

The Many Phases of Ice

Norman Anderson
Physics 511
Dr. Alex Travesset

Abstract

In this paper we will look at the various phases of ice, their structure, and some of their properties. While hexagonal ice is the most common form of ice there are twelve other phases that have currently been identified. We will look at these phases one by one and also their relation to each other. A phase diagram will also be presented to display the ordering of these phases.

Introduction

Ice is a very interesting and long known solid. Its composition is that of one of the most abundant liquids on Earth, and is the essential component of snow, rain, and the generation of thunderstorm electricity. Besides its environmental importance ice is also special because of the interesting phenomena contained within its structure. The crystal structure of ice is very unusual because, while the molecules lie on a regular crystal lattice, there is disorder in their orientations. This property leads to many interesting characteristics in electrical polarization and conductivity. While ice is commonly seen everyday this is only one phase of ice known as ice I_h . What is generally not emphasized is that ice actually has at least thirteen other crystalline phases which exist at various temperatures and pressures.

Ice I_h

Ice I_h is the most commonly known phase of ice. This phase is the normal form of ice obtained by freezing water at atmospheric pressure. The 'h' following the 'I' is used to designate that it is the normal hexagonal phase of ice. The commonly seen phase diagram for Ice I_h , water, and vapor is depicted in Figure 1.

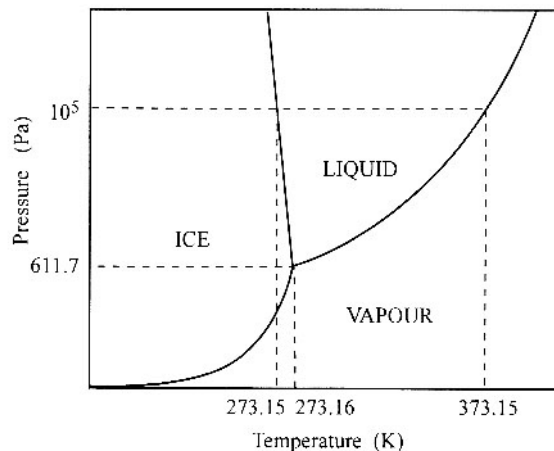


Figure 1: Phase diagram of Ice Ih

From the figure we can see that the triple point, point where all three phases are in equilibrium, occurs at 273.16 K and 611.7 Pa. In general we consider this type of ice to form at freezing temperatures above 150 K, with other phases of ice to form at lower temperatures. The negative slope seen in the melting curve is a consequence of the fact that water expands when it freezes. While this seems strange, silicon and germanium, which have similar low density structures, also exhibit this property. It is this expansion that causes ice to float in water. This expansion cause ice to be about 9% less dense than water. Using Archimedes' principle, since ice has a lower density it will float in water.

While there are many other phases of ice there are also some varieties of the ice Ih phase. S1 ice occurs when ice forms platelets lying on the surface with the c-axis vertical forming columnar grains. This is then considered a vertically growing ice such as that found on the sides of containers. If the ice is formed more rapidly, we have randomly oriented grains which grow perpendicular to the c-axis. This then represents a horizontally growing ice such as that formed on the top of lakes known as S2 ice. Polycrystalline ice then has randomly oriented grains in every direction and is known as T1 ice. This type of ice is very similar to Glacier ice. These types of ice all have the hexagonal crystal structure which will now be looked at in greater detail.

The basic structure of ice is shown in Figure 2. This is the model developed by Pauling in 1935 and later confirmed through neutron diffraction studies by Peterson and Levy in 1957. The oxygen atoms are shown by open circles and hydrogen atoms shown by dark circles.

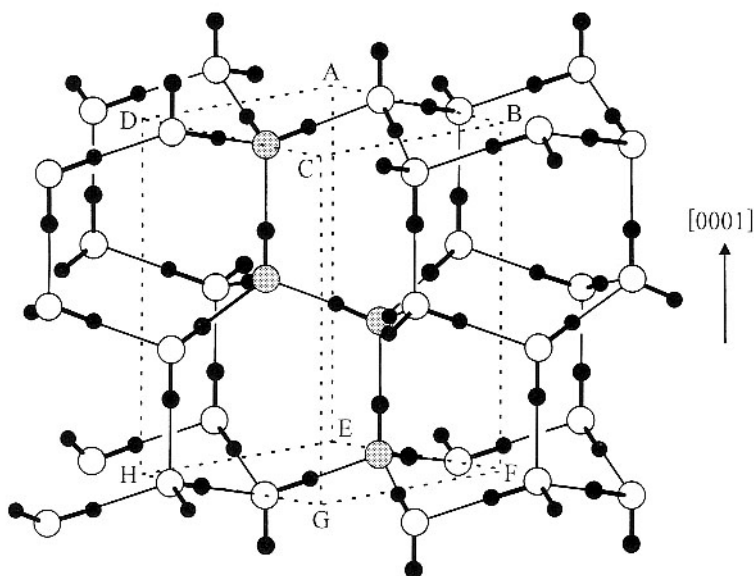


Figure 2: Crystal structure of ice Ih

As we can see from the figure, each oxygen atom has four nearest neighbors at the corners of a regular tetrahedron. The hydrogen atoms are covalently bonded to the

nearest oxygen atoms to form water molecules which are then linked to each other through hydrogen bonds. The layers of this structure are then stacked in an ABAB. . . repeating pattern. The main thing to note about this structure is that there is no long range order in the orientation of the water molecules or hydrogen bonds.

Ice Ic

Cubic ice or ‘ice Ic’ is a metastable variant of ice Ih. It was first discovered by Konig in 1943 using electron diffraction techniques. Here the oxygen atoms are arranged in the cubic structure of diamond rather than on the hexagonal lattice of ice Ih. As is the case with ice Ih, the water molecules of ice Ic still form four hydrogen bonds to its neighbors. The stacking sequence of this phase of ice is of the ABCABC . . . form as illustrated in Figure 3. Figure 3 shows both the cubic and hexagonal structures of ice projected on the $\{1\bar{1}20\}$ plane.

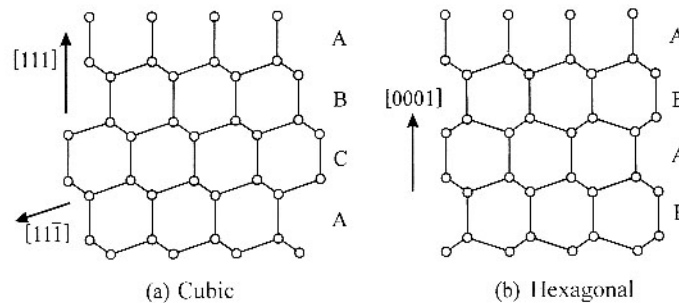


Figure 3: Comparison of the cubic and hexagonal structures of ice

In general the cubic form of ice is produced at freezing temperatures between 130 and 150 K with amorphous ice being produced at lower temperatures. While ice Ic is formed below 150 K, it is important to note that ice Ih does not become ice Ic at temperatures below 150 K. However, around 200 K cubic ice does transform into hexagonal ice.

Ice Ic is a very popular structure for theoretical modeling of ice because its high symmetry simplifies calculations. Molecular dynamic simulations were carried out by Svishchev et. al. in 1994 on the crystallization of ice from supercooled liquid water always produced ice Ic [2]. This never actually happens in macroscopic experiments and shows us how subtle the difference between ice Ic and ice Ih is.

Amorphous ice

There are two main forms of amorphous ice, low density and high density. Low density amorphs (LDA) have a density at atmospheric pressure of about 0.94 Mg m^{-3} . High density amorphs (HDA) are formed at high pressure but have an atmospheric density of about 1.17 Mg m^{-3} . A flowchart of the forms of amorphous ice and other phases of ice and water is displayed in Figure 4. In the diagram T_g signifies a glass transition and the dotted lines are used for a simplified approach where the entire region is considered LDA. Also amorphous solid water is designated by (ASW) and hyperquenched glassy water is designated by (HGW). In the diagram we see that ASW and HGW degrade into

‘Water A’, which is a metastable state. However, ASW and HGW more frequently transform into Ice Ic experimentally.

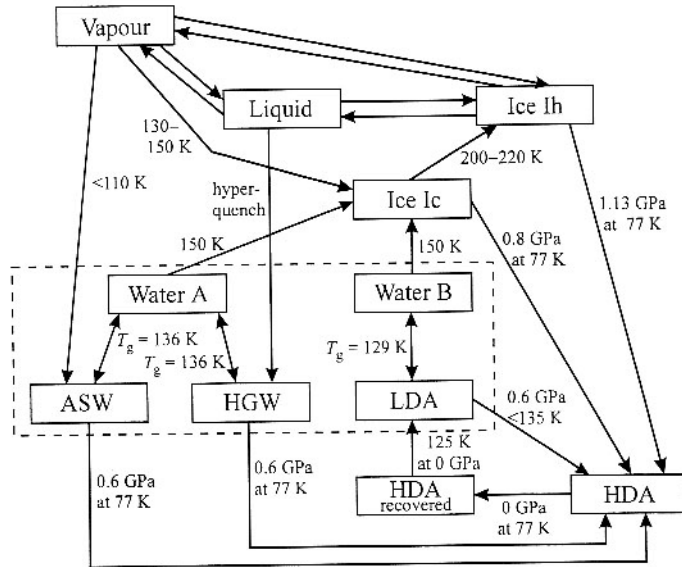


Figure 4: Flowchart of amorphous ice and other more common water/ice phases

Theoretical simulations carried out by Okabe et. al. show that ice I_h transforms to HDA at 1.27 GPa and 77 K. If we compare this to the diagram above we see very comparable results with just a 0.47 GPa difference in pressure. Furthermore the simulation also tells us that LDA can be formed by heating HDA to 160 K under no applied pressure. While this is higher than what we see in the diagram it is still consistent with the process.

While amorphous ice does exist, it has been shown recently by Schober et. al. that both LDA and HDA display many crystal like effects similar to those of ice I_c with LDA showing a higher degree of crystal like properties [3]. High frequency dynamics of both amorphous ices were measured using inelastic X-ray scattering and very narrow width phononlike excitations were observed. These excitations then are interpreted as a sign of low local disorder.

Still yet there has been much controversy on whether there are actually two phases of amorphous ice. Even more recently, however, Finney et. al. has provided strong proof using radial distribution functions (RDF) derived by neutron diffraction as shown in Figure 5.

We can see from this figure that there is a distinct difference in the RDF for LDA and HDA ice. This lends very convincing evidence to the case of two amorphous ice phases. It is also interesting to note here that the RDF determine by Okabe also differed for LDA and HDA ice.

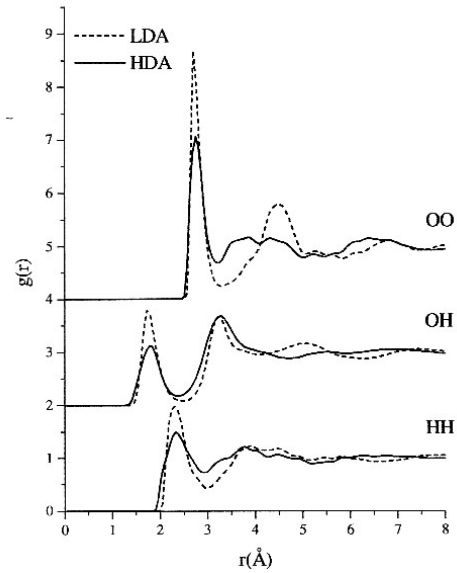


Figure 5: Radial distribution functions for LDA and HDA ice

Higher phases of ice

Before looking at each of the higher order phases of ice individually, we first look at the entire group of phases. Figure 6 shows a summary of the higher order phases of ice as well as the intersection with the liquid water phase. The other phases of ice have been labeled with Roman numerals from ice I to ice XII. Each phase is stable over a certain temperature range and pressure, but many of the phases are metastable outside of this given range. Figure 6 then shows the stable phases of the ice-water system.

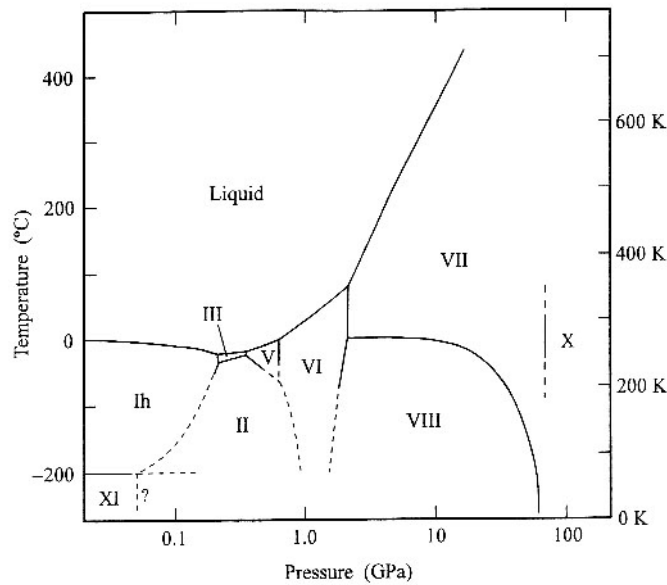


Figure 6: The stable phases of ice

The solid lines in the diagram represent experimental measurements and the dashed lines indicate extrapolated or inferred boundaries. The key features of the diagram are the triple points. Table 1 gives us a summary of the triple points of the various phases of ice. This gives us a summary of where the various phases of ice occur.

point	p (MPa)	T (K)
L-I _h -III	209	250.7
L-III-V	350	255.5
L-V-VI	632	273.1
L-VI-VII	2210	354.6
I _h -II-III	213	238.3
II-III-V	344	248.7
VI-VII-VIII	2100	273
I _h -XI-vapor	0	273

Table 1: Summary of triple points of ice phases

Ice II

Ice II has a truly ordered structure and is formed by compressing ice I_h at 190 to 210 K. If heated ice II becomes ice III but the reverse process is not readily accomplished. The unit cell is rhombohedral but the structure can also be described in a larger hexagonal cell of 36 molecules. It contains hexagonal rings linked to one another in which ice II achieves a higher density than ice I_h. Figure 7 shows a stereo-diagram of the crystal structure of ice II.

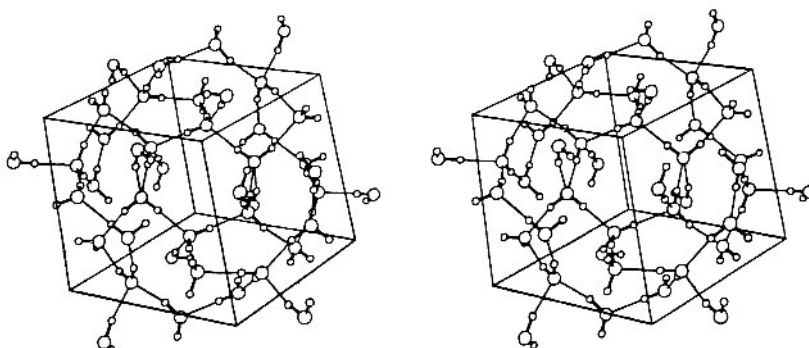


Figure 7: Stereo image of ice II

In the crystal, all water molecules are hydrogen bonded to four others, two as donor and two as acceptor. As the H-O-H angle does not vary much from that of the isolated molecule, the hydrogen bonds are not straight. The relationship of the structure of ice II to ice I_h can be visualized by detaching the columns of ice I_h rings, moving them relatively up or down at right angles to their plane, rotating them about 30° around this axis and re-linking the hydrogen bonds in a more compact way to give a density of 1.16 g cm⁻³. The hydrogen bonding is also ordered and fixed in ice II. However, some of these hydrogen bonds are bent and, consequentially, much weaker than the hydrogen bonds in hexagonal ice.

Ice III

Ice III is the least dense of the high-pressure phases of ice, but it is more dense than the liquid phase. Ice III is formed from water at 300 MPa by lowering its temperature to 250 K. Its unit cell forms tetragonal crystals. In the crystal, all water molecules are hydrogen bonded to four others, two as donor and two as acceptor. Ice III contains five membered rings joined as bicyclo-heptamers and has a density of 1.16 g cm^{-3} at 350 MPa. The hydrogen bonding is disordered and constantly changing as in hexagonal ice. The tetragonal crystal is pseudo-cubic and contains 12 water molecules. Its structure consists of tight right-handed four-fold helices, containing two thirds of the water molecules, connected by the remaining water molecules which, thus, experience a differing molecular environment.

Ice IV

Ice IV exists only as a metastable phase and it is not easily formed without the aid of a nucleating agent. Figure 8 shows a stereo image of the crystal structure of ice IV. The structure is rhombohedral with the three fold axis vertical in Figure 8.

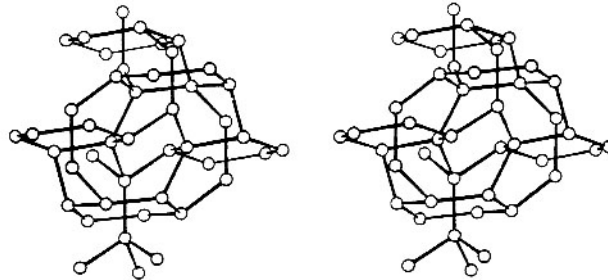


Figure 8: Stereo image of the structure of ice IV

Almost-planar-six membered rings of molecules lie perpendicular to this axis. There is also a hydrogen bond between a pair of different molecules passing through the center of each ring. Still, all molecules belong to a single hydrogen-bonded network.

Ice V

Ice V has the most complicated structure of all the ice phase. Ice V is formed from liquid water at 500 MPa by lowering its temperature to 253 K. Its unit cell forms monoclinic crystals with each unit cell containing 28 molecules. Ice V contains four-, five-, six- and eight-membered rings and groups of seven molecules at four different lattice sites with each experiencing a differing molecular environment. A chain of water molecules, with each forming a corner of two condensed four-membered rings, runs parallel to the a-axis. Also parallel run chains of two other alternating sites that are joined together through gaps in the first chain by the smaller number of the fourth type. All molecules form one connected lattice with a density of 1.24 g cm^{-3} at 350 MPa. The hydrogen bonding is disordered and constantly changing as in hexagonal ice.

Ice VI

The crystal structure of ice VI is tetragonal and the structure is formed from chains built up of hydrogen bonded molecules lying parallel to the fourfold [001] axis. The chains

centered on the corners of the unit cell are linked together by hydrogen bonds parallel to the a and b axes. The symmetry of this structure indicates that the hydrogen positions are disordered. Figure 9 depicts the crystal structure of this phase.

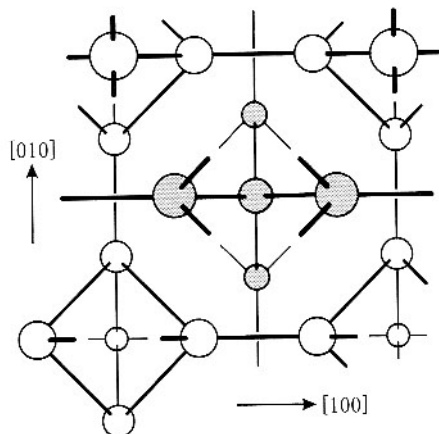


Figure 9: Crystal structure of ice VI

There are two separate interpenetrating networks, linked through the four equatorial water molecules in the hexamers. The two axial hexamer water molecules join the hexamers and experience a different molecular environment. Ice VI is formed from liquid water at 1.1 GPa by lowering its temperature to 270 K, and has a density of 1.31 g cm^{-3} at 0.6 GPa. It is also interesting to note that the permittivity of this phase exhibits Debye relaxation.

Ice VII

Ice VII has a cubic arrangement of oxygen atoms. It also has a very simple high density packing of water molecules. Ice VII is shown in Figure 10.

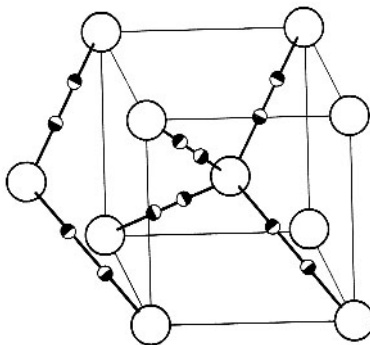


Figure 10: Crystal structure of ice VII

In this structure each oxygen atom has eight nearest neighbors but is tetrahedrally linked by hydrogen bonds to only four of them. There are two interpenetrating but independent sublattices each with the structure of cubic ice. It has a density of about 1.65 g cm^{-3} at 2.5 GPa, which is less than twice the cubic ice density.

Neutron diffraction data show that the hydrogen atoms are disordered. Because of this hydrogen disorder, the permittivity will exhibit a similar Debye relaxation to that of hexagonal ice.

Ice VIII

Ice VIII is the ordered structure of ice VII. Ice VIII is formed from ice VII by lowering its temperature. The hydrogen bonding is ordered and fixed as ice VII undergoes a proton disorder-order transition to ice VIII when cooled at about 5°C. Ice VII and ice VIII have identical structures apart from the proton ordering. Ice VIII forms a tetragonal crystal containing eight water molecules per unit cell, where all of the water molecules are hydrogen bonded to four others, two as donor and two as acceptor. Figure 11 shows the crystal structure of ice VIII.

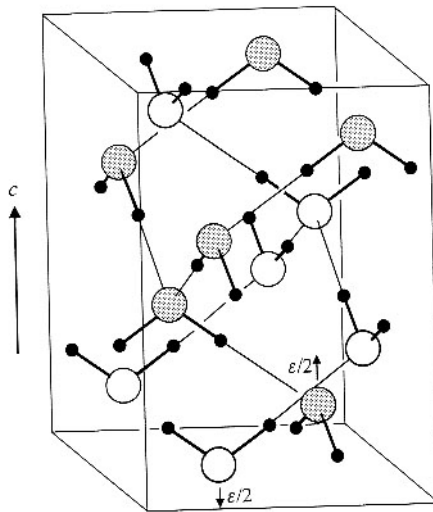


Figure 11: Crystal structure of ice VIII

Similarly to ice VII, ice VIII consists of two interpenetrating cubic ice lattices. It has a density of about 1.66 g cm^{-3} at 8.2 GPa and 223 K which is less than twice the cubic ice density.

Ice IX

Ice IX is formed by cooling Ice III. As we cool ice III from -65 to -108 °C, there is a gradual fall in permittivity as ice IX is being formed. Ice IX is very closely related to ice III having a similar crystal structure as well as other properties. The ordering of ice IX was determined by neutron diffraction to be antiferroelectric as is the case with ice III as well.

Ice X

Ice X was initially observed in 1984 by Hirsch and Holzapfel using Raman scattering. They observed some features which looked like a phase change around 40-45 GPa and called it ice X. Ice X is also known as the proton ordered symmetric ice. It is still under dispute whether ice X has indeed been verified experimentally. It is believed that ice

VIII can be transformed into ice X but there is yet to be experimental proof. It is also predicted that ice VII should transform into ice X at about 70 GPa.

Ice XI

Ice XI was initially observed by Kawada in 1972, however it took until 1984 when Tajima performed high precision calorimetry experiments for ice XI to be accepted as a new phase. Ice XI is the low-temperature equilibrium structure of hexagonal ice prepared from dilute KOH (10 mM) solution kept just below -201°C for about a week. The hydroxide ions create defects in the hexagonal ice allowing protons to jump more freely between the oxygen atoms. Figure 12 displays the crystal structure of ice XI.

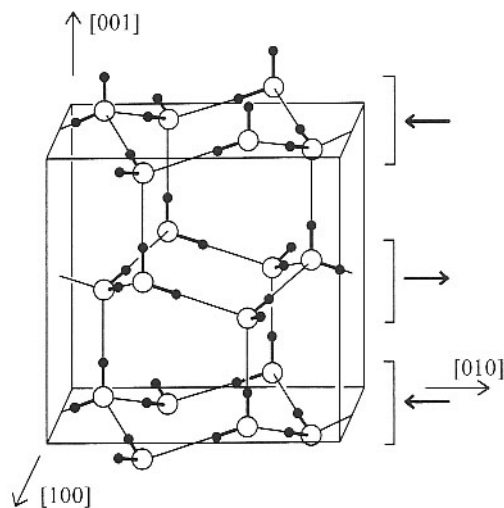


Figure 12: Crystal structure of ice XI

A loss of entropy by proton ordering occurs to give a more stable structure. The K^+ ions occupy interstitial sites in the hexagonal boxes but neither ion is shown in the given figure. Ice XI is the thermodynamically favored form of ice at atmospheric pressure at these low temperatures. It is a proton-ordered form of hexagonal ice forming orthorhombic crystals. All bonds are parallel to the c-axis and oriented in the same direction making ice XI a ferroelectric.

Ice XII

Ice XII may be formed by heating high-density amorphous ice at a constant pressure of 0.81 GPa from 77 K to ~ 183 K and recovered at atmospheric pressure at 77 K. Ice-twelve is metastable within the ice-five and ice-six phase space. It forms a tetragonal crystal. In the crystal, all water molecules are hydrogen bonded to four others, two as donor and two as acceptor. Ice-twelve contains a screw-type hydrogen bonded arrangement quite unlike that found in other crystalline forms of ice, with the smallest ring size consisting of seven molecules. It has a density of 1.30 g cm^{-3} at 127 K and ambient pressure, somewhat greater than ice-five whose density is 1.23 g cm^{-3} . The hydrogen bonding is disordered and constantly changing as in hexagonal ice.

Conclusion

In this paper we have looked at the many phases of ice. We have seen that there are currently thirteen well defined ice phases. The majority of these phases can be transformed into other phases of ice but some are yet to be well defined such as ice X. While ice is one of the most easily recognized and common solid seen in life, it still remains one of the most complex solids to understand. While many phases have been identified it does not mean that there are not more phases of ice especially as we look to higher and higher pressures.

References

- [1] Petrenko, V. F. and Whitworth, R. W., *Physics of Ice*, Oxford, (1999).
- [2] Svishchev, I. M. and Kusalik, P. G., *Crystallization of liquid water in a molecular dynamics simulation*, Physical Review Letters, **73**, 975, (1994).
- [3] Schober, H., et. al., *Crystal-like High Frequency Phonons in the Amorphous Phases of Solid Water*, Physical Review Letters, **85**, 4100, (2000).
- [4] Finney, J. L. et. al., *Structures of High and Low Density Amorphous Ice by Neutron Diffraction*, Physical Review Letters, **88**, 225503-1, (2002).
- [5] Okabe, I., Hideki, T., Nakanishi, K., *Structures and phase transitions of amorphous ices*, Physical Review E, **53**, 2638, (1996).
- [6] Pounder, E. R., *The Physics of Ice*, Pergamon, Oxford, (1965).
- [7] Bogorodskii, V. V., *The Physics of Ice*, Jerusalem, (1971).
- [8] Klotz, et. al., *Structure of High-Density Amorphous Ice under Pressure*, Physical Review Letters, **89**, 285502-1, (2002).
- [9] Riehl, N., et. al., *Physics of Ice*, Plenum Press, New York, (1969).
- [10] Dmitriev, V. P., Rochal, S. B., Toledano, P., *Theory of Ice Structures*, Physical Review Letters, **71**, 553, (1993).
- [11] Benoit, M., Bernasconi, M., Focher, P., Parrinello, M., *New High-Pressure Phase of Ice*, Physical Review Letters **76**, 2934, (1996).