

## Ice and Beyond: Tetrahedral Building Blocks in Crystals<sup>a</sup>

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**Abstract:** Tetrahedral building blocks are immensely important in inorganic materials. The structure of ice is ideal for presenting this concept, combined with an introduction to hydrogen bonding. Connecting tetrahedral building blocks is then extended to polymorphs of silica.

**Keywords:** 3D structures · Education · Hydrogen bond · Ice · Polymorph · Silica

Water, H<sub>2</sub>O, is essential to life. Our oceans make up 96.5% of the water present on our planet, but only 2.5% of Earth's water is non-saline (freshwater). Of the freshwater, around 70% is found in glaciers and ice-caps, and 30% in ground water.<sup>[1]</sup> Water and ice possess fascinating properties, and one well-known fact is that ice floats on water because the density of ice is lower than that of liquid water. Usually, the solid phase of a substance is denser than its liquid phase, and ice/water shows the opposite behaviour; we return to this phenomenon later. The word 'ice' encompasses 17 different (and experimentally proven as of June 2020) structural forms or *polymorphs* depending upon temperature and/or pressure.<sup>[2]</sup> When water freezes at normal atmospheric pressure, it forms 'ice Ih' (Fig. 1). The label *Ih* is composed of a Roman numeral (I) and the *h* specifies *hexagonal symmetry*, the latter leading to the hexagonal (or 6-fold) symmetry seen in well-formed snowflakes. High-pressure phases of ice probably do not exist naturally on Earth because of the huge pressures required to form them, but they are predicted to be present in the interiors of other planets and moons.<sup>[3]</sup> In the laboratory under controlled high-pressures and temperatures, polymorphs other than ice *Ih* can be formed, and their structures investigated.



Fig. 1. Ice crystals. ©Edwin C. Constable 2019

Like the other polymorphs of ice, ice *Ih* possesses a 3-dimensional structure, and critical to this rigid assembly is the presence of *intermolecular hydrogen bonds*. A hydrogen bond is formed

between an H atom attached to an electronegative atom, and an electronegative atom that possesses a lone pair of electrons. After fluorine, oxygen is the most electronegative element in the periodic table. The non-linear structure of a water molecule, and the positions of the lone pairs of electrons on the O atom, are shown in Figs. 2a and 2b. Each O–H bond is polar in the sense shown in Fig. 2b. In the structure of ice, we are concerned only with O–H...O hydrogen bonds. However, hydrogen bonding is hugely important in the solid-state structures of small molecules and in biological systems; F–H...F, O–H...F, O–H...O, O–H...N, N–H...F, N–H...O and N–H...N intermolecular interactions are especially important along with weaker C–H...O hydrogen bonds (sometimes called non-classical hydrogen bonds).<sup>[4]</sup> In an X–H...Y hydrogen bond, the X–H unit acts as a proton donor and Y is the proton acceptor. Fig. 2c illustrates one O–H...O hydrogen bond between two water molecules. The H atom is asymmetrically positioned between the two O atoms, being covalently bonded to one O atom and forming an electrostatic interaction (Hδ+...Oδ−) with the second O atom. The bond dissociation enthalpy of the covalent O–H bond is *ca.* 464 kJ mol<sup>−1</sup> and that of the O–H...O hydrogen bond is *ca.* 25 kJ mol<sup>−1</sup>. Typically, solid-state structures are determined using X-ray crystallography. However, X-rays are diffracted by electrons surrounding the nuclei and, because H has only one valence electron, it is usually difficult to accurately locate the position of H nuclei. X-ray diffraction can accurately determine the O...O distance, but not, usually, the O...H distances. The direct and accurate location of H atoms requires the use of neutron diffraction because neutrons interact with the nuclei of atoms. However, neutron sources are far less readily available than X-ray sources. Although the replacement of 1H by the heavier isotope deuterium (2H or D) is often used to aid the location of hydrogen atoms, it may lead to geometric changes in the hydrogen bond.<sup>[5]</sup> The shortest O...O distances in polymorphs of ice are around 280 pm, and this is typical of the asymmetrical O–H...O hydrogen bond depicted in Fig. 2c. However, not all O–H...O interactions are of this type. There are examples of symmetrical O–H–O hydrogen bonds (so-called 'strong' hydrogen bonds) in which the O...O distance is *ca.* 240 pm.<sup>[6]</sup>

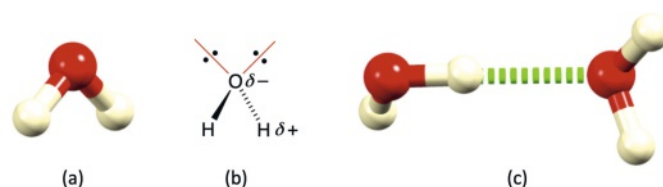


Fig. 2. (a) The non-linear structure of an H<sub>2</sub>O molecule; (b) the O atom has two lone pairs and each O–H bond is polar; (c) an O–H...O hydrogen bond.

In every polymorph of ice, a water molecule forms four hydrogen bonds. In two of these interactions, H<sub>2</sub>O acts as a donor and in two it acts as an acceptor. The O atom is in a tetrahedral environment (Fig. 3a). The different polymorphs arise by interconnecting these tetrahedral building blocks in different ways. Part of the solid-state structure of ice *Ih* is shown in Fig. 3b and the hexagonal symmetry is crystallographically imposed. A large-

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er part of the lattice (with only the O atoms included) is shown in Fig. 3c, and reveals the presence of open channels running through the structure. Channels actually run in three directions through the crystal lattice, leading to a very open network and therefore ice *Ih* has a relatively low density ( $0.92 \text{ g cm}^{-3}$ ). On melting at 273 K, some hydrogen bonds are broken, the lattice partially collapses, and the density increases reaching a value of  $1.00 \text{ g cm}^{-3}$  at 277 K. Hydrogen bonding between water molecules is not only important in the solid state. Even as water approaches its boiling point (373 K), hydrogen bonding within the bulk liquid is still significant and leads to water having a high value for the enthalpy of vaporization ( $40.7 \text{ kJ mol}^{-1}$ ).

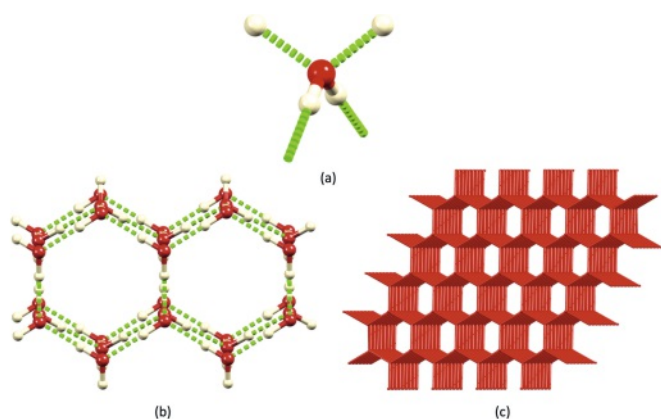


Fig. 3. (a) Each O atom in each polymorph of ice is in a tetrahedral environment; hydrogen bonds are shown in green. (b) Part of the 3D-structure of ice *Ih*. (c) A larger part of the structure (O atoms only are included) to show channels running through the lattice. (Crystal coordinates: R.T. Downs, M. Hall-Wallace, (2003) The American Mineralogist Crystal Structure Database.)

Of the remaining polymorphs of ice, we illustrate only the structures of ice II and ice IX (Fig. 4). Figs. 4a and 4c show details of the hydrogen-bonded assemblies in the high-pressure polymorphs ice II and ice IX, and inspection of these structures reveals the same tetrahedral building blocks present in ice *Ih*. Ice II comprises tube-like assemblies and Fig. 4b views part of the lattice looking down the tubes. One of these tubes forms the central motif in Fig. 4a and this diagram reveals the interconnection of the tubes by hydrogen bonds. Two excellent reviews by Salzmänn<sup>[2,3]</sup> provide structural details of all the polymorphs of ice and the conditions under which they form.

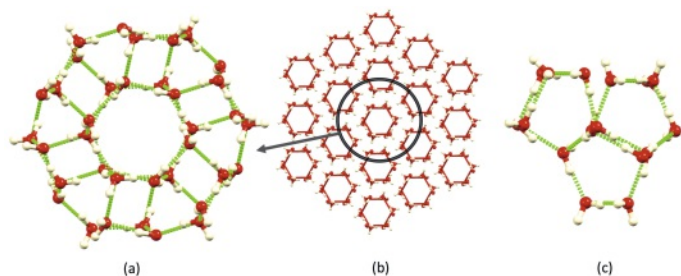


Fig. 4. Parts of the 3D-structures of (a), (b) ice II and (c) ice IX (ICSD codes 23703 and 28415, respectively). Hydrogen bonds are shown in green in (a) and (c). See text for explanations.

So far, we have focused only on the hydrogen-bonded networks in ice, and the key building block in all these structures is a tetrahedral unit (Fig. 3a). However, this is a good opportunity to expand the discussion to a range of inorganic materials, the structures of which are defined by tetrahedral building blocks. Most students are familiar with the structure of diamond comprising covalently bonded, tetrahedral carbon atoms. Three important classes of inorganic materials with related structures are silica,<sup>[7]</sup> sili-

cates and aluminosilicates, including zeolites. Elemental silicon does not occur naturally on our planet, but 27.7% of the Earth's crust is composed of  $\text{SiO}_2$  (e.g. sand and quartz) and silicate minerals. Common to all their structures is an  $\{\text{SiO}_4\}$ -building block, three representations of which are shown in Fig. 5a. While the Si atom is explicitly shown in the stereochemical structure on the left, the second and third representations depict only the tetrahedral shape defined by the O atoms. In  $\text{SiO}_2$ , each O atom is covalently bonded between two Si atoms, while in silicates or aluminosilicates, each O atom in an  $\{\text{SiO}_4\}$ -tetrahedron may be part of an Si–O–Si bridge or a terminal Si–O<sup>−</sup> unit. Polymorphs of  $\text{SiO}_2$  include  $\alpha$ - and  $\beta$ -quartz,  $\alpha$ - and  $\beta$ -tridymite and  $\alpha$ - and  $\beta$ -cristobalite. At room temperature and pressure, the thermodynamically stable form of  $\text{SiO}_2$  is  $\alpha$ -quartz, the structure of which is shown in Figs. 5b and 5c. The phase change from  $\alpha$ - to  $\beta$ -quartz occurs at 846 K (at atmospheric pressure) and a comparison of Figs. 5c and 5d reveals a change in symmetry.  $\alpha$ -Quartz has trigonal symmetry and  $\beta$ -quartz has hexagonal symmetry. The  $\text{SiO}_4$  units remain intact and there is a small change in the Si–O–Si bond angle from  $144^\circ$  to  $153^\circ$  on going from  $\alpha$ - to  $\beta$ -quartz.

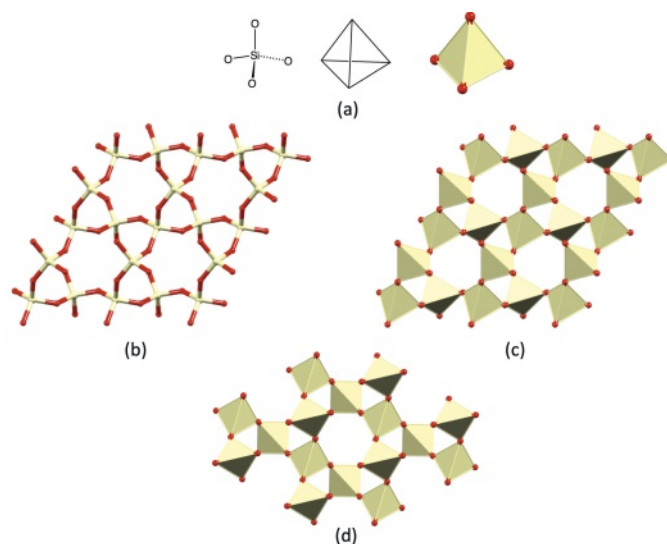


Fig. 5. (a) Three representations of a tetrahedral  $\{\text{SiO}_4\}$ -building block. The structure of  $\alpha$ -quartz (b) in a ball-and-stick representation (red, O; cream, Si) and (c) in a polyhedral representation. (d) Part of the 3D-structure of  $\beta$ -quartz. Data: ICSD codes 16331 and 93975.

This article has introduced the idea of tetrahedral building blocks in crystal lattices using hydrogen-bonded  $\text{H}_2\text{O}$  molecules in polymorphs of ice and covalently linked  $\{\text{SiO}_4\}$  units in silica as examples. The general concept of connecting tetrahedral units can be extended to diamond and inorganic materials such as silicates and zeolites, and we shall explore the structures of naturally occurring silicates and aluminosilicates in a future Education Column.

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<sup>a</sup>This column is one of a series designed to attract teachers to topics that link chemistry to Nature and stimulate students by seeing real-life applications of the subject.