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# Anomalies and phase transitions of dense ice

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## Abstract

The phase diagram of water ice, H2O is dominated above 3 GPa by several dense structures [1], which are all based on a body-centered cubic sub-lattice of O. In the ices VII and VIII the molecular integrity is preserved. Ice VII is disordered with the dipole of the water molecules pointing randomly along the three cartesian axis, such as the average structure is cubic. Ice VIII is an ordered low-temperature variant of ice VII with tetragonal symmetry, where the dipoles point along the fourfold symmetry alternatively up and down; the result is an antiferroelectric structure. Both ices VII and VIII exhibit anomalies in the diffraction pattern and Raman spectra inconsistent with their initial symmetry assignment. Beyond about 100 GPa the molecular integrity is lost and the structure, the ice X, becomes ionic. Here the H atoms are midway between their O neighbors, preserving the cubic symmetry.

First-principles calculations based on density-functional and density-function perturbation theories were performed to investigate the stability fields and the transition paths of these different high-dense ices.

We propose that the anomalies in ice VII and ice VIII can be explained by the formation of ferroelectric (FE) and anti-ferroelectric (AFE) domains. In the FE domains the dipoles point along the same direction along the 4-fold axis, while in AFE they point alternatively up and down. The splitting of the X-ray diffraction peaks and the appearance of new Raman modes are the result of different a/c ratios in the two FE and AFE parts of the structure [2,3].

Then, based on lattice dynamical calculations, we show that the transition between ices VII and VIII and ice X goes through a disordered phase X in the 60-115 GPa pressure range. In this regime the H atoms are allowed to freely bounce back and forth between their two O neighbors. Ice X is stable up to about 420 GPa. The first post-ice-X structure occurs due to a phonon softening in ice X. The resulting structure has orthorhombic symmetry [4,5,6]. We show that the softening is also visible in the development of an elastic anomaly after 160 GPa.

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## References

[1] R.J. Hemley, Effects of high pressure on molecules, Annu. Rev. Phys. Chem. Vol. 51, pp. 763-800, 2000).

[2] M. Somayazulu, J. Shu, C. S. Zha, A. F. Goncharov, O. Tschauner, H. K. Mao, and R. J. Hemley, In-situ high-pressure x-ray diffraction study of H2O ice VII, J. Chem. Phys., Vol. 128, 064510, 2008.

[3] R. Caracas R.J. Hemley, Ferroelectric high-dense ice, submitted, 2011.

[4] M. Benoit, M. Bernasconi, P. Focher, and M. Parrinello, New high-pressure phase of ice, Phys. Rev. Lett., Vol. 76, pp. 2934-2937, 1996.

[5] R. Caracas, Dynamical instabilities of ice X, Phys. Rev. Lett., Vol. 101, 085502 (2008)

[6] B. Militzer and H. F. Wilson, New phases of water ice predicted at megabar pressures, Phys. Rev. Lett., Vol. 105, 195701, 2010.