First-principles study of hydrogen bond symmetrization of phase D under high pressure

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ABSTRACT

We have investigated the physical and structural properties of phase D (MgSi2O6H2) at high pressure by means of a first-principles calculation method. Phase D is important as a dense hydrous magnesium silicate with high stability under pressure, and as one of the most likely candidates for a water reservoir in the Earth's lower mantle. The calculated compression behavior of phase D is in very good agreement with experimental results. We found a distinct but continuous change from asymmetric to symmetric hydrogen bonding in phase D at 40 GPa. This pressure-induced hydrogen bond symmetrization has a significant effect on the compression behavior of phase D. The bulk modulus increases by about 20% with this structural change. This behavior of pressure-induced hydrogen bond symmetrization is very similar to that previously reported by us for δ-AlOOH. The transition is reversible and second-order, and thus the high-pressure state is probably unquenchable.

INTRODUCTION

The question of the existence of water in the Earth's deep mantle is of interest because it is thought that water affects the physical properties of the Earth's constituent minerals. Numerous studies have been conducted in relation to the quest for stable hydrous or nominally anhydrous minerals in the Earth's interior (Smyth 1987; Inoue et al. 1995; Kohlstedt et al. 1996; Ono 1998; Ohtani et al. 2001; Murakami et al. 2002). While most hydrous minerals decompose by releasing water under high pressure and temperature, dense hydrous magnesium silicates (DHMS) are stable under the conditions of the slab's geotherm. Therefore, they are believed to be major resources of water in subducting slabs. Among them, phase D is the strongest candidate for water supplier to the lower mantle, since it is the highest pressure DHMS known. It has been experimentally reported that phase D is stable under the pressure and temperature conditions of the upper part of the lower mantle along cold slab geotherms (Liu 1987; Frost and Fei 1998, 1999; Shieh et al. 1998, 2000; Angel et al. 2001).

In many hydrous minerals, the hydrogen atom is covalently bonded to oxygen as hydroxyl and is also weakly attracted to a neighboring oxygen atom on the opposite side. This hydrogen bonding attraction is explained as being predominantly electrostatic and partly covalent (Isaacs et al. 2000). The hydrogen bonding energies range from 0.1 to 15 kcal/mol, and thus they are usually much weaker than common chemical bonds (80–100 kcal/mol). The strength of hydrogen bonds is approximately estimated by their interatomic distances, and more precisely, by their stretching vibration frequencies. It is well known that as the strength of the hydrogen bond O⋯H increases, that of the O-H bonding decreases. Vibrational spectroscopic studies show that a decrease of O-H frequency is commonly observed under high pressure and is interpreted as indicative of increasing hydrogen bond strength. However, it has also been shown that the strength of the hydrogen bonding can either increase or decrease under high pressure, depending on crystal structure and chemical composition (Kagi et al. 2000; Williams and Hemley 2001 and references cited therein; Kleppe et al. 2003; Bradbury and Williams 2003). The effect of pressure upon hydrogen bonding in DHMS is still not well understood and minute investigation of the interaction of hydrogen bonds with surrounding atoms is needed to understand their physical properties.

We reported first-principles investigations of the structural and physical properties of the recently discovered high pressure hydrous phase of AlOOH (δ-AlOOH), which is also a possible supplier of water to the lower mantle (Tsuchiya et al. 2002). According to this study, δ-AlOOH has a very strong hydrogen bond even at ambient pressure. The stable hydrogen position in this phase shifts to the middle point of two neighboring O atoms under lower mantle pressure conditions at about 28 GPa. We found that this symmetrization of the hydrogen bond strongly affects the compression behavior of δ-AlOOH. The bulk modulus increases by more than 20% with symmetrization. The predicted transition pressure of 28 GPa corresponds to the depth of the upper part of the lower mantle. If δ-AlOOH forms in the lower mantle, it would have a symmetric hydrogen bond. A similar hydrogen bond compression behavior can also be expected in phase D. In this study, we mainly focus on the hydrogen bond properties of phase D as a function of pressure. Our aim is to clarify the relationship between the hydrogen bonding and the compression mechanism of phase D using a first-principles theoretical method.

Phase D was first reported by Liu (1987) as a high-pressure product of serpentine. Another new DHMS phase, reported by Ohtani et al. (1997), was revealed to be identical to phase D.