

Elasticity and acoustic velocities of δ -AlOOH at extreme conditions: A methodology assessmentChenxing Luo (罗晨星)¹, Yang Sun (孙阳)^{2,*} and Renata M. Wentzcovitch^{1,3,4,5,6,†}¹Department of Applied Physics and Applied Mathematics, [Columbia University](#), New York, New York 10027, USA²Department of Physics, [Xiamen University](#), Xiamen 361005, China³Department of Earth and Environmental Sciences, [Columbia University](#), New York, New York 10027, USA⁴Lamont–Doherty Earth Observatory, [Columbia University](#), Palisades, New York 10964, USA⁵Data Science Institute, [Columbia University](#), New York, New York 10027, USA⁶Center for Computational Quantum Physics, [Flatiron Institute](#), New York, New York 10010, USA

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Hydrous phases play a fundamental role in the deep-water cycle on Earth. Understanding their stability and thermoelastic properties is essential for constraining their abundance using seismic tomography. However, determining their elastic properties at extreme conditions is notoriously challenging. The challenges stem from the complex behavior of hydrogen bonds under high pressures and temperatures (P, T s). In this study, we evaluate how advanced molecular dynamics simulation techniques can address these challenges by investigating the adiabatic elasticity and acoustic velocities of δ -AlOOH, a critical and prototypical high-pressure hydrous phase. We compared the performances of three methods to assess their viability and accuracy. The thermoelastic tensor was computed up to 140 GPa and temperatures up to 2700 K using molecular dynamics with a DeePMD machine-learning interatomic potential based on the SCAN meta-GGA functional. The excellent agreement with ambient condition single-crystal ultrasound measurements and the correct description of velocity changes induced by H-bond disorder-symmetrization transition observed at 10 GPa in Brillouin scattering measurements underscores the accuracy and efficacy of our approach.

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I. INTRODUCTION

Water is an active participant in dynamic processes that shape the Earth. Typically incorporated in hydrous minerals or nominally anhydrous minerals (NAMs), water contributes to slab subduction and mantle convection by facilitating rock deformation and reducing melting temperatures of mantle silicates [1]. However, accurately quantifying water content in the mantle, particularly in the lower mantle, remains challenging because of the need for more relevant thermoelastic and sound velocity data for hydrous minerals necessary for interpreting seismic observations [2]. The complexity of measurements under extreme pressures and temperatures (P, T s) is exacerbated by hydrogen bonds' intricate behavior, e.g., strong anharmonicity, disorder-symmetrization transition, transition to a proton superionic behavior, dehydration, all difficult to quantify and might affect mechanical properties significantly.

To evaluate (a) the challenges that arise in determining the thermoelastic properties and sound velocities in hydrous systems and (b) how advanced computational simulations may address them, we investigate δ -AlOOH [3,4], a prototypical high-pressure hydrous mineral. According to previous studies, δ -AlOOH withstands the extreme pressure of the deep-lower mantle (up to 140 GPa) [4–8]. Its Al-O octahedron

forms a post-stishovite-like framework structure, representative of coexisting hydrous systems, e.g., MgSiO_4H_2 phase H [9], ϵ -FeOOH [10], and hydrous aluminous silica [11–13]. It is the simplest and one of the most well-studied high-pressure hydrous minerals [6,7]. δ -AlOOH undergoes H-bond disorder-symmetrization transition at ~ 5 –20 GPa at 300 K [8,14,15] and high-temperature proton diffusion above 1500 K [8]. This comprehensive understanding of δ -AlOOH's stability, structural transitions, and unique challenges make it ideal for understanding how well-advanced atomistic simulations can address elasticity and sound velocities for H-bonded systems under the mantle's extreme P, T s.

Previous studies have determined δ -AlOOH's elasticity and acoustic velocities in a limited P - T regime, revealing velocity profiles similar to those of anhydrous minerals (e.g., perovskite-type MgSiO_3 , stishovite-type SiO_2 , etc.) rather than typical hydrous minerals or NAMs [6,16]. However, they have anomalies, especially across the H-bond disorder-symmetrization transition [16,17]. Static *ab initio* calculations based on density functional theory (DFT) with the generalized gradient approximation (GGA/PBE) [17,18] up to 60 GPa predicted an anomalous jump in the elasticity and acoustic velocities due to “H-bond symmetrization” at 30 GPa. Brillouin scattering measurements of shear wave (V_S) and compressional wave (V_P) speeds on polycrystalline samples [16] to 120 GPa and 36.3 GPa, respectively, confirm this overall trend. However, the pressure-induced anomalies were observed at a much lower pressure, ~ 10 GPa. Meanwhile, a recent ultrasound measurement on single-crystal at ambient

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conditions [19] obtained velocities lower than the previous Brioullion scattering measurements. To reconcile these discrepancies and to determine these parameters under the lower mantle's more extreme P, T s, more accurate determinations of δ -AlOOH's elastic and acoustic properties over a broader pressure and temperature range are necessary.

Ab initio calculations using the quasiharmonic approximation and stress-strain relations have accurately predicted elastic properties of minerals at mantle conditions as long as harmonic vibrations are warranted at high pressures [20–23]. This method is not applicable for hydrous phases at mantle conditions, and one must resort to molecular dynamics (MD) simulations to address the strongly anharmonic behavior of H bonds. As an active research topic, the effectiveness of several MD simulation methods to compute high-temperature elasticity, including the strain vs stress method, strain fluctuation under isobaric conditions [24,25], and stress fluctuation under isentropic and isothermal conditions [26,27], are subjects of ongoing debate. Clavier *et al.* [28] presented an insightful overview of these methodologies. Additional discrepancies in finite-temperature elasticity may originate from definitions of elasticity under finite P, T s. For instance, the difference between isothermal (C_{ijkl}^T) and adiabatic elastic tensors (C_{ijkl}^S) is a non-negligible distinction at temperatures exceeding a few thousand Kelvin; the difference between the thermodynamic elastic tensor (A_{ijkl}) and the effective elastic tensor (C_{ijkl}) [29] under finite pressure still needs clarification. Given the need to derive sound velocities for meaningful comparisons with measurements, our objective here is also to derive the adiabatic effective elastic tensor, clarify these differences, and understand their implications.

In this study, we perform MD simulations using the deep potential (DP) neural network interatomic potential [30,31] developed [8] to accurately reproduce *ab initio* forces and energies obtained with the strongly constrained and appropriately normed (SCAN) meta generalized gradient approximation (meta-GGA) functional [32]. We evaluate δ -AlOOH's thermoelastic properties and acoustic velocities over the broad P, T range of the mantle, i.e., up to 140 GPa and 2700 K. SCAN-DPMD has proven effective in replicating measured pressure vs volume (P - V) relations at high P, T s [8] for δ -AlOOH, even with protons in the superionic regime. In addition, our previous studies suggested that meta-GGA functionals can accurately predict ionic solids' elastic and mechanical properties at extreme pressure and temperatures, particularly for hydrous systems [33,34]. Therefore, δ -AlOOH's thermoelastic properties should be equally well predicted. Based on these results, we highlight different definitions of elasticity and clarify the implications of different approaches at high P, T s.

The paper is structured as follows: Section II describes the methods used in this study, Sec. III presents the studies' findings, and Sec. IV presents our conclusions.

II. METHOD

In the subsequent sections, C_{ij} in uppercase represents the elastic tensor, c_{11} , c_{12} , etc., in lowercase represent the tensor components. Section II A uses the full Cartesian notation to describe the elastic tensor, while Sect. II B uses the Voigt

notation to describe the aggregate (isotropic) elastic coefficients. These are the standard notations for discussing these topics.

A. Formalisms for thermoelasticity

Here, we summarize three major approaches for computing the *adiabatic effective* thermoelastic tensor through MD simulations. While other methods exist, our study tests the techniques presented here.

1. The stress-fluctuation formalism

The *thermodynamic* elastic tensor A_{ijkl} ($i, j, k, l = 1, 2, 3$) is defined as the second-order strain derivative of the free energy (F) density for a system in equilibrium in MD simulations with a fixed simulation box of volume V . It is given by [26,35–37]

$$A_{ijkl}(T, V) = \frac{1}{V} \frac{\partial^2 F}{\partial \epsilon_{ij} \partial \epsilon_{kl}} = \langle A_{ijkl}^B \rangle - \frac{V}{k_B T} [\langle \sigma_{ij} \sigma_{kl} \rangle - \langle \sigma_{ij} \rangle \langle \sigma_{kl} \rangle] + \frac{N k_B T}{V} (\delta_{il} \delta_{jk} + \delta_{ik} \delta_{jl}), \quad (1)$$

where “ $\langle \cdot \rangle$ ” denotes the ensemble average over the simulation run time, ϵ_{ij} denotes the infinitesimal strain tensor, N the number of atoms, T the temperature, and δ_{ij} the Kronecker delta. The stress and Born matrix tensors (σ_{ij} and A_{ijkl}^B) are defined as the *instantaneous* first- and second-order derivative to the internal energy density (U/V) with respect to infinitesimal strains ϵ_{ij} , i.e.,

$$\sigma_{ij} \equiv \frac{1}{V} \frac{\partial U}{\partial \epsilon_{ij}} \quad \text{and} \quad A_{ijkl}^B \equiv \frac{1}{V} \frac{\partial^2 U}{\partial \epsilon_{ij} \partial \epsilon_{kl}}. \quad (2)$$

They are evaluated and recorded periodically during an equilibrated MD run. In practice, A_{ijkl}^B converges faster than σ_{ij} , but because it has more terms (21 for A_{ijkl}^B vs six for σ_{ij}) less frequent sampling of A_{ijkl}^B helps reduce storage requirements without compromising accuracy (see Sec. III D). In our calculation, A_{ijkl}^B is recorded every 200 MD steps and σ_{ij} is recorded every 20 steps. We evaluate A_{ijkl}^B through numerical differentiation via [36]

$$A_{ijkl}^B = \frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}} + \sigma_{il} \delta_{jk} + \sigma_{ik} \delta_{jl}. \quad (3)$$

For a simulation run with an average stress σ_{ij} , the *effective* elastic tensor C_{ijkl} is given by [29,38,39]

$$C_{ijkl} = \frac{1}{V} \frac{\partial^2 F}{\partial \epsilon_{ij} \partial \epsilon_{kl}} - \sigma_{ij} \delta_{kl} + \frac{1}{2} (\sigma_{ik} \delta_{jl} + \sigma_{kj} \delta_{il} + \sigma_{il} \delta_{jk} + \sigma_{lj} \delta_{ik}), \quad (4)$$

it is further simplified when the stress is hydrostatic, i.e., $\sigma_{ij} = -P \delta_{ij}$ [39],

$$C_{ijkl} = \frac{1}{V} \frac{\partial^2 F}{\partial \epsilon_{ij} \partial \epsilon_{kl}} + P (\delta_{ij} \delta_{kl} - \delta_{il} \delta_{kj} - \delta_{ik} \delta_{jl}), \quad (5)$$

where P denotes the pressure $P \equiv -\frac{1}{3} \text{Tr}(\sigma_{ij})$. A_{ijkl} is not equal to C_{ijkl} unless the system is free of any external pressure or stress. For an *NVE* run, Eqs. (1) and (5) give the adiabatic

elastic tensors A_{ijkl}^S and C_{ijkl}^S , and for an NVT run [27], Eqs. (1) and (5) give the isothermal elastic tensors A_{ijkl}^T and C_{ijkl}^T [36].

2. The stress vs strain method

Alternatively, the *effective* thermoelastic tensor C_{ijkl} can be evaluated using the stress vs strain approach. The components of C_{ijkl} are obtained via numerical differentiation of the recorded stress tensor (σ_{ij}) with respect to the strain tensor (ϵ_{kl}), i.e.,

$$C_{ijkl} = \partial \sigma_{ij} / \partial \epsilon_{kl}, \quad (6)$$

where σ_{ij} denotes the stress tensor components, and ϵ_{kl} the imposed strain tensor. For an NVE run, Eq. (6) gives the adiabatic elastic tensor C_{ijkl}^S , and for an NVT run [27], Eq. (6) gives the isothermal elastic tensor and C_{ijkl}^T .

3. Adiabatic correction

If one has already derived the isothermal tensor, the adiabatic tensor could be derived by applying the adiabatic correction. For an orthorhombic system, the diagonal and off-diagonal components of the adiabatic tensor C_{ijkl}^S are connected to the isothermal tensor C_{ijkl}^T by [22,23,40]

$$C_{iikk}^S = C_{iikk}^T + \frac{TV}{C_V} \lambda_i \lambda_k \quad (i, k = 1, 2, 3). \quad (7)$$

Here, λ_i is given by [40]

$$\lambda_i = -\alpha_k C_{iikk}^T, \quad (8)$$

where α_k , the linear thermal expansion coefficient at constant pressure, is defined by

$$\alpha_i = \left. \frac{\partial \ln a_i}{\partial T} \right|_P \quad (9)$$

and is obtained by numerical differentiation of the lattice parameter $a(T)$ with respect to T . C_V denotes the constant volume-specific heat. It can be calculated in the NVT ensemble using [41]

$$NC_V = \frac{\text{var}(U)}{k_B T^2} = \frac{1}{k_B T^2} [\langle U^2 \rangle - \langle U \rangle^2], \quad (10)$$

where N denotes the number of atoms and U denotes the internal energy. This correction is temperature dependent and is more relevant at high temperatures.

B. Elastic moduli and acoustic velocities

The bulk modulus (K) and shear modulus (G) are derived from the C_{ij} as Voigt-Reuss-Hill (VRH) averages [42], i.e.,

$$K_H = \frac{1}{2}(K_V + K_R) \quad \text{and} \quad G_H = \frac{1}{2}(G_V + G_R), \quad (11)$$

where K_H , G_H represent the Hill averages; the Voigt averages, K_V , G_V , and Reuss averages K_R , G_R , are given by [42,43]

$$9K_V = (c_{11} + c_{22} + c_{33}) + 2(c_{12} + c_{23} + c_{31}), \quad (12a)$$

$$15G_V = (c_{11} + c_{22} + c_{33}) - (c_{12} + c_{23} + c_{31}) + 3(c_{44} + c_{55} + c_{66}), \quad (12b)$$

$$1/K_R = (s_{11} + s_{22} + s_{33}) + 2(s_{12} + s_{23} + s_{31}), \quad (12c)$$

$$15/G_R = 4(s_{11} + s_{22} + s_{33}) - 4(s_{12} + s_{23} + s_{31}) + 3(s_{44} + s_{55} + s_{66}), \quad (12d)$$

where s_{ij} represents the components of the elastic compliance tensor, which are inversely related to the stiffness tensor ($S_{ij} = C_{ij}^{-1}$). The acoustic wave speeds, V_S and V_P , are

$$V_P = \sqrt{(K + \frac{3}{4}G)/\rho} \quad \text{and} \quad V_S = \sqrt{G/\rho}. \quad (13)$$

C. DPMD simulations

DPMD simulations were performed in LAMMPS [44] with deep potential (DP) neural network interatomic potential [30,31] implemented in the DEEPMD-KIT v2.0 package [45,46]. The potential was trained based on the SCAN meta-GGA functional's [32] description of δ -AlOOH's force and energy implemented in the VIENNA AB-INITIO SIMULATION PACKAGE (VASP) [47] with 520 eV energy cutoff for plane-wave basis set sampled over a $2 \times 2 \times 2$ Monkhorst-Pack k -point mesh for 128-atom supercells [8]. At 3000 K, the highest benchmarked temperature used, this SCAN-DP reaches an accuracy of ~ 2 meV/atom root mean squared error (RMSE) in energy and ~ 0.12 eV/Å RMSE in force compared to SCAN-DFT [8].

The components of the C_{ij} tensor were determined in a dense P, T mesh, every 5 GPa up to 150 GPa, and every 600 K from 300 K to 2700 K using SCAN-DPMD on 8192-atom supercells. To obtain the cell shape at a given temperature, constant pressure (NPT) DPMD simulations were performed for 0.1 ns with a timestep of 0.2 fs and the Nosé-Hoover thermo-baro-stat that incorporates modular invariance [48–50] to equilibrate the cell shape at given P, T s. For subsequent simulations, we start from a cell shape equal to those equilibrated in the NPT runs.

To derive the elastic tensor using the stress-fluctuation method [Eqs. (1) and (5)], we performed NVT simulations to generate atomic coordinates and velocities at desired temperatures. These runs were followed by NVE runs for at least 4 ns with a timestep of 0.5 fs to determine the components of the *adiabatic* C_{ij}^S tensor under the specified conditions.

To derive the adiabatic (isothermal) elastic tensor using the stress vs strain method [Eq. (6)], we started from a cell shape equilibrated with constant pressure MD at specific P, T conditions. Then, we fixed the cell shape and conducted NVT simulations to reach the target equilibrium temperature. After removing the thermostat, we deformed the cell shape by imposing a 1% strain, followed the state with an NVE (NVT) run, and recorded the average stress response over an MD run of 12.5 ps with a timestep of 0.5 fs. Details regarding the calculation of C_V for adiabatic correction [Eqs. (7)–(10)] were presented earlier in our previous paper [8].

III. RESULTS AND DISCUSSION

A. Compressive behavior and thermal expansion

In Fig. 1, we evaluate the accuracy of SCAN-DPMD in predicting the compressive behavior of the system by comparing its predictions with x-ray diffraction measurements [6,51–53], available over a wide P, T range. Both density-pressure relations [ρ vs P , Fig. 1(a)] and axial compressions

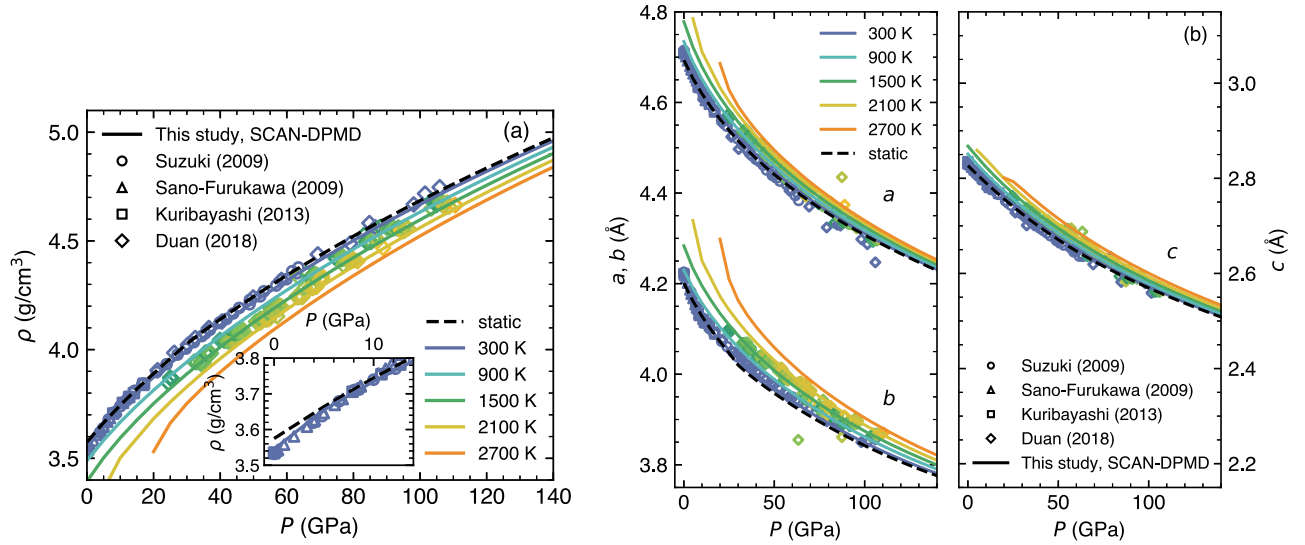


FIG. 1. Compressive behavior of δ -AlOOH at 300–2700 K and under static condition predicted by SCAN-DPMD compared to x-ray diffraction measurements by Sano-Furukawa *et al.* [51], Suzuki [52], Kuribayashi *et al.* [53] (300 K), and by Duan *et al.* [6] (300–2500 K): (a) isothermal density-pressure relations (ρ vs P); (b) isothermal axial compressive behavior (a, b, c vs P).

[a, b, c vs P , Fig. 1(b)] are accurately reproduced in DPMD simulations at finite temperatures.

δ -AlOOH's 300 K compression curve was measured extensively below 30 GPa. Our results agree well with these measurements. In particular, we fully reproduced the compressibility change at 5 GPa, driven primarily by the change in the a and b axes [51]. These compressibility changes are less noticeable at $900 < T < 1500$ K. However, anomalies reappear at $2100 < T < 2700$ K for pressures below 40 GPa. For $P > 40$ GPa, no change in compressive behavior is seen at any T . Above 60 GPa, the discrepancies between SCAN-DPMD predictions and experimental data slightly increase, likely caused by the more significant uncertainties in the measurements, evident from the wider spread of experimental data at higher pressures [6]. The differences between SCAN-DPMD prediction and measurements are comparable to experimental uncertainties. The increasing uncertainties in the axial compressive behavior measurements highlight experimental challenges at elevated pressures.

Using these results, we determined δ -AlOOH's volume thermal expansivity, $\alpha = \partial \ln V / \partial T|_P$, via numerical differentiation (see Fig. 2). Our calculations indicate δ -AlOOH's α decreases with pressure. At 900 K, it increases from $\sim 2.2 \times 10^{-5} \text{ K}^{-1}$ at 30 GPa to $\sim 0.9 \times 10^{-5} \text{ K}^{-1}$ at 150 GPa. At high temperatures, first, δ -AlOOH's α increases gently. Above ~ 1000 – 1500 K, and depending on the pressure, it abruptly increases with T , suggesting significant anharmonicity at high temperatures. These positive curvatures of $\alpha(T)$, i.e., $\partial^2 \alpha / \partial T^2|_P > 0$, usually occur as a precursor to phase transitions, and in this case, correlated with the melting of the H sublattice that leads to the diffusive boundary to superionic behavior reported earlier [8]. Our calculation suggests that the curvature increases significantly at ~ 1000 K at 30 GPa and 1500 K at 150 GPa. This temperature is lower than the normal mantle and the slab geotherm [54,55].

In summary, the consistency between our SCAN-DPMD simulations and measurements across a broad temperature

range underlines this method's potential to predict elastic properties accurately. The strong anharmonicity implied by $\alpha(T)$ at extreme P, T s demands the application of SCAN-DPMD for such calculations.

B. Elastic tensor

δ -AlOOH is an orthorhombic crystal, characterized by an elastic tensor (C_{ij}) with nine distinct components: c_{11} , c_{22} , c_{33} , c_{12} , c_{13} , c_{23} , c_{44} , c_{55} , and c_{66} [56]. We evaluate

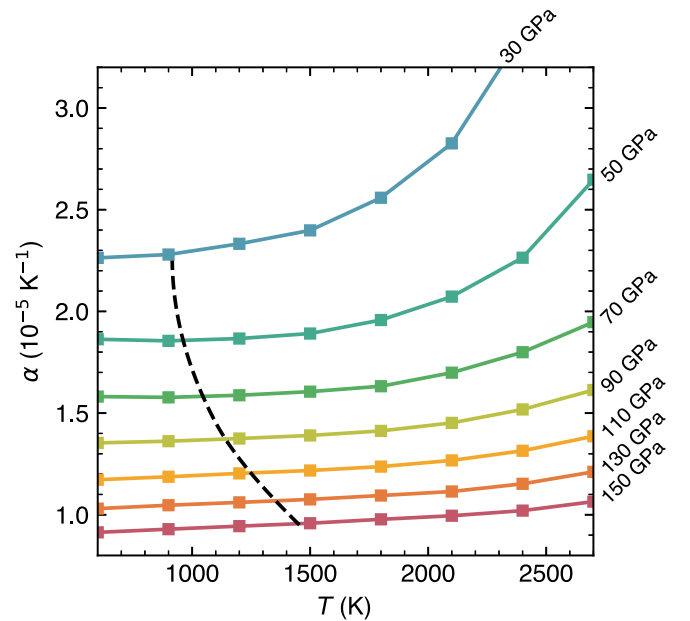


FIG. 2. Thermal expansivity (α) of δ -AlOOH predicted by SCAN-DPMD. The dashed-black curve indicates the critical temperatures where the curvature of $\alpha(T)$ alternates, defined by $\partial^2 \alpha / \partial T^2|_P = 0$. The curvature $\partial^2 \alpha / \partial T^2|_P$ vs T is shown in Fig. S1 within the SM [57].

TABLE I. Comparison of elastic constants and other properties at ambient conditions (0 GPa, 300 K) between SCAN's predictions and various studies.

	Wang (2022) [19] Single crystal	Mashino (2016) [16] Polycrystal	Li (2006) [18] GGA static	Tsuchiya (2009) [17] GGA static	This study SCAN static	This study SCAN 300 K MD
ρ (g/cm ³)	3.536(1)	3.593	3.532	3.383	3.575	3.545
c_{11} (GPa)	375.9(9)		416	314	394.2	364.9
c_{22} (GPa)	295.4(11)		509	306	381.8	310.7
c_{33} (GPa)	433.5(12)		418	391	463.5	441.4
c_{44} (GPa)	129.2(6)		133	117	151.5	142.4
c_{55} (GPa)	133.4(7)		124	115	141.9	135.0
c_{66} (GPa)	166.4(6)		229	152	184.0	168.0
c_{12} (GPa)	49.7(9)		137	34	50.4	21.8
c_{13} (GPa)	91.9(15)		93	95	108.0	101.5
c_{23} (GPa)	52.8(21)		84	67	89.8	74.3
K_V (GPa)	166.0(13)		219.1	155.9	191.1	168.0
G_V (GPa)	146.5(3)		166.0	131.1	160.6	150.4
K_R (GPa)	159.8(48)		216.4	128.8	189.2	159.7
G_R (GPa)	144.0(15)		157.4	123.0	159.7	148.0
K_{VRH} (GPa)	162.9(31)		217.7	153.5	191.1	163.8
G_{VRH} (GPa)	145.2(13)		161.7	130.0	160.6	149.2
V_P (km/s)	10.04(7)	9.54(7)	11.11	9.83	10.65	10.11
V_S (km/s)	6.41(3)	5.89(10)	6.77	6.20	6.70	6.49

these adiabatic tensor components using the stress-fluctuation method in DPMD simulations within the NVE ensemble [26,27,35–37]. For compactness, we use the Voigt notation (C_{ij} , $i, j = 1$ to 6) instead of the full Cartesian notation (C_{ijkl} , $i, j, k, l = 1, 2, 3$). The elastic tensor presented in this section was the adiabatic effective elastic tensors (C_{ij}^S) derived using the stress-fluctuation method. Our comparisons indicate that all these methods give similar results. For a detailed discussion and comparison of these methods, please refer to Secs. III D and III E.

In Table I, we compare the computed C_{ij} components at 0 GPa under static and 300 K conditions to previous DFT-GGA/PBE calculations [17,18] and ultrasound single-crystal measurements [19]. Tsuchiya *et al.*'s GGA/PBE-based predictions [17] significantly underestimate the elastic stiffness tensor component by 15–30%, and in some cases, by as much as 60 GPa, compared to single-crystal measurements [19] and our SCAN predictions. Their underestimation could be attributed to the PBE's overestimation of pressure, ~ 5 –6 GPa [15], producing a larger equilibrium volume V_0 and smaller bulk modulus K_0 . Conversely, Li *et al.*'s GGA/PBE-based results [18] are generally more significant, particularly for the components c_{11} , c_{22} , and c_{33} . The reasons for this discrepancy between similar calculations are unclear, but these studies used different computational tools and pseudopotentials: Li *et al.* [18] employed VASP with the projector augmented wave (PAW) pseudopotentials, whereas Tsuchiya *et al.* [17] utilized QUANTUM ESPRESSO with norm-conserving pseudopotentials. Additionally, using different H-bond configurations that coexist at 0 GPa [15,58] could contribute to the observed differences.

Benefitting from SCAN's more faithful reproduction of the compression curve, we have achieved a more accurate prediction of V_0 . Our fully anharmonic predictions of C_{ij}^S at 300 K resemble much more closely the single-crystal ultrasound

measurements [19]. Differences between our predictions and these measurements, ~ 10 –20 GPa, are all within the experimental uncertainties, except for c_{22} , which is ~ 10 GPa outside the experimental uncertainty range. Overall, the agreement is excellent, especially considering that the joint experimental determination of these coefficients can compensate for underestimating some coefficients by overestimating others.

Figure 3 shows the pressure dependence of δ -AlOOH's adiabatic elastic tensor C_{ij}^S at various temperatures. At 300 K, within the 0–15 GPa pressure range, the diagonal components c_{11} and c_{22} start softer than c_{33} but undergo a steep increase under pressure. This pattern underpins the axial compression trends observed in Fig. 1(b) and in experiments [51], where the a and b axes are notably more compressible within the same pressure range. Conversely, c_{33} , off-diagonal, and shear components exhibit milder anomalies under pressure, indicating they are less affected by the disorder-symmetrization transition. The higher compressibility pressure range extends to ~ 15 GPa, ~ 7 –9 GPa beyond the experimental transition pressure at ~ 6 –8 GPa at 300 K [14,51].

Except for c_{44} and c_{55} , which nearly plateau at higher pressures, C_{ij}^S s become more linearly dependent on pressure above 15 GPa at 300 K. Here, c_{11} and c_{22} become similarly stiff or stiffer than c_{33} . At around ~ 90 GPa, we observed a subtle change in the rate of stiffening in c_{22} and c_{33} : first, $P < 90$ GPa is a deceleration regime, then, after $P > 90$ GPa is an acceleration regime. They are likely associated more with the system's anharmonicity until δ -AlOOH's "full symmetrization", i.e., the potential energy surface for proton at the center of two O ions becomes truly harmonic at ~ 100 GPa [8]. It affects δ -AlOOH's c_{22} and c_{33} rate of increase with pressure but does not change the overall monotonic trend.

Between 900–1500 K, the observed anomaly and subtle behavior of the C_{ij} tensor become less pronounced, yet they persist. Above 2100 K and below 40 GPa, the steep increases

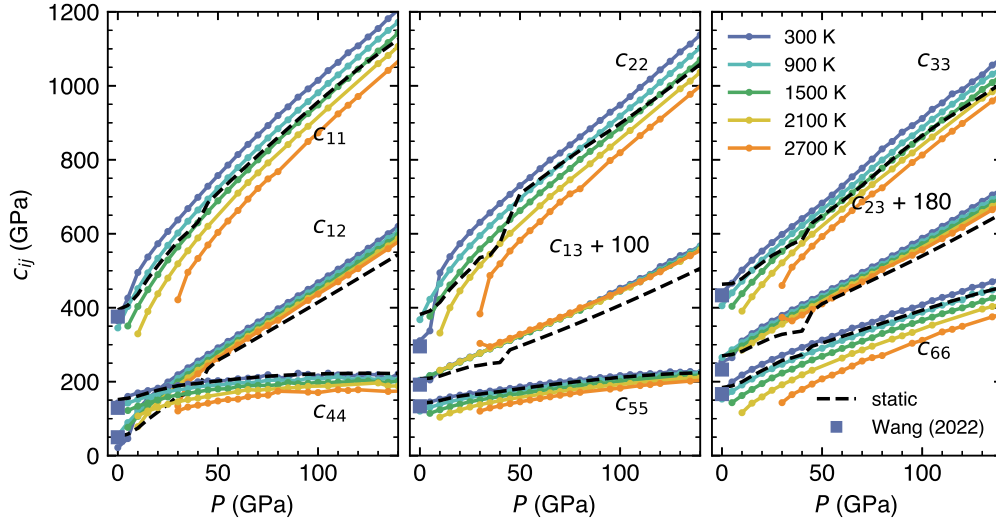


FIG. 3. Comparison between static elastic tensor (black-dashed curves) and adiabatic thermoelastic tensor components (solid-colored curves) of δ -AIOOH calculated using SCAN-DP. Ultrasound measurements at ambient conditions on single crystal reported on [19] are included for reference.

in C_{ij} intensify across all components as a precursor to the instabilities and potential dissociation or dehydration observed experimentally in this P, T range [5–7].

Compared with the 300 K SCAN-DPMD simulations, static SCAN-DP underestimates C_{ij} components across the entire pressure range. This underestimation is caused by the missing H-bond disorder and dynamic effects [14], which leads to an overestimation of the transition pressure by ~ 30 GPa. The discrepancy reinforces the necessity of employing MD to capture finite-temperature effects, especially across a phase transition, for accurate modeling. Notably, our static SCAN-DP’s prediction is qualitatively similar to previous static GGA/PBE-DFT studies, which also report the jump in C'_{ij} s around 30 GPa [17].

C. Elastic moduli, acoustic velocities, and anisotropies

Based on the calculated C_{ij}^S , we first determine the bulk and shear moduli (K and G) using Eqs. (11) and (12), then determine the compressional and shear velocities (V_P and V_S) using Eq. (13). Figure 4 shows these results vs P, T .

At 300 K within the 5–10 GPa range, we observe a pronounced “jump” in both K and V_P , alongside a more gradual yet anomalous increase in G and V_S . These can be attributed to the anomalous changes in C_{ijkl}^S and $P(V)$ compression curve in this pressure range as discussed above (see Fig. 1). Beyond 30 GPa, all properties, K , G , V_S , and V_P , display a smooth monotonic increase with pressure.

The elastic moduli and acoustic velocities all soften with increasing temperature. However, we do not identify a signal related to the onset or enhancement of the protons’ superionic behavior [8]. This is confirmed by fitting V_P and V_S above 90 GPa to a polynomial second order in P and first-order in T , $f(P, P^2, T)$. Without a super-linear T dependence, the model still describes V_P and V_S at high P, T s quite accurately, even above the superionic transition boundary starting at ~ 2100 K at ~ 60 GPa [8]. The model parameters for V_P

and V_S are given in Table SI, and their validation is shown in Fig. S2 within the Supplemental Material (SM) [57]. The term linear in T captures the V_S ’s and V_P ’s dependences on T over the entire pressure range quite well. The deviation from the linear model observed at $V_P < 12$ km/s and $V_S < 7$ km/s corresponds to $P < 15$ GPa at 300 K and up to $P < 45$ GPa at 2700 K, a regime where δ -AIOOH’s H bonds are asymmetric and V_P and V_S behave differently from higher pressures where H bonds are symmetric. The absence of higher-order dependence on T suggests that the Al-O framework predominantly dictates the overall properties of δ -AIOOH after the H-bond disorder-symmetrization transition. This observation explains why δ -AIOOH’s elastic properties are more similar to those of typical nonhydrous high-pressure systems rather than those of hydrous phases or NAMs [6,16].

Compared with measurements, our predicted V_P and V_S align closely with recent ambient-condition single-crystal measurements [19] but are faster than those obtained from polycrystalline measurements [16]. Our results systematically overestimate these parameters by 5% across the entire pressure range of measurements on the polycrystalline sample. This is not unexpected since grain boundaries and pores are known to reduce acoustic velocities [19,59,60]. The Voight-Reuss bounds outlined in shaded color appear marginal for this system and cannot accommodate such discrepancies.

The azimuthal anisotropy of each acoustic velocity mode is further quantified by the anisotropy factor (AV), defined by

$$AV = \frac{V_{\max} - V_{\min}}{V_{\max} + V_{\min}} \times 200\%, \quad (14)$$

where V_{\max} and V_{\min} denote the maximum and minimum velocities over all azimuthal directions. The three velocity modes, V_P , V_{S1} , and V_{S2} , are the solutions to the Christoffel’s equation [61] at direction represented by the unitary vector

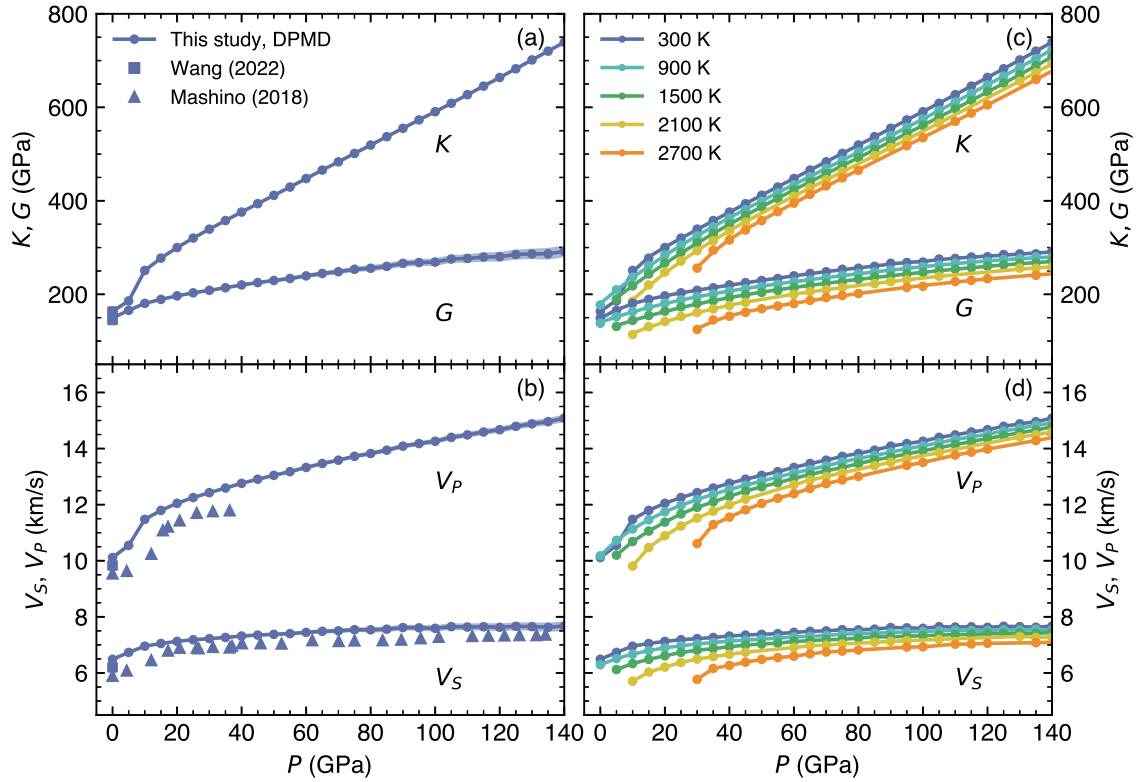


FIG. 4. Predicted (a) bulk modulus (K) and shear modulus (G), (b) compressional velocity (V_P), and shear velocity (V_S) of δ -AlOOH vs P predicted by SCAN-DPMD at 300 K compared to ultrasound measurements on a single-crystal sample at ambient conditions by Wang *et al.* [19] and Brillouin scattering under pressure on a polycrystalline sample at room temperature by Mashino *et al.* [16]. (c) and (d) are similar predictions at high temperatures. The shaded regions indicate the Voigt-Reuss-Hill (VRH) bounds at 300 K.

$$\hat{n} = (n_1, n_2, n_3),$$

$$|C_{ijkl}n_jn_l - \rho V^2\delta_{ik}| = 0. \quad (15)$$

Figure 5 shows AV_P , AV_{S1} , and AV_{S2} vs P . The AV s generally increase with pressure except for dips in AV_P and a jump in AV_{S2} in the 0–40 GPa range, depending on the temperature. The dips correspond to the anomalies in C_{ij}^S , but their effects are enhanced here. The necking in C_{ij}^S seen in Fig. 5 likely corresponds to the end of the complete disorder-symmetrization transition, which changes the pressure dependence of AV_P from super-linear to linear. The AV s slightly decrease with increasing temperature. δ -AlOOH is significantly less anisotropic than serpentines [62,63] but considerably more anisotropic than the major anhydrous mantle components, e.g., MgO periclase and [64] and MgSiO₃ perovskite [34,64].

D. The stress vs strain method

We compare the adiabatic tensor C_{ijkl}^S derived using the stress-strain relation with the one derived from the stress-fluctuation method. We expect that the result might differ slightly from the stress-fluctuation method because energy is not fully conserved during the simulation box deformation. The first law of thermodynamics states that

$$\Delta U = Q - W = T\Delta S - P\Delta V,$$

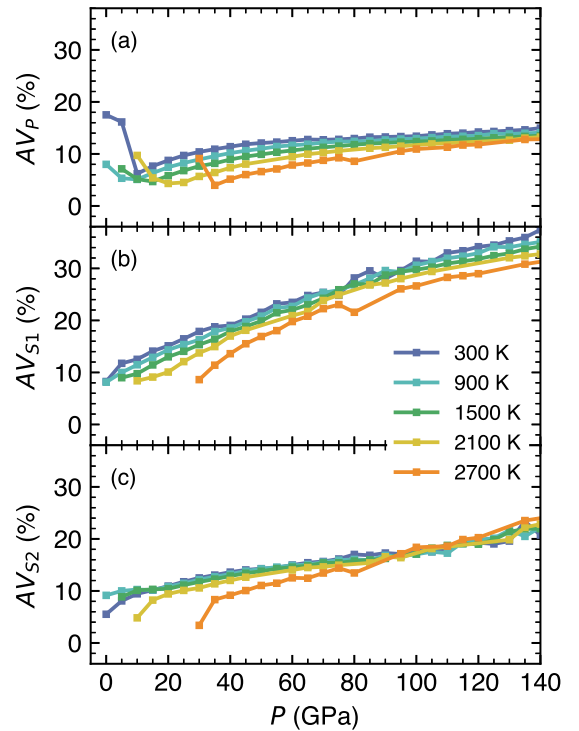


FIG. 5. P, T dependencies of δ -AlOOH's azimuthal anisotropy factors (AV s) for δ -AlOOH vs P predicted by SCAN-DPMD simulations.

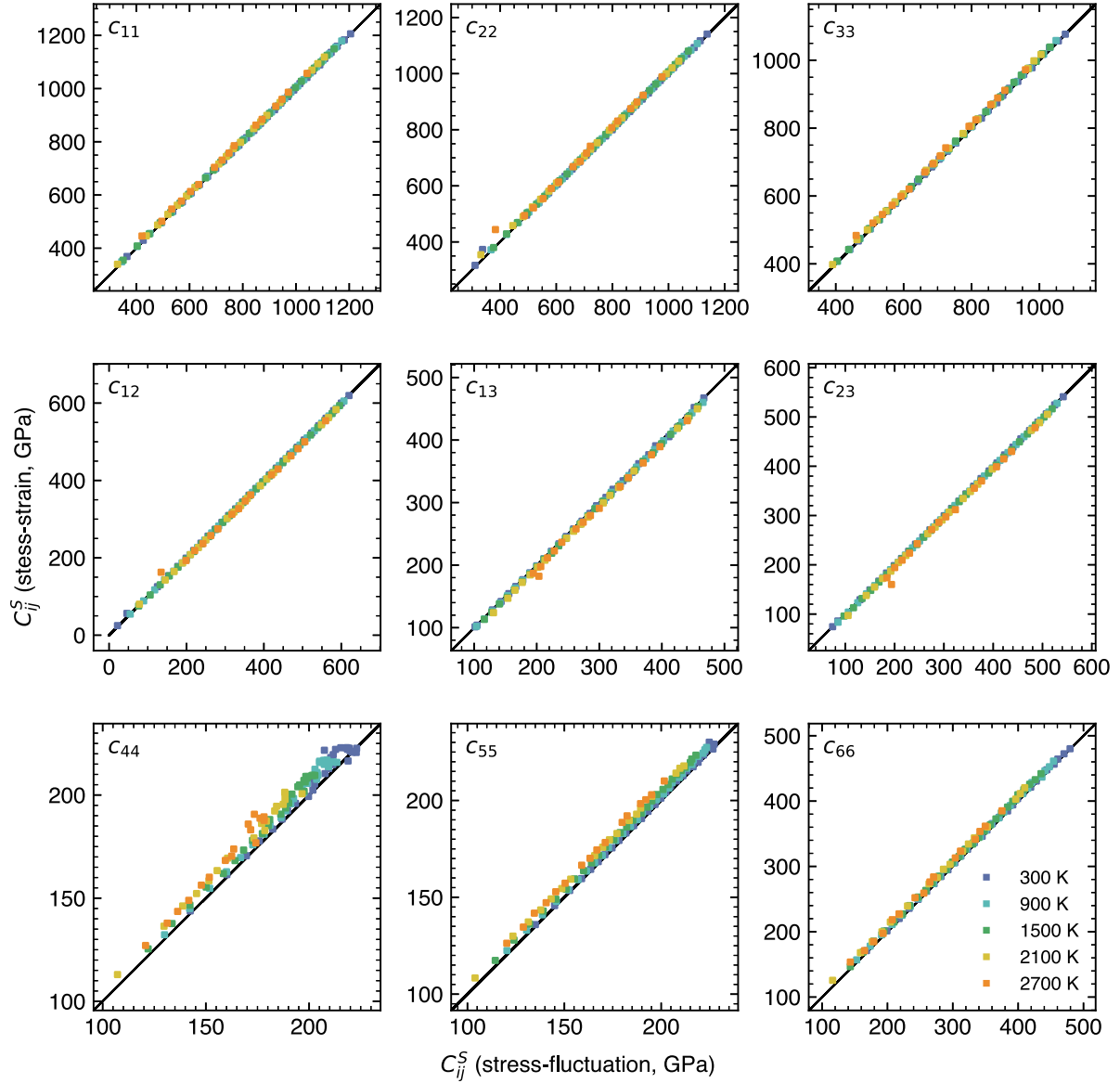


FIG. 6. Comparison of C_{ij}^S components obtained with stress-fluctuation and the stress-strain approaches using SCAN-DPMD within the NVE ensemble at various P, T conditions.

where ΔU represents the change in the internal energy $U = E_k + E_p$, and $W = -P \Delta V$ is the work done by the system. A true isentropic process implies $\Delta S = 0$, and $\Delta U = W = -P \Delta V$. Both ΔU and $W = -P \Delta V$ can be obtained throughout the deformation simulation, and our calculation indicates that the condition $\Delta U = -P \Delta V$ is not strictly guaranteed, but it is close (see Fig. S3 within the SM [57]). To ensure a proper isentropic process, adjustments to E_k (the scaling of the velocities) are necessary. This implies potential discrepancies with the stress-fluctuation method, even when running an MD simulation in a constant energy (NVE) ensemble.

Compared with the stress-fluctuation method (Fig. 6), we observe a deviation of less than 10 GPa in C_{ij}^S components. This deviation is quite small, or less than 2%, for diagonal and off-diagonal components. Still, it translates to a 10% overestimation for the shear components because of their relatively small absolute values. The horizontal spread indicates the challenge in converging the stress-fluctuation

calculations for the c_{44} and c_{55} components (see Fig. S4 within the SM [57]).

Practically, the stress-fluctuation method offers a streamlined approach for obtaining C_{ijkl}^S through MD simulations, eliminating the need for multiple MD simulations and offering a mathematically rigorous solution. Our tests suggest that employing both a larger simulation cell and an extended simulation timescale enhances the convergence of stress-fluctuation calculations. The Born matrix term, i.e., $\langle A_{ijkl}^B \rangle$ in Eq. (1), converges rapidly to an uncertainty < 0.1 GPa, often within a few thousand timesteps (e.g., Fig. S4 within the SM [57]). However, converging the stress-fluctuation term (i.e., $V/k_B T [\langle \sigma_{ij} \sigma_{kl} \rangle - \langle \sigma_{ij} \rangle \langle \sigma_{kl} \rangle]$) proves to be substantially more challenging, particularly at low- T and high- P conditions, where low-frequency vibrational modes are relatively more important. Small timesteps must be used in systems such as δ -AlOOH, which contain light and faster-moving ions, to ensure numerical accuracy in the equation of motion

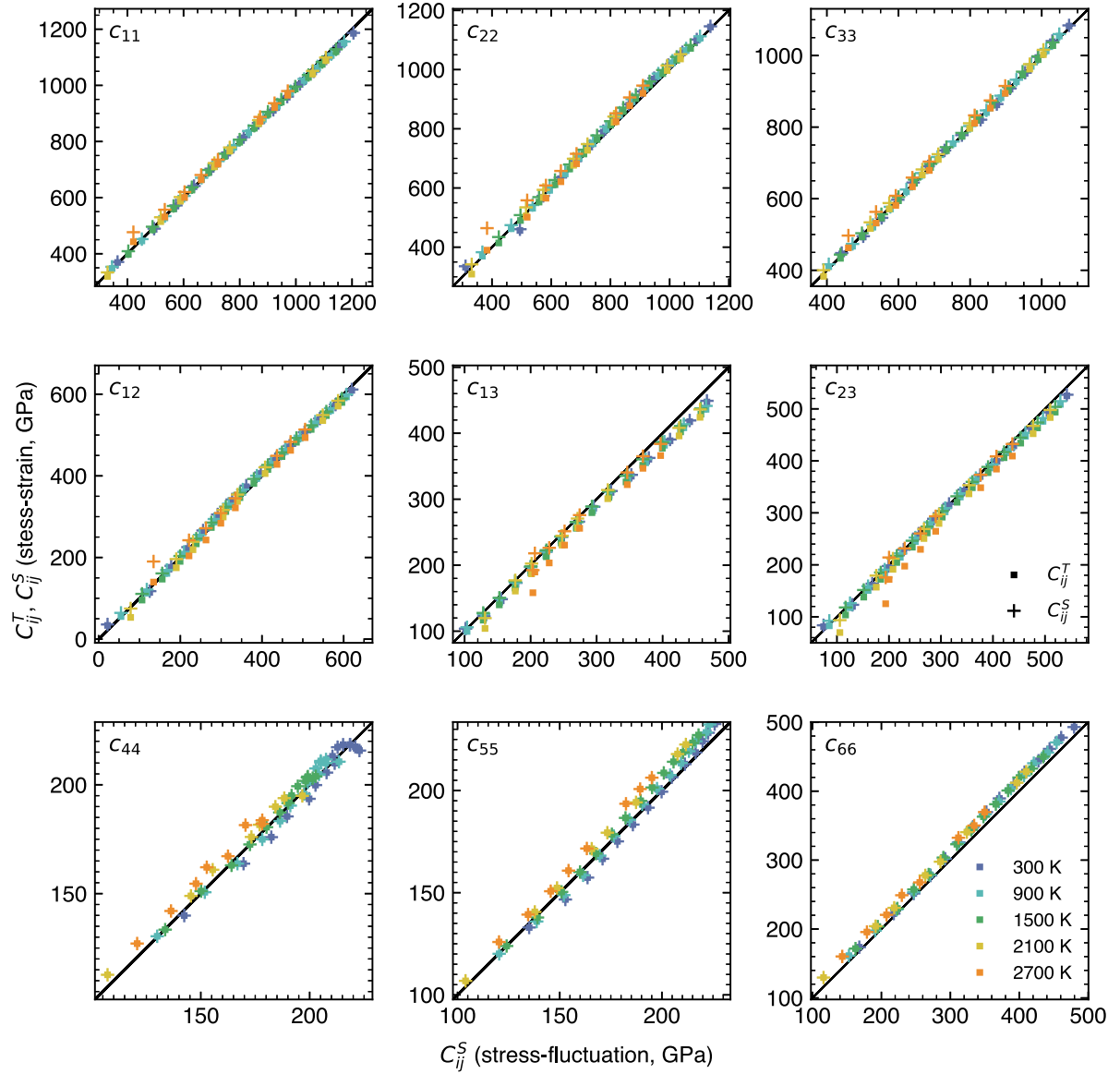


FIG. 7. Isothermal, C_{ij}^T (solid squares), and adiabatic, C_{ij}^S (crosses), elastic tensor components computed using stress-strain relations (y-axes) plotted against adiabatic elastic tensor, C_{ij}^S , computed using the stress-fluctuation method (x-axes).

integration. The simultaneous need for short timesteps (0.2–0.5 fs) and long simulation run times (~ 10 ns) to converge the stress covariance term in Eq. (1) make these simulations more challenging (see convergence test in Fig. S4 within the SM [57]). In this case, the less straightforward stress vs strain approach to compute C_{ij}^S is useful.

E. Adiabatic vs isothermal elastic tensor

To compare the adiabatic and isothermal elastic tensors and to test the adiabatic correction, we also performed stress-strain calculations within the NVT ensemble to derive the isothermal tensor C_{ijkl}^T then applied the adiabatic correction [Eq. (7)] to derive C_{ijkl}^S . We compared these results to C_{ijkl}^S derived from the stress-fluctuation analysis in Fig. 7. For diagonal components, C_{ijkl}^T obtained from the strain-stress

relation does not significantly deviate from C_{ijkl}^S . The second term in Eq. (7) increases their values slightly, but the overall change is not significant. Results at low P and high T become even worse compared to C_{ijkl}^S obtained using the stress-fluctuation analysis. The effect is more pronounced at higher T s when thermal expansivity increases anomalously with hydrogen diffusion (see Fig. 2) [8]. For the off-diagonal components (c_{12} , c_{13} , and c_{23}), the second term in Eq. (7) noticeably mitigates temperature-dependent discrepancies. It significantly improves the agreement with C_{ijkl}^S obtained from the stress-fluctuation analysis. The correction does not affect shear components. They behave similarly to C_{ijkl}^S obtained via the stress-strain relation directly in the NVE ensemble (Fig. 6). Overall, the adiabatic correction in Eq. (7) is necessary at high temperatures, especially for superionic systems. Practically, deriving α_i numerically presents significant

challenges. Because of the absence of an explicit relation, deriving α_i from the box shapes requires dense P, T sampling, particularly for systems at high temperatures where α_i exhibits a super-linear temperature dependence T . In comparison, the stress-fluctuation calculations are more straightforward and more manageable.

IV. CONCLUSIONS

This study employs SCAN-DPMD simulations to investigate the thermoelastic properties and acoustic velocities of δ -AlOOH at the P, T 's up to 2700 K and 145 GPa, corresponding closely to subducting slab conditions in the mantle. The predicted C_{ij} components agree well with previous single-crystal ultrasound measurements at ambient conditions [19]. The pressure dependence of sound velocities at high pressures is similar to those measured at 300 K in polycrystalline samples by Brillouin scattering [16], including the steep increase in K and V_p caused by the disorder-symmetrization phase transition at ~ 10 GPa and 300 K. However, the predicted velocities are faster than the Brillouin scattering measurements by $\sim 5\%$. The difference falls outside the Voigt-Reuss bounds and likely originates in significant effects caused by grain size, grain boundaries, and possibly pores. The impact of proton diffusion at high temperatures on sound velocities does not seem obvious.

Under P, T 's relevant to the Earth's lower mantle, δ -AlOOH has a significantly faster velocity than typical hydrous minerals. Its elastic properties are more similar to those of anhydrous phases, e.g., stishovite-type SiO_2 . The phase equilibrium between phase Egg (AlSiO_3OH) [65–68], δ -AlOOH, and stishovite-type SiO_2 with hydrous defects [69–74], i.e., $\text{Egg} \rightleftharpoons \delta\text{-AlOOH} + \text{Stv}$, is relevant to the Earth's deep water cycle [13,19] and it is desirable to recognize it in seismic tomography. Because of phase Egg's significantly slower sound velocity [19,75] than those of δ -AlOOH and stishovite, the formation (or decomposition) of phase Egg in the mantle would cause a decrease (or increase) in velocity. Since this behavior is different from near-ambient conditions, and single-crystal elasticity measurement is only available at

ambient pressure and temperatures before the pressure-induced H-bond transitions in δ -AlOOH, single crystal measurements at high pressures and temperatures after the phase transitions are highly desirable.

MD simulations are necessary to investigate systems with strong anharmonicity at high temperatures. Because of its rigorous mathematical framework, the stress-fluctuation method with the NVE ensemble remains a cornerstone among various MD methods for computing adiabatic thermoelastic properties. However, despite its trade-offs in energy conservation during deformation, the stress vs strain approach within the NVE ensemble still stands as a practical alternative, especially when convergence in stress fluctuation becomes more challenging. Determining the isothermal thermoelastic tensor first via the strain-stress relations with the NVT ensemble, followed by an adiabatic correction, is less practical because it involves calculations of linear thermal expansion coefficients, which, due to the lack of an explicit volume-temperature relationship, relies on numerical differentiation on a densely-sampled P, T grid. The differences in individual C_{ij} components calculated by various methods are at most 20 GPa at all pressures, hardly affecting polycrystalline averages for elastic moduli and sound velocities.

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SUPPLEMENTARY INFORMATION

Elasticity and acoustic velocities of δ -AlOOH at extreme conditions: a methodology assessment

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This PDF file includes:

- Tables SI
- Figures S1 to S4

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TABLE SI – Parameter describing the SCAN-DPMD predicted sound velocities of δ fitted to $M_0 + (\partial M/\partial P) P + (\partial^2 M/\partial P^2) P^2 + (\partial M/\partial T) T$.

	M_0 (km/s)	$\partial M/\partial P \times 10^{-2}$ (km · s ⁻¹ · GPa ⁻¹)	$\partial^2 M/\partial P^2 \times 10^{-5}$ (km · s ⁻¹ · GPa ⁻²)	$\partial M/\partial T \times 10^{-4}$ (km · s ⁻¹ · K ⁻¹)
V_P	11.61	3.28	-5.06	-3.10
V_S	6.85	1.33	-4.74	-2.67

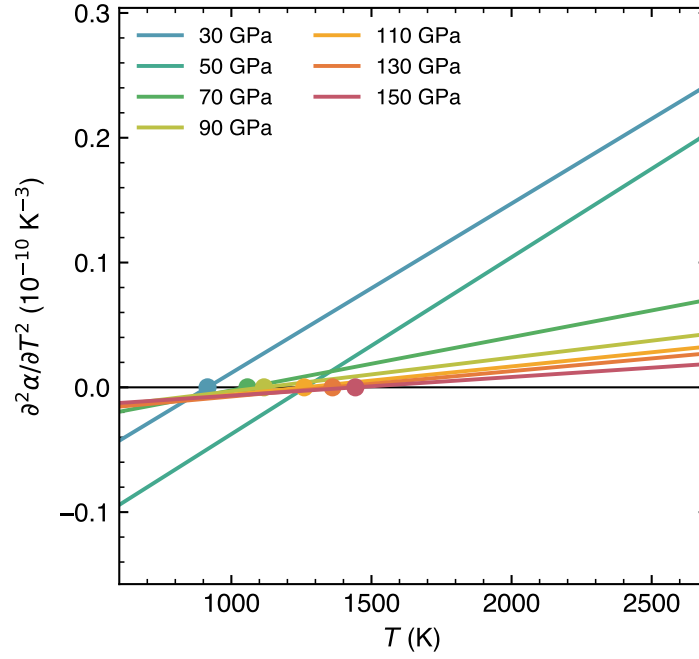


FIG. S1 – The curvature of the thermal expansivity α ($\partial^2\alpha/\partial T^2$) vs. T at various pressures. Solid dots indicate zeros. At each pressure, $\ln V(T)$ was fitted to a fourth-order polynomial; the first-order derivative of the polynomial is the thermal expansivity, $\alpha(T)$, and the third-order derivative of the polynomial was the curvature of α vs. T .

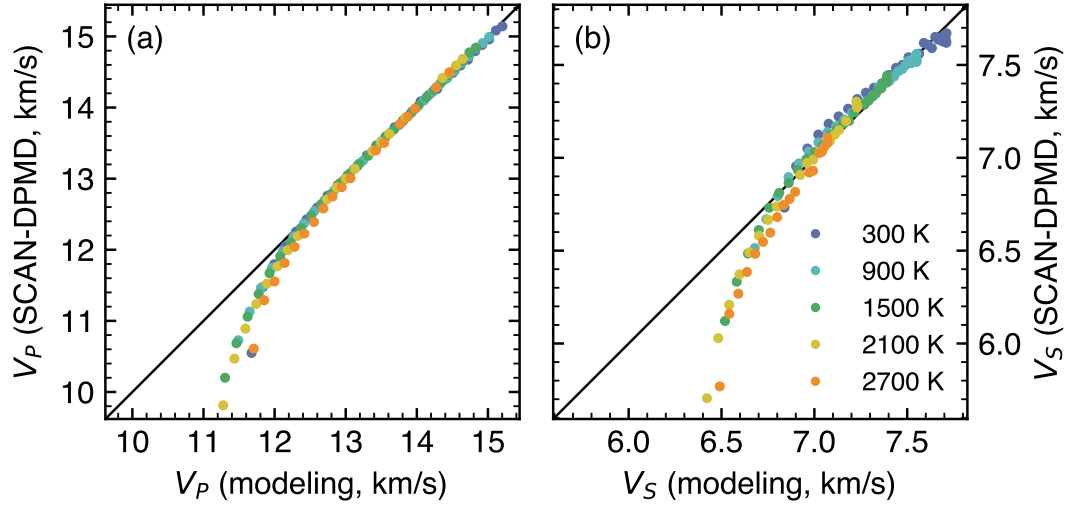


FIG. S2 – Modeling and validation of (a) V_P and (b) V_S at $T > 90$ GPa using a linear model of P , P^2 , and T and validation over the entire pressure range.

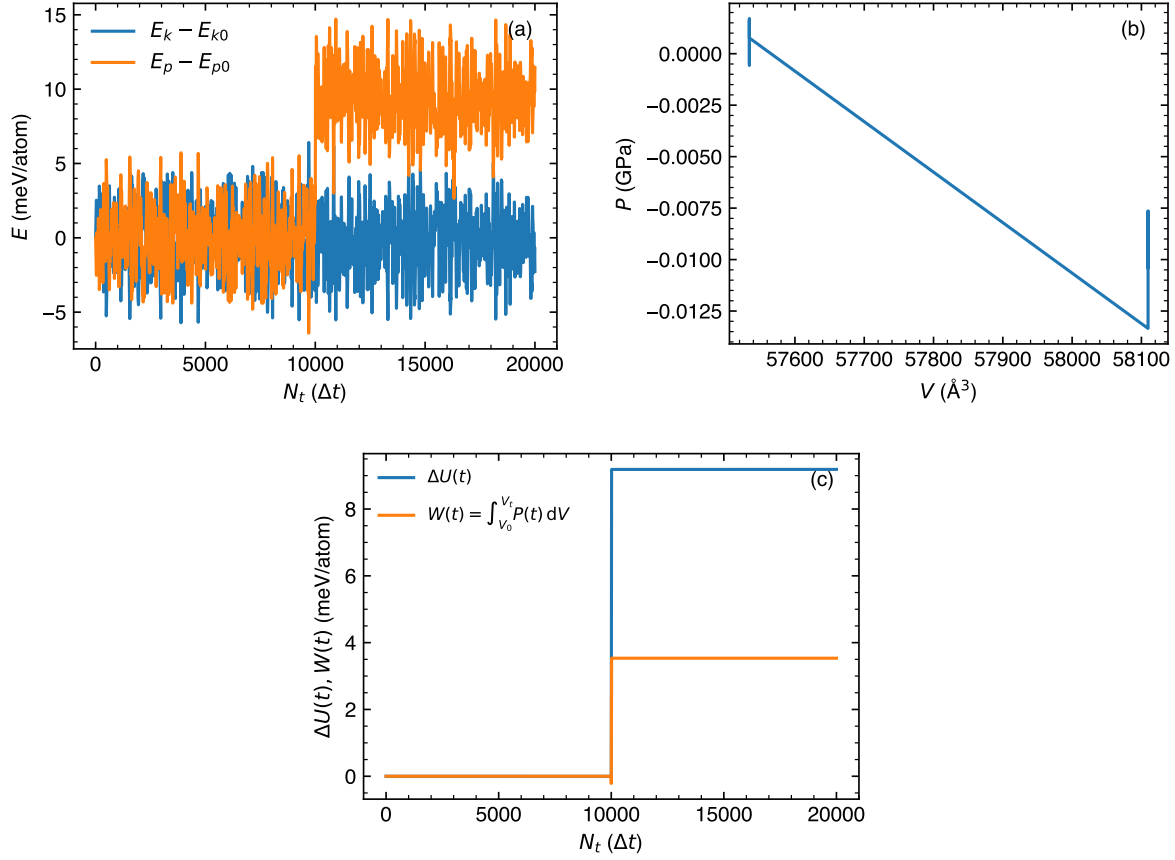


FIG. S3 – Analysis of the *NVE* simulation deformation process with a 1,024-atom cell. For a system equilibrated with an *NVT* simulation at 0 GPa and 300 K. We first performed a 10,000-step *NVE* simulation. A 1% strain was then applied to the system, after which another 10,000-step *NVE* simulation was conducted using the deformed configuration. Here, we show (a) energy differences before and after deformation; (b) P - V relation diagram throughout the deformation process; (c) calculation of the internal energy difference $\Delta U = \Delta E_k + \Delta E_p$ and the work done W during deformation. The relationship $W = \Delta U$ should hold for an ideally adiabatic process.

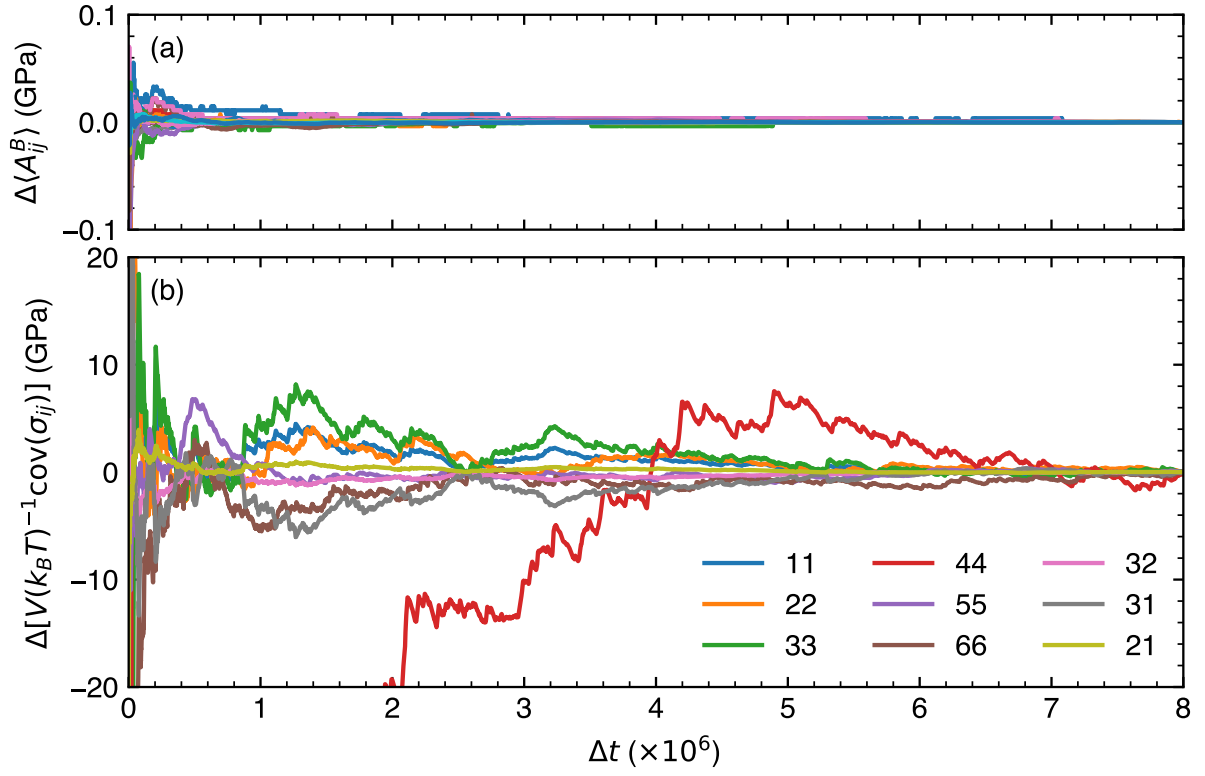


FIG. S4 – Convergence of (a) $\langle A_{ijkl}^B \rangle$ and (b) $V/k_B T [\langle \sigma_{ij} \sigma_{kl} \rangle - \langle \sigma_{ij} \rangle \langle \sigma_{kl} \rangle]$ term components w.r.t. simulation time step (i.e., rolling averages compared to the final values) at 300 K, 105 GPa.