Revisit to the structure of Ice XV: a DFT study

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There are open questions in the study of ice XV, the ordered phase of ice VI. The previous studies give inconsistent results between permittivity measurement (Johari & Whalley, 1976), neutron diffraction study (Saltzmann et al. 2009), and theoretical studies (Kuo & Kuhs, 2006; Knight & Singer, 2005). Permittivity measurements and theoretical study suggest that ice XV is ferroelectric, whereas neutron diffraction study suggests that ice XV is anti-ferroelectric.
To obtain the consistent result, we classified 45 possible hydrogen configurations using a newly developed invariant, and then performed neutron Rietveld analyses and DFT calculations for every 45 possible configurations. The Quantum Espresso (Giannozzi et al. 2009) was used for the DFT calculations (Hohenberg and Kohn, 1964; Kohn and Sham, 1965). Quantum Espresso is a package for the calculation of electronic structure properties using a plain-wave basis set and pseudopotentials. We used Perdew-Burke-Ernzerhof type non-empirical exchange-correlation functionals (Perdew et al, 1996) for this study. PBE type Xc/Corr energy form gives similar energy tendency (del Ben et al., 2014) with approximations from wave function theory such as a MP2 (Head-Gordon et al. 1988) and RPA (Macher et al., 2014). The pseudopotentials are derived using Troullier-Martins Method (Troullier and Martins, 1991). The enthalpies of 45 possible configurations for ice XV were calculated within an unit cell with the kinetic energy cutoff of 70 Ry and the Brillouin zone k mesh of 5 x 5x 6. The cell and atomic parameters were optimized using BFGS quasi-Newton method (Broyden, 1970; Fletcher, 1970; Goldfarb, 1970; Shanno, 1970) at atmospheric pressure. The phonons were calculated using density functional perturbation theory (Baroni et al., 2001). To correct the effect of zero-point motions of atoms, we added calculated phonon energy ($=1/2\Sigma_n\omega_n$) to the enthalpies from structural optimizations for each configuration. The effect of ferro-electricity were corrected by the Ewald construction, the same as the previous work about ice XV (Del Ben et al., 2014).
A consistent result was obtained about the structure of ice XV that the experimentally obtained ice XV have *Pmmn* space group, that is, the structure of ice XV is partially ordered structure. Our DFT calculations with surface effect corrections suggest that the energy difference between 45 possible patterns is between 0.05 eV (20 K in the reduced temperature). Moreover, the energy differences among several lower energy configurations are within 0.01 eV. Such a small energy difference gives us an interpretation of our experimental result that the ice XV has a *Pmmn* space group as time-space averaged structure.

Keywords: Ice, Density Functional Theory