to ask Dr Whitworth what he thinks about basal and non-basal glide in the light of his core theory; is his model able to predict the large difference between non-basal and basal glide? I wonder, from Johari's points about the inhomogeneity of HF-doping in ice, whether the core model is more helpful because with re-orientation at the core the dopant need only go into the core; therefore we need not worry about inhomogeneities in the lattice.

I have another question. What do we think about the role of recrystallization in mechanical deformation and can we separate the effects of fabric formation from dynamic recrystallization?

WHITWORTH: The basic answer to your first question is that we do not have a model. The point that really comes out is that none of the models that have been worked on can explain the speed at which dislocations are observed to move and we are left with the only other possibility—which has not been formulated yet! There is little prospect of explaining why we

get slip on one plane rather than another if we cannot explain slip on the simplest plane. If a suitable model were worked out in detail then it might be possible to explain why one plane differs from another.

One thing is, I think, fairly clear and that is that all the difficulties in explaining dislocation movement on the basal plane apply equally seriously to any plane of the structure, and the sort of features which I discussed would be common to any glide system.

**GLEN:** I suspect the question is: if you have a liquid core and it is reasonably big, why does the Burgers vector matter much?

**GOODMAN:** Why is there a difference between the two systems? We know that the non-basal system is harder than the basal.

**WHITWORTH:** I must insist that I have not put forward a model, and I said that I was forced to a conclusion which is a very dangerous one. It was put up to encourage thought about a problem in the ice system which we really do not know how to think about yet. When we have thought about it we may decide it is not really a workable scheme either and then we have to find some other way of allowing dislocations to move more quickly.

But there is one other thing in connection with these ideas and I think it relates to your second point. That is, in all these mechanical tests we have got to discriminate carefully between the two components which are mixed up in any measurement of a deformation: dislocation density and dislocation velocity. When we are talking about the shape of creep curves and the interaction with obstacles, precipitates, and so on, we are back in the more common areas that one encounters in metals, of dislocations moving past obstacles, hardening, line tension, and so on, rather than in the area of free single dislocations moving through the lattice. If you are doping you have got to be careful which part of the deformation you are affecting: you may be speeding up or slowing down a dislocation velocity, alternatively you may be introducing defects which are obstacles or which are sources of cross-slip and dislocation multiplication.

**GOODMAN:** I think the experiments of Joncich and others (1978) were in the direction we need to take if we are to separate dislocation density effects from velocity effects; if we are going to use mechanical properties at all to examine the relationship of dislocation velocity against stress.

**WHITWORTH:** Those measurements are extremely good at sorting out the way in which velocity depends on stress, but by their very nature, they do not give you the constant of proportionality. If you change from a pure specimen to a doped specimen you lose the constant which you need to know.

**GOODMAN:** The dopant may also change the dislocation density.

**GLEN:** We are pretty sure that most of the ways of introducing dopants do change the dislocation density; is this not true from the Ottawa work, even if you introduce the dopant by diffusion?

**WHITWORTH:** Yes, but it is more serious than that. You can change the dislocation density by adding a dopant and you can observe this by X-ray topography. However, even if you put in a dopant that only affects the dislocation velocity, then, in a mechanical test the dislocation density will adjust itself to a different value from that in a similar test on the undoped crystal.

GOODMAN: Could we move on to recrystallization and its effect on the mechanical properties? Recrystallization has hardly been mentioned in this Symposium.

I would like to draw attention to a deformation map which I showed during the discussion of Dr Baker's paper (Fig. D3, p. 499). Dr Baker talked about the possible creep mechanisms occurring at low stresses. In Cambridge, we believe that creep by diffusional flow will eventually become faster than creep by dislocation glide as the stress is decreased. Diffusional creep is characterized by a linear dependence of the strain-rate on the stress; to my knowledge no experiment has conclusively shown the existence of a linear creep mechanism at low stresses. However, by using constitutive equations derived for other materials (Ashby and Verrall, 1973) we have marked an area on the diagram where diffusional flow might be expected.

On the diagram the line marked with depths is the stress-temperature profile of the "Byrd" bore hole through the Antarctic ice sheet. From the diagram you can see that the upper parts of the ice sheet will be deforming by diffusional creep. The vertical dashed line represents the boundary above which recrystallization effects are likely to be seen (Barnes and others (1971), observed recrystallization in their experiments when the temperature was above  $-8^{\circ}\text{C}$ ). I would like to ask those present who are interested in recrystallization what they think about the effect of recrystallization on creep.

Gow and Williamson (1976) found that the fabric diagram for the "Byrd" core changed from a strong single pole to a multi-pole diagram at about 1 800 m. 1 800 m corresponds to the point where the recrystallization boundary intersects the stress-temperature profile. I would like to ask whether there are any comments on the way fabric develops in the lower part of the ice sheet. Is the multi-pole fabric due to the increased temperature or to the greater strain-rates?

W. F. BUDD: I would like to show a couple of diagrams dealing with this problem which show the compatibility between the stress configuration and the crystallography, for example from our Cape Folger bore hole. We have a stress system at the surface which is longitudinal tension and vertical compression. We get a two-maximum fabric with the maxima tending to be perpendicular to the maximum shear directions (Fig. 1(a)). Figure 1(b) shows a situation in which the vertical compression exists with slightly more extension in one horizontal direction than in the other. The fabric develops with a two-maximum girdle. As we go down through the ice, the horizontal shear becomes more dominant and the single maximum approaches the vertical until there is almost a very strong, single vertical maximum.

Now, what this means is that the ice is growing and recrystallizing, and developing a form compatible with the stress. So, if one starts measurements in the laboratory on ice which is not originally compatible with its stress, then one might expect that if one left it long enough under those conditions, it might develop and become compatible. This is, in fact, what we find with tertiary creep. If one is studying ice, initially in primary creep, that is randomly oriented and one deforms it to the tertiary stage then the ice changes and it does not have the same fabric any more. As a result, we have all tended to look at the minimum creep rate.

I shall now show a diagram (Fig. 2) which shows the flow rates of these samples of ice subject to the horizontal shear stress and what one finds is that under those conditions the shear stress increases very rapidly at the zone where the crystals are well aligned. The diagram shows creep curves and strain-rate-time plots with time along the abscissa, for samples from different depths. The top-most curve shows the strain-rate for the sample where the basal planes are almost horizontal and it is many times larger than the bottom curve which is that of randomly-oriented ice, the other ice samples are from the various other depths. As you can see, these tests have been going on for a long time (over six months) and they take a long time to reach steady-state. What we are finding (these tests still continue—one has been going on

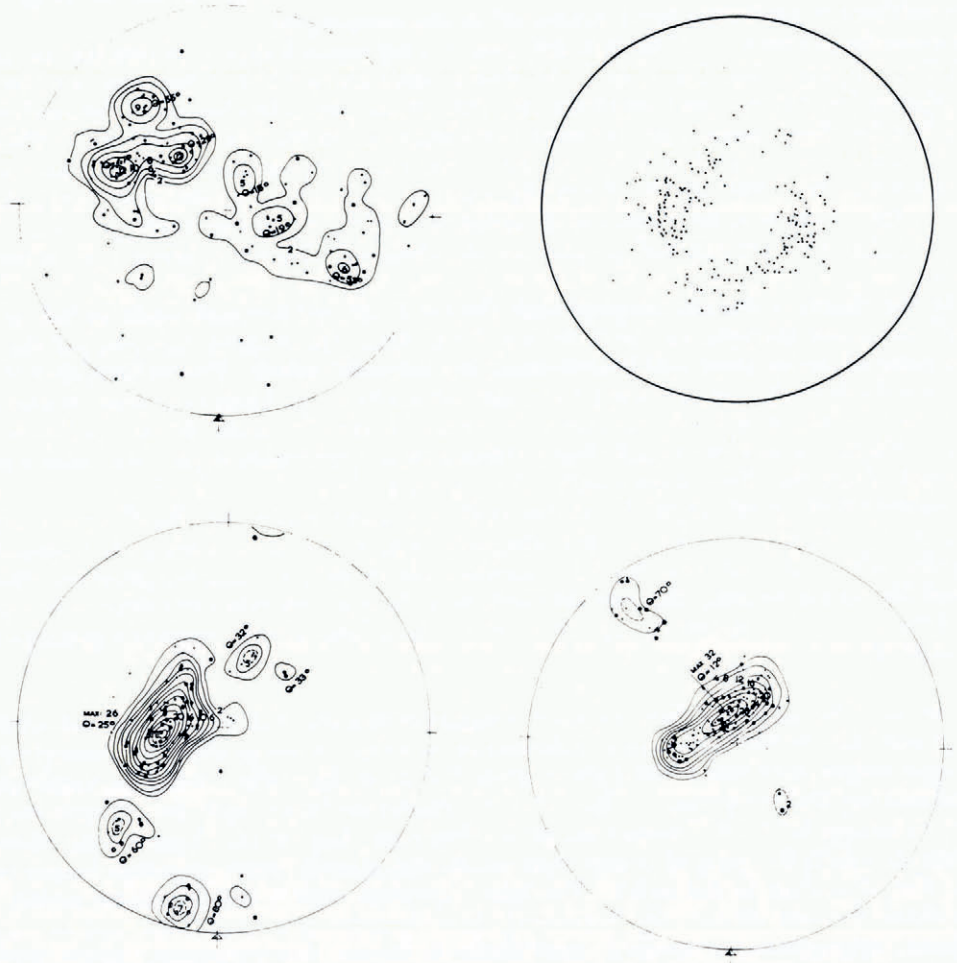


Fig. 1. Cape Folger ice-crystal orientation fabrics from Budd (1972).

- (a) A horizontal section from 30 m depth showing two broad maxima in the line of flow associated with the longitudinal extension with negligible transverse extension.
  - (b) A horizontal section from the edge of Cape Folger where the transverse extension is appreciable compared to the longitudinal extension.
  - (c) A horizontal fabric from 126 m depth showing the one larger broad maximum becoming dominant and orientated closer to the vertical as the horizontal shear increases.
  - (d) A horizontal section from 241 m (where the ice thickness is c. 360 m) showing the dominance of the single broad maximum, centred  $12^\circ$  from the vertical, due to the effect of the increasing horizontal shear.
- The fabrics (a), (c), and (d) were measured by G. Wakahama and (b) by J. Hollin.

for two years now) is that the lowest curves tend to turn up to tertiary, but the top ones are already in tertiary and are tending to creep steadily in spite of the very long time.

The top right diagram (inset on Figure 2) shows the ratios of strain-rates at various depths for randomly-oriented ice. One sees that there is a narrow zone, something like three-quarters of the way down, where ice strains ever so much faster with that stress configuration than any of the other depths. Similar things can be got from other stress configurations like simple compression and so on. I think they all seem to fit this general pattern.

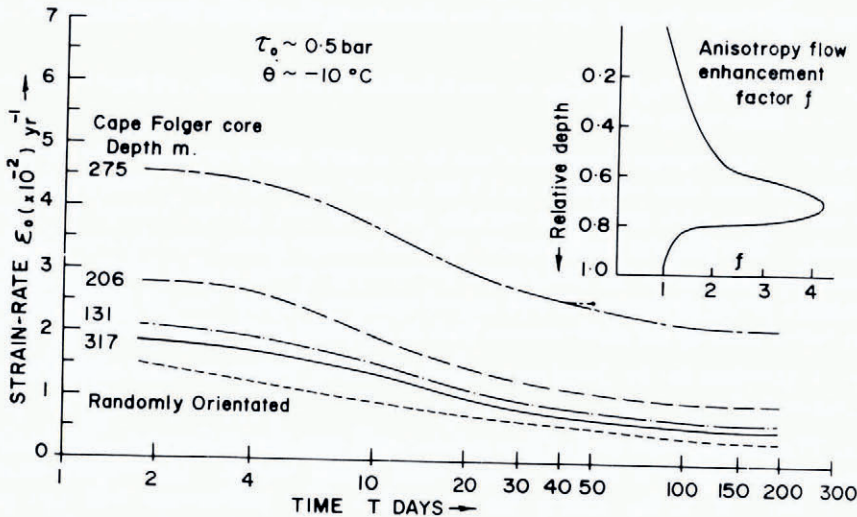


Fig. 2. Cape Folger ice-core shear strain-rates, measured by D. S. Russell-Head. Octahedral shear strain-rates versus time (on a log scale) are shown for simple shear tests on ice in the in situ stress configuration with 0.5 bar octahedral shear stress at  $-10^{\circ}\text{C}$ . The depths of the ice are indicated in metres from 131 to 317 m and results for randomly orientated laboratory-made ice are also shown.

*Inset, the relative strain-rate (with respect to the randomly orientated ice) is shown as a function of relative depth, thus defining a flow-rate enhancement factor depending on the crystal anisotropy.*

GLEN: I think the one moral which we can draw from this is that these deformation maps which sometimes have grain sizes on them may have regions where that grain size just is not stable. I imagine that is so.

Another question which seems to me to come from this is that if you change region on the deformation map (which I think is Dr Goodman's point) this might have some fairly profound effects on a theory. I wonder if this relates to what Lile was doing in that he was attempting to produce a law which would work for the polycrystals of various orientations given what we know about the random orientation. Would this work if one moved across a boundary where one went to a grain-boundary-controlled region?

R. C. LILE: I have made the fundamental assumption that for compatibility between the orientation fabric and the specimen configuration, strain-rate is governed by the resolved shear stress on basal planes. My experiments at low stress and temperature tend to bear out the validity of this assumption. Additional work is under way to investigate the results which could be expected when one moves away from this region of the deformation map.

GLEN: Do we think that if we go to the top right-hand region of Figure D3 (p. 499) that the assumption is no longer true? Is fabric still controlled by where the basal planes are? Dr Goodman is probably as good a person to ask as any.

GOODMAN: There is not a reasonable equation for the recrystallization mechanism.

GLEN: So that is a thing which is still to be worked out. We have identified another thing which looks like a big query mark on the map.

GOODMAN: What I am trying to say is that we are very concerned about a dislocation glide mechanism and that we are putting a lot of effort into understanding such a mechanism. But for the understanding of ice sheets in general, we need also an equation which will tell us how a fabric develops or, having attained a particular fabric, what the strain-rates are.

GLEN: One might have thought this was also important knowledge for the study of temperate glaciers.

GOODMAN: As we saw in Budd's film, at much higher stress the effect of recrystallization must dominate over dislocation effects.

BUDD: That film showed what happens if you have a stress that is too high for a given situation. Other long-term tests that Matsuda and I have done at compatible stress levels and higher temperatures began with randomly-oriented ice with tiny grains instead of crystals with aligned grains. The aligned grains break up into smaller grains but the randomly-oriented grains gradually grow into well interlocked glacier-type grains with a fabric compatible with the appropriate stress situation. In the experiments we carried out we ended with the two-maximum fabric exactly the same as one finds in the field under the same stress situations.

P. DUVAL: A question for Dr Goodman: why is there no region on your map where creep is recovery controlled?

GOODMAN: We assume from what Glen said in 1968 that the dislocation glide controlled by proton re-arrangement is a slower process than climb control. The crucial experimental evidence is that HF-doping affects the dislocation glide mechanism but does not affect diffusion rates—if it did affect diffusion rates we would not be able to rule out diffusion control of climb.

GLEN: But is recovery not, in fact, involved in that top right-hand corner we have been talking about?

GOODMAN: We think that in a recrystallization mechanism the change of shape of the grain is by dislocation glide (i.e. by proton-reorientation-controlled glide). That is why there is a dotted line on the deformation map; it is still controlling the rate.

GLEN: It might not be, we have already put a big query mark against it.

DUVAL: I have a comment on tertiary creep and specially on the processes which produce the increase in creep rate during tertiary creep. The first is the modification of fabric, principally in simple shear. The second is dynamic recrystallization. In this latter case, the variation in creep occurs without modification of the fabric.

GOODMAN: We are only trying to construct, with the deformation map, a framework within which to discuss the mechanisms which govern ice. So we only plot secondary creep rates.

GLEN: Yes, but of course if you are talking about creep which goes on for a long time then it is the point at which tertiary creep settles down that you are interested in.

GOODMAN: I could suggest a possible low-stress-creep experiment here. Paterson (1977) has recently published a paper on bore-hole closure rates. I think that it is perfectly feasible to make a device which can measure bore-hole closure continuously and which could be put into the bore hole. Stress in the ice is a function of depth and it would be possible to fill the bore hole with a liquid of say half the density of ice so that there would be a stress distribution down the bore hole. The closure rate would be a function of that stress and so one could do creep experiments at very low stresses.

GLEN: I think one would have to be very careful what the liquid was and whether it came into contact with the ice or not because of the things which we discussed earlier this afternoon. I believe that the "Byrd" bore hole had ethylene glycol in it, and goodness knows what that did. One of the things that has been reported is, of course, a measurement of dielectric properties around the bore hole (Rogers and Peden, 1973) and they proved to be quite different from any other dielectric measurements on polar ice. Our group, at least, is worried that this might be due to the ethylene glycol.



C. J. L. WILSON: A comment to Dr Goodman about his deformation maps. The ice of the Cape Folger Antarctic core, and a number of other cores that I have observed, often contains small misorientations and these could be called sub-grains within the large grains. On these sub-grain boundaries there are a great many very small bubbles. Is there any way that your deformation map can take into account these small bubbles and the presence of inclusions on the sub-grain boundaries?

GOODMAN: No, such effects have not been included in the constitutive equations used to construct the maps. If the constitutive equation which is used to describe diffusional creep at high homologous temperature (Nabarro–Herring creep) is applied to ice with a grain size of 0.1 mm (a typical sub-grain size, say) the diffusional creep rate would be faster than dislocation creep at 0.1 MN m<sup>-2</sup> and -10°C. We know linear creep, which characterizes diffusional creep, is not observed for this temperature and stress, and therefore we could conclude that diffusional creep does not occur between sub-grains. The sub-grain boundary cannot be a good source or sink of vacancies or interstitials.

Inclusions on the grain boundaries will affect first the ease with which recrystallization can take place and secondly, although probably not significantly, the movement of vacancies or interstitials around or to the grain boundaries?

GLEN: Are there any other topics? Time is getting on.

O. E. MOGENSEN: I would like to ask what really is the resolution of the Lang camera technique? If I understand it correctly the resolution is something like one micrometre and that means that any three-dimensional cluster of vacancies, or any bubble containing less than one billion molecules has not been studied. A two-dimensional dislocation loop if it contains less than 10<sup>6</sup> molecules has not been studied either. It could be that clusters play a role also in all the electrical measurements.

HIGASHI: The resolution of X-ray diffraction topography is about 10 μm so what you say is correct. As far as dislocations are concerned, they can be quite well detected due to the elastic distortion around them, but I do not think we can identify vacancies.

GLEN: Let us be clear on this—the resolution is of that magnitude but this does not mean that an object has to be that large for us to see it as a spot. You could see something smaller, but you could not resolve two things.

MOGENSEN: No, but as far as I know, the bubbles and the vacancy clusters do not give rise to any kind of spot because they have little or no lattice strain associated with them.

GLEN: But a dislocation loop which introduced a stress field might be. It is a useful technique but it will not solve all our problems.

WHITWORTH: If one is just looking for small objects then I would have thought we could do better than X-ray topography by looking at things with light, say with an ultramicroscope. I wonder to what extent people have looked very carefully at ice with optical scattering techniques.

SINHA: I am examining this problem very carefully, and obviously the problem is the resolution of the microscope, particularly at high magnification, and the interference produced by internal reflection within the ice crystal—that is the biggest problem—even with the resolution of a good microscope the scattered light destroys the image. I have tried some scattered laser light but the scattered light coming out of separate angles from the beam was again reflected between the multiple surfaces.

HALLETT: I think perhaps it might be worth reminding ourselves here that just by using ordinary thin-film interference we can go down to resolutions, in some forms of epitaxial ice growth, of a few hundreds of ångströms. This gives us some feeling for the surface structure; steps of height down to about 200 Å have been observed.

KASSNER: As far as individual inclusions are concerned perhaps 0.1  $\mu\text{m}$  is about the best that we can do just by observing the optical scattering, and even that will be difficult.

GLEN: I think the time has come when I should draw this discussion to a close. We have ranged quite widely; I think we have identified some interesting problems and I hope to see the solutions to some of these problems in the literature in the not too distant future. Finally, I would like to thank the participants to this discussion for their contributions to it.

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