X-ray diffraction study of ice VIII at low temperature and high pressure

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Introduction

Molecular phases VII and VIII of ice appear at high pressure above 2 GPa [1]. Their crystal structures are constructed essentially by the body-centered lattices of oxygen atoms with disordered protons in a high-temperature phase VII (cubic — P*n*3*m*) and with ordered protons in low-temperature phase VIII (tetragonal —$I4_1/amd$). Recent infrared [2-4] and Raman [5] experiments have revealed that the transition from ice VII to an atomic phase X with hydrogen-bond symmetrization at 58 GPa and room temperature. The structural study of ice VIII is crucial for understanding of the mechanisms of the order–disorder transition (VIII–VII) and of the hydrogen-bond symmetrization (VIII–X) at low temperature.

Experimental

High pressure was generated with a gas-driven diamond-anvil cell (DAC). Powdered ice was prepared by grinding ice in a mortar cooled by liquid nitrogen. Pressure was determined on the basis of ruby fluorescence method.

Powder x-ray diffraction patterns were measured on the beamline 18C at the Photon Factory, KEK. The DAC was placed in a cryostat with a helium gas refrigerator. The x-ray was monochromatized to 20.00 keV. Diffraction rings from the powder sample were recorded on an imaging plate with a typical exposure time of 10 min.

Results and Discussion

Powder x-ray diffraction patterns of ice were obtained as a function of pressure at 266±2 K and at 87±3 K. The pressure variation of unit-cell volume measured for ice VIII at 266 K shows a step of about 0.1 cm^3/mol near 17 GPa, indicating a phase transition. The transition from VIII to VII was identified in the observed diffraction patterns, which showed peak unification associated with the structural conversion from the tetragonal to cubic lattice.

The volume of ice VIII at 87 K decreases continuously up to 50 GPa, indicating no signature of phase transition (Fig. 1). The compression data were fitted by a Birch-Murnaghan equation of state, giving B_0 = 28.7 GPa and B_0' = 3.9; the V_0 value was fixed to 12.04 cm^3/mol calculated for ice VIII at 0.1 MPa and 85 K [6]. The similarity between the compression curve of ice VIII and that of ice VII at 300 K is intuitively understood because these high-pressure ices have essentially the same body-centered oxygen lattices. In addition, the tetragonal lattice in ice VIII approaches to the cubic lattice as pressure increased.

An isobar experiment provided the thermal expansion for ice VIII. A decrease in volume from 9.85 to 9.73 cm^3/mol was obtained with a temperature decrease from 300 to 140 K at about 8 GPa. We assumed little change in volume at the VII–VIII transition, and obtained an averaged thermal expansion coefficient $\alpha = 8\times10^{-5}\ K^{-1}$.

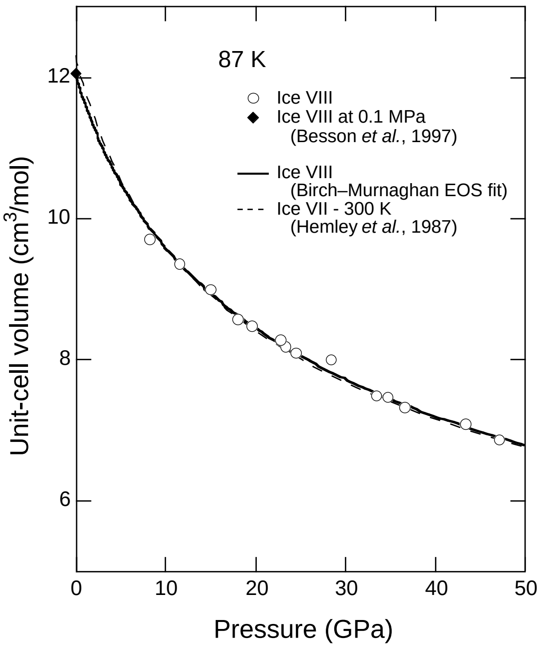

Figure 1 Variation of unit-cell volume against pressure for ice VIII at 87±3 K. A solid line shows the compression curve fitted by a Birch–Murnaghan type equation of state. A dashed line shows the compression curve of ice VII at 300 K (Hemley *et al.* [7]).

References

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