Vibrational properties of $\delta$-AlOOH under pressure

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**ABSTRACT**

We have performed first-principles calculations to investigate the behavior of the hydrogen bond in $\delta$-AlOOH under pressure. The highest OH-stretching $A_1$ and $B_2$ mode frequencies decrease under pressure leading to hydrogen bond symmetrization. After hydrogen bond symmetrization, the corresponding frequencies gradually increase. This softening and subsequent hardening of the OH bonds is a good spectroscopic indicator of hydrogen bond symmetrization and is observed in our GGA static calculations at $\approx 30$ GPa without considering tunneling effects. We have also carried out calculations of Raman peak intensities in several supercells with various hydrogen orderings to investigate the potential effect of H-disorder on the Raman spectrum of $\delta$-AlOOH. Our results suggest that the four broad Raman bands observed experimentally in the range of OH-stretching mode frequencies could originate in H-disorder in this phase.

**Keywords:** Hydrogen bond, hydrous mineral, first-principles calculation, vibrational property, high pressure

**INTRODUCTION**

The existence of water in deep Earth minerals is known to affect their viscosity, melting temperature, and elastic properties. It is believed that water is transported into the deep mantle by hydrous minerals in subducting cold slabs. Although some experiments showed destabilization and decomposition of hydrous minerals and release of water at high pressures and temperatures (e.g., Ono 1998; Okamoto and Maruyama 1999; Irifune et al. 1998), $\delta$-AlOOH has been shown to be stable from 40–130 GPa and 1270–1750 K (Sano et al. 2006). Because of this extraordinary stability, this phase is a potential water reservoir in cold slabs and a carrier of water into the deep mantle (Ohtani et al. 2001; Sano et al. 2006).

A powder-crystal X-ray diffraction experiment demonstrated that the crystal structure of $\delta$-AlOOH without H atoms can be assigned as orthorhombic with the space group $P2_1nm$, which is very close to the CaCl$_2$ structure (Suzuki et al. 2000). Single-crystal X-ray diffraction experiments identified the symmetry of $\delta$-(Al$_{0.84}$Mg$_{0.07}$Si$_{0.09}$)OOH to be $Pmn2_1$. This structure has H atoms in two distinct sites, one forming a bifurcated hydrogen bond and the other situated $\approx 0.3$ Å away from O···O line with O-H···O angle of $\approx 154^\circ$. (Kudoh et al. 2004). Single-crystal X-ray diffraction experiment of $\delta$-AlOOH recently confirmed the space group $P2_{1}nm$ with ordered H position (Komatsu et al. 2006).

The stability of these hydrogen sites of $\delta$-AlOOH have also been investigated theoretically by means of first-principles techniques (Tsuchiya et al. 2002). Two types of low-pressure phases characterized by asymmetric hydrogen bonds were predicted and H-bond symmetrization was found in both at $\approx 30$ GPa using generalized gradient approximation (GGA, Perdew et al. 1996) as the exchange-correlation functional. A similar first-principles calculation of $\delta$-AlOOH also identified a symmetric H-bond phase even at 0 GPa (Panero and Stixrude 2004), though their calculation was performed using local density approximation (LDA). This discrepancy is clearly caused by difference between GGA and LDA, since LDA has been shown to be unsuitable for describing H-bond systems (Hamann 1997) and its deficiency is too large to be compensated by other factors (temperature and quantum zero-point motion effects).

Though vibrational and tunneling effects might modify the transition pressure, it suggested that $\delta$-AlOOH probably exists in the symmetric hydrogen bond form at lower mantle pressure conditions. Raman spectroscopy measurements of the OH vibrations in $\delta$-AlOOH at ambient conditions (Ohtani et al. 2001; Xue et al. 2006) have reported four broad unassigned peaks in the OH stretching vibration region between 2000 and $2800 \text{ cm}^{-1}$, indicating strong and asymmetric hydrogen bonds.

Recent experiments have reported that $\alpha$-AlOOH (diaspore), a lower-pressure phase of $\delta$-AlOOH, persists up to $\approx 50$ GPa at room temperature (Friedrich et al. 2007a). The theoretical phase boundary between $\alpha$ and $\delta$ phase is reported by Li et al. (2006) to be $\approx 18$ GPa at static 0 K condition. Although this suggests discrepancy between experiment and theory, this difference is simply because in the room-temperature experiments, the transition from diaspore to $\delta$-AlOOH was kinetically hindered and diaspore was observed to exist metastably beyond its stable pressure range. Instead, high-temperature experiments (Suzuki et al. 2000; Ohtani et al. 2001; Sano et al. 2004) already report the phase boundary between diaspore and $\delta$-AlOOH is about 17 GPa, which is in excellent agreement with the GGA transition pressure.