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A Critical Point of Ice VII

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Ice VII is a crystalline phase of water ice under high pressure, which forms cubic crystal of space group Pn-3m, being stable in a wide pressure range between 2.2 GPa and 60 GPa at room temperature. Although ice VII is traditionally considered as a single phase of water ice, there have been several reports on the transition of its structure and properties around 10-20 GPa[1]. Here we propose to interpret these transitions as the continuous crossover between two states of ice VII across the Widom line (the phase boundary extended over the critical point) of a solid-solid critical point (T_c≈100 K, P_c≈14 GPa) in the metastable region of ice VII, below which metastable ice VII separates into a 'rotational' phase at low pressure and an 'ionic' phase at high pressure. Various structural and spectroscopic anomalies reported for ice VII may be interpreted as the supercritical phenomena of the solid-solid critical point. In particular, the structure transition proposed by Guthrie *et al.[2]* is discussed in this talk.

1. Introduction

Water is a mysterious molecule. Its peculiar nature is sometimes related to the existence of a critical point, a point in the phase diagram where a phase boundary terminates and the distinct phases merge into a homogeneous supercritical state. Above the vapor-liquid critical point of water (Tc=647 K, Pc=22.064 MPa), distinct liquid water and vapor phases merge into a supercritical fluid, which has properties of both vapor and liquid. A hypothetical liquid-liquid critical point (Tc≈220 K, Pc≈100 MPa)[3] has been proposed deep in the supercooled region of liquid water, below which homogenous liquid water separates into a low-density liquid and a high-density liquid. The liquid-liquid critical point is believed to be the origin of various anomalous properties of liquid water including the maximum density at 4℃.

At 2 GPa and room temperature, water transforms from ice VI to ice VII, which consists of water molecules forming bcc oxygen lattice and random hydrogen bond network. The network forms two interpenetrating but independent sublattices with the structure of ice Ic. As pressure increases from 2 GPa to 60 GPa, the bcc oxygen lattice remains stable with reduced lattice constants, while the hydrogen bond network evolves from the statically random to the dynamically random and eventually to the symmetric state. Ice VII exhibits many phenomena originating from the complex proton dynamics, of which X-ray diffraction provides very little information.

Here we speculate the existence of a solid-solid critical point (T_c≈100 K, P_c≈14 GPa) in the metastable region of ice VII (Fig. 1), which is related to the recent Raman spectroscopy measurement[4]. The critical point may be the origin of the two states of Ice VII, and various structural and spectroscopic anomalies reported for ice VII may be interpreted as the supercritical phenomena: transition of electric charge carrier around 10 GPa was observed by impedance spectroscopy[5]; the pressure dependence of dissociation rate of water molecules was observed with X-ray Raman Spectroscopy(XRS)[6, 7]; Guthrie *et al.[2]* reported that the neutron diffraction pattern of deuterated ice VII starts to deviate at 13GPa from the ideal pattern of ice VII structure. They proposed the high pressure structure with dissociated D_2O molecules and substantial deuteron density (occupancy~1) at the octahedral interstitial sites.

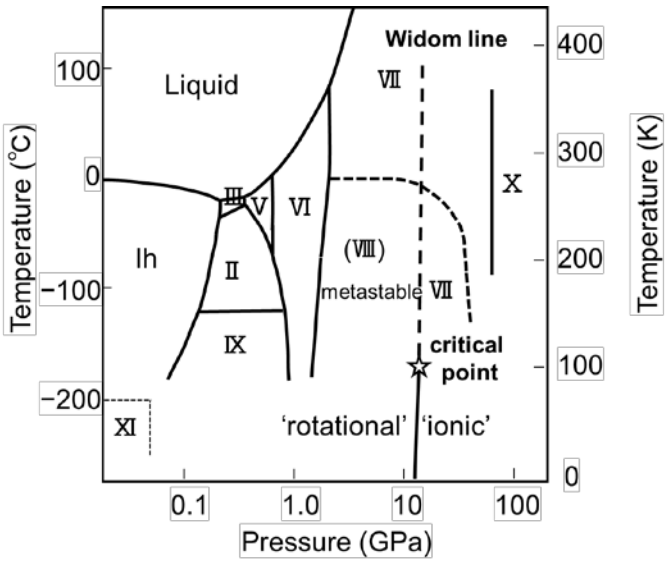

Figure 1: Proposed phase diagram of H_2O

2. Computational

Considering the similarity in transition pressures and transition manners, the transitions observed in the neutron experiment and impedance spectroscopy may have the same origin, i.e., the speculated solid-solid critical point. Therefore, it would be interesting to examine the details of the proposed interstitial model. First, *ab initio* molecular dynamics simulations of ice VII at 300 K and various pressures for 100 ps were performed in order to study the pressure dependence of interstitial occupancy. Second, the XAS (XRS) spectra were calculated for the normal ice VII and for the interstitial model in order to see if they are distinguishable.

3. Results and Discussion

Although the deviation in the diffraction pattern above 13 GPa clearly implies a change of crystal structure, which is consistent with our speculation and worth further investigation, the simulations suggest that the interstitial model needs more careful examination by XRS measurement. Spontaneous dissociation of water molecule of such high degree at this pressure range should be detectable with XRS. The better fit in neutron diffraction pattern does not always mean that the model structure is correct.

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