Absence of proton tunneling during the hydrogen bond symmetrization in δ-AlOOH

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δ-AlOOH is of significant crystallochemical interest due to a subtle structural transition near 10 GPa from a P21 nm to a Pnnm structure, the nature and origin of hydrogen disorder, the symmetrization of the O-H⋯O hydrogen bond and their interplay. We perform a series of density functional theory based simulations in combination with high-pressure nuclear magnetic resonance experiments on δ-AlOOH up to 40 GPa with the goal to better characterize the hydrogen potential and therefore the nature of hydrogen disorder. Simulations predict a phase transition in agreement with our nuclear magnetic resonance experiments at 10−11 GPa and hydrogen bond symmetrization at 14.7 GPa. Calculated hydrogen potentials do not show any double-well character and there is no evidence for proton tunneling in our nuclear magnetic resonance data.

INTRODUCTION

Hydrogen is an important chemical component in the Earth’s mantle, as even a small amount can strongly affect key properties of minerals, such as melting temperature, rheology, electrical conductivity and atomic diffusion [1–4]. Therefore, over the past 20 years, many hydrous minerals, such as dense hydrous magnesium silicates [5], have been synthesized at high-pressure (P) and high-temperature (T) conditions and investigated as potential candidates for hydrogen transport to the lower mantle. However, most of these minerals decompose at P < 60 GPa, where phase H breaks down to MgSiO3 bridgmanite and a fluid component [6–8].

In 2017, AlSiO3(OH) was found in diamond inclusions [9] from the mantle transition zone at a depth of 410-660 km. High-P, high-T experiments revealed that this phase can form from hydrous sediment components at upper mantle conditions (10 - 12 GPa) [10], and decomposes to δ-AlOOH and SiO2 stishovite at conditions similar to those found at the base of the mantle transition zone (P >20 GPa) [11]. δ-AlOOH is particularly interesting as it shows a wide stability range including conditions along the geotherm of a subducting slab [12–14] and may therefore be a potential host of hydrogen in Earth’s lower mantle.

δ-AlOOH crystallizes in a primitive orthorhombic lattice with space group P21 nm at ambient conditions [12, 13, 16]. Its structure corresponds to distorted rutile, with Al and O atoms located on mirror planes (Fig. 1). AlO6 octahedra share edges along the c axis and these octahedra chains are connected via corners (Fig. 1). There are two distinct oxygen positions (O1 and O2) at the vertices and in the equatorial plane, respectively. Layers of AlO6 octahedra oriented in different directions are connected with an asymmetric hydrogen bond between the layers.
ice-X transition [24–26]. No direct evidence of tunneling has been found to date, however.

We investigate the phase transition, hydrogen bond symmetrization (a central uni-modal proton distribution between the two respective oxygen atoms) and the possibility of proton tunneling in $\delta$-AlOOH, combining density functional theory (DFT) based calculations and high and low field high-$P$ nuclear magnetic resonance (NMR) spectroscopy. With DFT, we perform a stepwise optimization of the host lattice and the hydrogen positions over a wide volume ($V$) range and analyze the potential seen by the hydrogen atoms as well as the geometry of the AlO$_6$ octahedra. We analyze the signal shift as well as the full width at half maximum (FWHM) of the high-field NMR experiments at $P$ up to 40 GPa (c.f. Fig. S1 of the supplementary material [27]), searching for characteristic features of a phase transition, and use low-field NMR data at 5.6 GPa to investigate indications of proton tunneling [25].

**FIG. 2.** Comparison of normal (dotted) and inverse (solid) sampling (Fig. S2 in the supplementary material [27]) of the potential seen by the hydrogen atom. At large volumes (low $P$), normal sampling leads to a symmetric and inverse sampling to an asymmetric single-well potential with a significantly lower energy ($\sim 0.2$ eV). With increasing compression, this difference vanishes as the two oxygen positions become equivalent. By construction, the potentials are equivalent at the central position (indicated by the vertical dashed line).

**COMPUTATIONAL DETAILS**

All DFT simulations are performed using the Quantum Espresso package [28, 29], where possible GPU-accelerated [30]. We use projector augmented wave atomic files for Al, O and H based on the PBEsol [31] approximation to exchange-correlation which was previously found to show excellent agreement with experimental data [22]. For Al the $2p$ electrons and lower and for O the $1s$ electrons are treated as semi-relativistic core states. Convergence tests with a threshold of $10^{-5}$ Ry/atom lead to a Monkhorst-Pack k-point grid [32] of $12 \times 8 \times 8$ for primitive unit cells and a cutoff energy for the plane wave expansion of 140 Ry. We use the FINDSYM code [33] for symmetry analysis and VESTA 3 [34] for visualization of structures.

**EXPERIMENTAL DETAILS**

High-$P$ cells with pairs of 250 $\mu$m culet diamond anvils are used, and the preparation of the NMR experiments closely follows the procedure outlined in our previous work [35]. 3.2 mm excitation coils are formed from single turn cover inductors made from 50 $\mu$m copper-coated teflon foil. The diamond anvil is coated with 1 $\mu$m of copper using physical vapor deposition, and subsequently Lenz lens resonators are cut out of this layer using focused ion beam milling.

A $20 \mu$m$^3$ crystal of $\delta$-AlOOH (synthesis described in [36]) is placed in the sample chamber and the DAC is filled with neon as a $P$-transmitting medium. Both excitation coils are mounted central to the diamond anvils and connected in a Helmholtz coil arrangement after closing the cell. For the high-field measurements, 1045 mT with a corresponding $^1$H resonance frequency of $\sim 45$ MHz in an electromagnet is used. Additional homonuclear $^1$H-$^1$H decoupling experiments are conducted using a Lee-Goldburg [37] saturation pulse of 25 W prior to the spin excitation to obtain high resolution $^1$H-NMR spectra. An additional DAC prepared in a similar manner is filled with distilled H$_2$O and used as a resonance shift reference. Low-field measurements are performed at 125 mT and a resonance frequency of $\sim 5$ MHz, using the same electromagnet. Resulting spectra are analyzed by line form matching to the experimental signal [38]. Pressure is calculated from the Raman signal of the diamonds [39, 40] and the AlOOH volume using the equation-of-state (EOS) from Simonova et al. [36].

**STRUCTURAL OPTIMIZATION & HYDROGEN POTENTIAL**

In the computations, we start structural optimization with reported experimental low-$P$ structures from Komatsu et al. [15] and Sano-Furukawa et al. [20] and optimize the hydrogen position for $V$ between 57 and 47 Å$^3$. We sample and optimize the hydrogen positions along the diagonal oxygen-oxygen direction first, relax the coordinates of all atoms, perform a second sampling and
optimization of the hydrogen positions, relax the cell parameters and perform a final sampling and optimization of the hydrogen positions. Both initial structures \[15, 20\] converge to the same coordinates within the first steps of the relaxation.

We sample configurations by displacing the hydrogen atoms along the diagonal oxygen-oxygen direction in the \(a\)-\(b\) plane by starting with both hydrogen atoms being close to the respective oxygen atom with the smaller \(b\) coordinate (normal configuration) and from the configuration shown in Fig. 1 (inverse configuration), c.f. Fig. S2 of the supplementary material \[27\]. From the energy obtained in each sampling step, we construct the potential seen by the hydrogen atom, similar to our previous work on the ice-VII to ice-X transition \[20\] via spline interpolation at each sampled \(V\) for both configurations. The final positions of the hydrogen atoms are obtained as the minima of the respective spline interpolation (Fig. 2).

We find distinctly different potential symmetries for normal and inverse sampling with respect to the center of the diagonal oxygen-oxygen distance: normal sampling results in a symmetric potential, inverse sampling in an asymmetric potential (\(\sim 0.2\) eV lower in energy). Under compression the potentials become narrower in both sampling types, and for inverse sampling asymmetry decreases. At \(V \leq 52.4 \pm 0.1\) \(\text{Å}^3\) the potential obtained by inverse sampling becomes symmetric and the energy difference between the two potentials approaches zero, with the inverse sampling remaining slightly lower in energy over the full \(V\) range.

Contradicting prior suggestions \[21, 22\], both potentials do not show any double-well character, even though calculating the potential seen by the hydrogen atom from Kohn-Sham DFT should strongly overestimate the potential well without further consideration of the quantum nature of the hydrogen atoms \[22, 26, 41\].

After each optimization step, we analyze the space group of the resulting cell and track the rotation of AlO\(_6\) octahedra using angles \(\omega\) and \(\omega'\) as defined by Sano-Furukawa et al. \[20\] as a function of compression (Fig. 3).

We find an increase in the angle of \(\sim 0.6^\circ\) when compressing from 57 \(\text{Å}^3\) to \(\sim 53\) \(\text{Å}^3\), followed by a decrease at higher compression for both \(\omega\) and \(\omega'\). The angles are in general \(\sim 0.5^\circ\) larger than the experimental values by Sano-Furukawa et al. \[20\] which show large scatter; the difference between \(\omega\) and \(\omega'\) and the \(P\) dependence they report are in very good agreement with our calculations.

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

NMR experiments employing Lee-Goldburg decoupling pulses lead to line widths of \(\sim 1.5\) ppm (shown for 8 and 11 GPa in Fig. 4) which permits the analysis of chemical shifts with \(\sim 10\) ppm (Fig. 4c). For the chemical shift, we find an abrupt change at \(P = 9.9\pm0.6\) GPa from \(\sim 5\) ppm to \(>12\) ppm, indicating a structural change in the chemical environment of the hydrogen atoms as expected for a phase transition. We find a single proton signal over the full pressure range indicating a unique, geometrically well defined proton position, in agreement with an earlier NMR study at ambient conditions by Xue and Kanzaki \[42\].

Lee-Goldburg decoupling, while retaining information about the isotropic chemical shift interactions and strongly focusing the line width, leads to a cancellation of the non-secular parts of the total spin Hamiltonian and thus to a loss of information about spin interactions due to chemical shift anisotropy, direct homo- and heteronuclear dipole-dipole as well as first order quadrupolar interactions. Therefore, we additionally analyze the line shape of \(^1\)H-NMR solid-echoes (Fig. S1 of the supplementary material \[27\]) and find a minimum in the line width at \(P = 12.7\pm0.4\) GPa (Fig. 4d), indicating a change in proton mobility.

Proton tunneling should lead to a zero field splitting accompanied by detectable tunneling side bands as it introduces an exchange between allowed magnetic transi-
In work on the ice-VII to ice-X transition in high-$P$ H$_2$O [25], we showed that such tunneling side bands can be resolved at high $P$ using low-field NMR, and that NMR is sensitive to changes in the tunneling rate during compression. We therefore employ the low-field setup at $P = 5.6$ GPa (Fig. 4b) and find no indication for tunneling side-bands in $\delta$-AlOOH, in agreement with the $P$ evolution of the calculated potentials, showing no double-well character over the respective compression range.

**EQUATION-OF-STATE**

In order to convert $V$ of the simulation cells to $P$, we use the optimized structures from the inverse configuration and fit a third order Birch-Murnaghan (BM3) EOS to total energy. We use the $V$ at which the potential symmetrizes ($52.4$ Å$^3$) to split the $E - V$ results in two sets and calculate an EOS for (i) the full $V$-range, (ii) $57 \geq V \geq 53.5$ Å$^3$ and (iii) $52 \geq V \geq 47$ Å$^3$ (Fig. 5a). We calculate the intersection of the enthalpy curves for (ii) and (iii) and estimate the transition $P$ as $11.3 \pm 0.6$ GPa (horizontal line in Fig. 5a), where the error is estimated from the shift when the point closest to the transition in the potential is in-/excluded from the respective $V$ ranges. The phase transition is of second order as we do not find a $V$ collapse.

The calculated EOS parameters (low-$P$: $V_0 = 56.0$ Å$^3$, $K_0 = 183$ GPa, $K'_0 = 3.7$ and high-$P$: $V_0 = 55.5$ Å$^3$, $K_0 = 224$ GPa, $K'_0 = 4.0$) are in good agreement with partial EOS parameters by Simonova et al. [36] (low-$P$: $V_0 = 56.51(8)$ Å$^3$, $K_0 = 142(5)$ GPa; high-$P$ part $V_0 = 55.56(8)$ Å$^3$, $K_0 = 216.0(5)$ GPa with $K'_0 = 4.0$ in both cases) and data from Suzuki et al. [44] and Kuribayashi et al. [18] at $V < 55$ Å$^3$ (Fig. 5b). At larger $V$, our EOS slightly underestimates $P$ compared to the experimental EOS, which is most likely caused by thermal effects not being included in the calculations.

Using the respective low-$P$ and high-$P$ EOS parameters, we convert all $V$ dependencies to $P$ dependencies and find potential symmetrization at $P = 14.7 \pm 0.4$ GPa and the maxima in $\omega$ and $\omega'$ at $P = 13.1 \pm 0.7$ GPa (Table I).

**DISCUSSION & CONCLUSION**

We have analyzed different properties of $\delta$-AlOOH that can be directly linked to the phase transition (chemical shift, EOS) and hydrogen bond symmetrization (potential symmetry), but also properties that should record an influence of both processes (angles $\omega$ and $\omega'$ as well as the NMR line width). We find features in the same three $P$ regions: (i) The phase transition characterized by the change in chemical shift at $9.9 \pm 0.6$ GPa and the change in the slope of the $E - V$ curve (and therefore splitting of the EOS) at $11.3 \pm 0.4$ GPa; (ii) a maximum in the angles $\omega$ and $\omega'$ at $13.1 \pm 0.7$ GPa and a minimum in the line width at $12.4 \pm 0.3$ GPa; (iii) the symmetrization of
FIG. 5. (a) Third order Birch-Murnaghan (BM3) equation-of-state fit to the total energy of the optimized structures from the inverse configuration sampling. The full $V$-range is fitted by the black curve, $V > 53.5 \text{ Å}^3$ by the blue curve and $V < 52 \text{ Å}^3$ by the teal curve. The vertical line shows the estimated transition from the potential analysis, and the horizontal line the intersection of the enthalpy calculated from the two partial BM3 fits. The inset shows a zoom of the area where low and high-$P$ partial EOS intersect. (b) Comparison of different $V - P$ data and equation-of-states from our calculations with literature data by Kuribayashi et al. [18], Simonova et al. [36] and Suzuki [44].

TABLE I. Calculated values of the transition pressure from the low-$P$ $P_{21}nm$ to the high-$P$ $P_{nm}$ structure of AlOOH. For the line width analysis, errors are estimated from the $P$ error and for the chemical shift from the $P$ resolution of the measurement. For the simulations, errors are estimated from the $P$ resolution of the sampling and for the EOS calculation as the difference between the intersection $P$ of the low-$P$ and high-$P$ sub-EOS (Fig. 5). The last three columns show literature data from Simonova et al. [36] (S+ 2020), Sano-Furukawa et al. [20] (SF+ 2018) and Pillai et al. [21] (P+ 2018).

| Criterion | NMR Shift | EOS | $<$AlOAl$>$ angles | NMR line width | Potential | S+ 2020 | SF+ 2018 | P+ 2018 |
|-----------|-----------|-----|-------------------|----------------|-----------|---------|---------|---------|
| $P$ (GPa) | $9.9 \pm 0.6$ | $11.3 \pm 0.6$ | $13.1 \pm 0.7$ | $12.4 \pm 0.3$ | $14.7 \pm 0.4$ | $>10$ (structural) | $9/18.1$ | $8/15$ |

Comparing our results with recently published experiments [20, 36] and computations [21, 22], we find that we match the phase transition measured via neutron diffraction by Sano-Furukawa et al. [20] and X-ray diffraction by Simonova et al. [36] at $\sim 10$ GPa in the NMR experiments and the calculations. Furthermore, we reproduce the hydrogen bond symmetrization estimate from the calculation of elastic constants by Cortona [22] and Pillai et al. [21] at $\sim 15$ GPa in our potential analysis. For angles $\omega$ and $\omega'$, we find the same increase in slope as Sano-Furukawa et al. [20], with a maximum at $13.1 \pm 0.7$ GPa. We take a closer look at the data by Sano-Furukawa et al. [20], values for the angles $\omega$ and $\omega'$ at the highest three $P$ points ($P \geq 13$ GPa) appear to decrease linearly with $P$, in agreement with our computational results (Fig. 3). The large scatter and limited $P$-range in the experimental data impedes a more detailed analysis, comparison and discussion, however.

The absence of a double well in our mapping of the hydrogen potential at any $V$ is supported by low-field NMR measurements which do not show any indication of tunneling side bands. Therefore, we conclude that, contrary to the ice-VII to ice-X transition [25, 26], there is no tunneling-induced proton disorder in $\delta$-AlOOH. The only observation directly linked to a double-well potential are the Fourier difference maps by Sano-Furukawa et al. [20] that describe an asymmetric proton distribu-
tion at $P > 9.5$ GPa, followed by a bimodal distribution to $P \lesssim 15$ GPa and a symmetric unimodal distribution at $P = 18$ GPa. According to our results and data, the intermediate (bimodal) state is not characterized by proton disorder. Rather, it reflects order with weak asymmetry that gradually decreases. Therefore, we suggest the following interpretation of the neutron data: As O1 and O2 become symmetrically equivalent during the structural transition from $P2_1/nm$ to $Pnnm$ at $\sim 10$ GPa, asymmetry can no longer be associated to an O1-H-...O2 bond, but an averaged picture emerges where protons are closer to former O1 and O2 atoms, which may be visible in the Fourier difference maps and lead to the bimodal distribution if projected onto a $Pnnm$ unit cell.

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