Progress in Solid State Chemistry 43 (2015) 71–81

Contents lists available at ScienceDirect

Progress in Solid State Chemistry

journal homepage: www.elsevier.com/locate/pssc

Water's phase diagram: From the notion of thermodynamics to hydrogen-bond cooperativity

Xi Zhang [a, b], Peng Sun [a], Tingting Yan [c], Yongli Huang [d], Zengsheng Ma [d], Bo Zou [c], Weitao Zheng [e], Ji Zhou [f], Yinyan Gong [a, *], Chang Q. Sun [g, *]

[a] Institute for Coordination Bond Metrology and Engineering, College of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, China
[b] Institute of Nanosurface Science and Engineering, Shenzhen University, Shenzhen 518060, China
[c] State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China
[d] Key Laboratory of Low-dimensional Materials and Application Technology (MOE) and School of Materials Science and Engineering, Xiangtan University, Xiangtan 411105, China
[e] School of Materials Science, Jilin University, Changchun 130012, China
[f] State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China
[g] NOVITAS, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore

ARTICLE INFO

Article history:
Available online 1 April 2015

Keywords:
Water
Ice
Hydrogen bond
Phase diagram
Pressure
Temperature

ABSTRACT

This presentation features recent progress in understanding the phase diagram of water and ice from the perspective of hydrogen bond (O:H–O) cooperative relaxation with focus on how the segmental length and the containing angle of the O:H–O bond change with mechanical compression and thermal excitation. By interplaying theoretical predictions, numerical computations, and phonon spectrometrics, we firstly examined the relaxation dynamics of O:H–O bond segmental length and phonon stiffness of: i) liquid water at 300 K and ice at 80 K as a function of pressure, ii) liquid water cooling from 350 K to 80 K under the ambient pressure, iii) mechanical freezing of the ambient water under compression up to 1.83 GPa, and, iv) liquid water heating from 253 to 753 K under 30 MPa pressure. Observations allow us to classify the $T_C(P)$ phase boundaries of water and ice into four types according to their slopes and then formulate them in terms of hydrogen bond relaxation in segmental length and containing angle. Observations reinforce the essentiality and effectiveness of hydrogen bond notion in dictating the unusual behavior of water and ice and clarify the bonding dynamics during phase transition, which is beyond the scope of classical thermodynamics.

Contents

---

[*] Corresponding authors.
E-mail addresses: ygong2007@163.com (Y. Gong), ecqsun@ntu.edu.sg (C.Q. Sun).

http://dx.doi.org/10.1016/j.progsolidstchem.2015.03.001
0079-6786/

1. Introduction

Water is ubiquitously important to all lives and it is too strange, too anomalous, and too challenge. Understanding the anomalous behavior of water and ice remains incomprehensive despite extensive dedications in past decades. Alternative ways of thinking and approaching are indispensable though the classical thermodynamics and the contemporary quantum mechanics have contributed significantly. Consideration is necessary from the perspective of the asymmetrical, local, and short-range inter- and intra-molecular interactions within the hydrogen bond (O:H–O) and the involvement of Coulomb repulsion between electron pairs on oxygen ions [1].

Appendix shows the phase diagram of water and ice. Ice formed by water behaves strangely at lower temperatures and higher pressures. Water–H_2O – seems to be a simple molecule: two hydrogen atoms connected to a central oxygen atom in a V-shape. In everyday ice cooled from liquid water, which scientists call Ice Ih, the water molecules line up in a hexagonal pattern; this is why snowflakes all have six-sided patterns (The “h” stands for hexagonal). A variation called Ice Ic at lower temperatures, found in ice crystals floating high up in the atmosphere, forms cubic crystals, in fogs and clouds. The crystal structure of the ice is fairly loose – the reason that ice Ih is less dense than liquid water – and the O:H intermolecular nonbonds become longer and weaker but the intramolecular H–O bonds become shorter and stiffer than they are in liquid water.

At higher pressures, the usual hexagonal structure breaks down, and the bonds rearrange themselves in more compact, denser crystal structures, neatly labeled with Roman numerals: Ice II, Ice III, Ice IV and so on. Scientists have also discovered several forms of ice in which the water molecules are arranged randomly, as in glass. At a pressure of about 200 MPa, Ice Ih turns into a different type of crystalline ice, Ice II. Ice II does not occur naturally on Earth. Even at the bottom of the thickest portions of the Antarctic ice cap, the weight of three miles of water and ice pushes down at only one-quarter of the pressure necessary to make Ice II. But planetary scientists expect that Ice II, and possibly some other variations, like Ice VI (around 1 GPa ~10^4 atm pressure), exist inside icier bodies in the outer solar system, like the Jupiter moons Ganymede and Callisto.

With pressure high enough, the temperature need not even be cold for ice to form. Scientists considered what happens to tectonic plates after they are pushed back down into Earth's interior. At about 100 miles down, the temperature of these descending plates is 300–400 °C – well above the boiling point of water at the surface – but cool compared with that of surrounding rocks. The pressure of 2 GPa at this depth could be great enough to transform any water that was there into a solid phase known as Ice VII. No one knows whether ice can be found inside Earth, because no one has yet figured out a way to look 100 miles underground. Just as salt melts ice at the surface, other molecules mixing with the water could impede the freezing.

Ice also changes its form with dropping temperatures. In hexagonal ice, the usual form, the oxygen atoms are fixed in position, but the O:H nonbonds between water molecules are continually breaking and reattaching, tens of thousands of times a second. At temperatures cold enough – below −200 °C – the nonbonds freeze as well, and normal ice starts changing into Ice XI (orthorhombic structure). Astronomers were probably already looking at Ice XI on the surface of Pluto and on the moons of Neptune and Uranus. But instruments currently are not sensitive enough to distinguish the slight differences among the ices.

From ice XII to ice XVI, found just a decade ago are also with many new features. For instance [2], the cadge-structured ice XVI has a density of 0.81 g/cm^3 as the stable low-temperature phase of water at negative pressures (that is, under tension). This hollow hydrate structure exhibits cooling expansion below about 55 K, and that it is mechanically more stable and has at low temperatures larger lattice constants than the filled hydrate. When pressure is increased to 60 GPa, ice X phase forms with identical H–O and O:H length of 1.1 Å, corresponding to density of 1.84 times that of water at 4 °C [3,4].

Ice can turn to be partially ionic ($2H_2O \rightarrow H_3O^{\delta+}$(one lone pair) + $HO^{\delta-}$($\delta = 0.62$; three lone pairs), which is realized by exchanging H with an electron at extremely high pressure (2 TPa) and high temperature (2000 K) [5]. The occurrence of this ionic phase follows the break-up of the typical O–H covalently bonded tetrahedrons in the hydrogen symmetric atomic phases and is originated from the volume reduction favorable for a denser structure packing.

The contribution to the lattice energy from the O:H intermolecular interaction increases and that from the intramolecular H–O bonding decreases when pressure is increased up to 2 GPa, as calculated using first principle and Quantum Mote Caro calculations [6]. The elegantly used TIPnP (n varies from 1 to 5) model series and the TIP4Q/2005 modeled water ice but they exclude the possibility of bond relaxation and charge polarization. These rigid non-polarizable models can hardly reproduce the anomalies of water ice with high satisfaction [7,8].

One often connects the structure and property Q of a substance directly to the external stimuli such as pressure, volume, entropy, and temperature $Q(PV, ST, \ldots)$, which is exactly that the classical thermodynamics deals with large trunks. Such treatment employs concepts of entropy, enthalpy, Gibbs and Helmholtz free energy, and so on so forth with standard deviation δ depending on the sample size N in the form of $\sigma \propto N^{-1/2}$. This approach provides little information on how the chemical bond responds to external stimulus.

A number of formulas exists describing the $T_C(P)$ phase boundaries of water ice from the classical thermodynamic point of view, for the Liquid–Vapor phase transition. Unfortunately, few approaches are available for formulating the boundaries in general cases. For instances, Clausius–Clapeyron equation [9] describes water vapor under typical atmospheric conditions (near standard temperature and pressure) and August–Roche–Magnus formula [10] approximates the temperature dependence of the saturation vapor pressure P_S: