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Report:

The purpose of the project was to establish whether there is a relation between the favoured grain boundary angles in ice and the polymer-ice structures that form in freezing PVP-water solutions. In such solutions, layer structures, cubic bicontinuous structures or hexagonal columnar structures have been shown to form,dependent on the initial concentration of the easily supercooling solutions. It could be that water partakes in such structures simply as molecules interacting with the polymer.At the other hand, ice formation could preceed the structure formation and thus form its backbone.

Although the origonal purpose was to go to high pressure and low temperature. so as to have the possibilty to change to different ice polymorphs, we first determined the relaxation behaviour of ice I_h, when put under uniaxial stress.

SAXS measurements on ID 2 with 10 m and 3.5 m detector distance show a pretty complete picture of the crystal relaxing its strain. After application of a stress of 0.1 kbar at -20 C the ice crystal devellops arrays of line dislocations forming grain boundaries. In well alligned samples, c-axis parallel to the beam, and stress applied in the <110> direction, one can distinguish between gram boundaries in many different orientations by virtue of the different patterns that such boundaries cause in the two dimensional images.

The general trend in such low temperature samples is that the applied stress, in first instance, generates dislocations and grainboundaries in very many different directions.Moreover, the patterns once formed, show very little change. Only when the samples are raised in temperature to about -5 C, recrystallization becomes so fast a process, that some of the boundaries disappear and are replaced by others. After ca 2000 seconds the remaining boundaries are mainly small angle boundaries around $(11\bar{2}0\}$ planes with arrays of line dislocations lying in the $[1\bar{1}00]$ directions and the Burgers vector b parallel with $[11\bar{2}0\}$. From the temperature dependence of the rate of these changes we estimate a free enthalpy of activation of about 10^{-18} to 10^{-19} J.

A very important conclusion can be drawn from these experiments concerning the possibility to determine the influence of the geometry of ice on PVP-water structures under equilibrium conditions for other ice forms. The slowness of the stress relaxation at low temperatures practically prohibits the use of low temperature ice forms. Only ice V, stable at 273K and pressures above 8 kbar, could relax the initially applied stress within a time suitable for the experiment. We shall therefore submit a new proposal conforming to this conclusion.

A second very important observation was made in PVP-water solutions of such high concentration, 64%, that no ice is formed at all, not even at -30 C. SAXS from a drop of such a solution, shows different combinations of sharp Bragg peaks that arise and disappear within seconds. Very often it is possible to map such combinations on a plane hexagonal reciprocal lattice, giving shortest distances of about 0.4 to 0.6 nm^{-1}, corresponding with a real space hexagonal columnar structure with neighbour distance between columns of 10 to 16 nm. This partially answers the original question, ice formation or ice form does not play a role in the formation of three dimensional PVP-water structures. For the layer structures this of coarse remains to be seen.