

Ab initio molecular dynamics simulations for thermal equation of state of B2-type NaCl

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The pressure as a function of volume and temperature has been investigated for B2-type NaCl over the pressure range of 20–360 GPa and at temperatures between 300 and 3000 K. The simulations were performed using *ab initio* molecular dynamics method within the density-functional theory framework. A Vinet equation of state fitted to the 300 K data yielded a bulk modulus of $B_{Ta} = 128.66$ GPa and a pressure derivative of $B'_{Ta} = 4.374$ at standard state pressure of 30 GPa. The thermal pressure contribution was determined to be of the form $\Delta P_{th} = [\alpha B_T(V_a) + (\partial B_T / \partial T)_V \ln(V_a/V)] \Delta T$. When $\alpha B_T(V_a)$ is assumed to be constant, the fit to the data yielded $\alpha B_T(V_a) = 0.0033$ GPa/K at standard volume, corresponding to the pressure of 30 GPa. In contrast, the volume dependence of the thermal pressure was very small, and fitting yielded $(\partial B_T / \partial T)_V = 0.00087$. © 2008 American Institute of Physics. [DOI: 10.1063/1.2832632]

I. INTRODUCTION

The high pressure and temperature properties of solids are important both in theory and in application. For instance, the thermal properties of matter at high pressure and temperature are essential in the study of the interior of the Earth in geophysics and for the study of the evolution of stars in astrophysics. A particular difficulty with performing experiments at high pressure is knowing what the pressure in the experiment actually is. NaCl is one of the most widely used internal pressure standards in high pressure diffraction experiments due to the availability of accurate experimental data. For instance, the equation of state for B1-type NaCl has been investigated in several studies up to the limit of its stability.^{1–8} It is also known that the B1-type NaCl is only stable up to a pressure of about 30 GPa, where the occurrence of a pressure-induced phase transition from B1 type (rocksalt) to B2-type (cesium chloride) has been reported.^{9–15} Although it is experimentally possible to study the B2-type NaCl at elevated pressures, its equation of state has not been investigated well yet, especially at high temperatures. This, therefore, limits the use of NaCl as a pressure standard to relatively low pressures and temperatures. Therefore, the P - V - T equation of state reported in this article will be fundamentally important for extending its scientific and engineering applications including its usefulness as a pressure calibrant.

It is the purpose of this paper to present the equation of state for B2-type NaCl using *ab initio* molecular dynamics simulation, which has been shown to be a successful approach for the prediction of quantitative thermodynamic data for a wide class of crystals. Below, we will present the equa-

tion of state for B2 NaCl over a wide range of pressures and temperatures.

II. METHODS

The electronic structure was calculated using the projector augmented wave implementation of the density-functional theory using the Vienna *ab initio* simulation package (VASP).^{16–18} For the exchange-correlation potential, the PW91 functional¹⁹ was used in the generalized gradient approximation (GGA) calculations. The core radii are 2.5 a.u. for Na and 1.9 a.u. for Cl. A plane-wave cutoff of 262.4 eV was used. The *ab initio* molecular dynamics (AIMD) simulation at constant volume was carried out using 54 atoms for the B2-type NaCl and 64 atoms for the B1-type NaCl. We used a single k point, the Γ point, for sampling the Brillouin zone. To validate the use of the Γ point, we performed ground state calculations of the lattice constant, bulk modulus, and cohesion energy both for a primitive unit cell at 220 k points (a $20 \times 20 \times 20$ Monkhorst–Pack shift grid) and for a simple cubic supercell containing 54 atoms (equivalent to 27 primitive unit cells) at the Γ point. The results obtained from the two calculations showed no significant discrepancy and are in agreement with experimental data. The number of atoms was found to be satisfactory, as discussed in more detail below. Our AIMD simulations were performed in the (N , V , T) ensemble and the Nosé thermostat²⁰ was used to keep the temperature constant with a time step of 1 fs. The computation time to reach equilibration varied among configurations and depended on the starting atomic positions, velocities, temperature, and pressure. After the confirmation of equilibrium of the system (3–10 ps), the pressure and temperature of the system were calculated. In order to assess the reliability of our method, the elastic properties of B1-type NaCl were also calculated and compared with the elastic properties which have been reported in a number of experimental studies.

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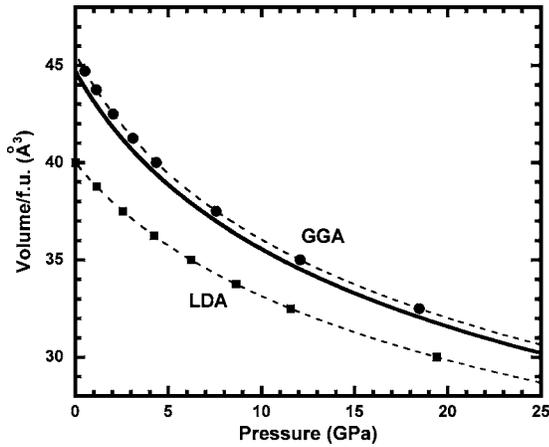


FIG. 1. Pressure-volume data for *B1*-type NaCl. The circles and squares denote the volumes from GGA and LDA calculations at 0 K. The solid line denotes the pressure-volume curve at 300 K based on the experimental data (Ref. 7).

III. METHOD OF ANALYSIS

The form of the most appropriate equation of state for solids has been discussed in many previous studies (e.g., Refs. 21 and 22). One of the general forms of the equation of state for solids is

$$P(V, T) = P(V, 0) + P_{\text{th}}(V, T). \quad (1)$$

$P(V, T)$ represents the total pressure P at volume V and temperature T . The first term on the right side of Eq. (1) is the pressure-volume relationship at 0 K, and the second term is the thermal pressure. In general, the difference in pressure between a reference state and a high P - T state is an important quantity. The equation of state can be written as follows:

$$P(V, T) - P(V_a, 300) = \Delta P(V_a \rightarrow V, 300) + P_{\text{th}}(V, 300 \rightarrow T). \quad (2)$$

The subscript a denotes the reference state. In this equation, the pressure change from the reference condition to higher P - T conditions can be obtained from the change in pressure due to the isothermal compression at ambient temperature and the thermal pressure change due to an isochoric temperature change. In this article, we have used the Vinet equation of state²³ for the first term on the right hand side of Eq. (2),

TABLE I. Bulk modulus of *B1* NaCl. The Birch–Murnaghan equation of state was used to calculate the bulk moduli of *B1*-type NaCl. B_0 : isothermal bulk modulus; B'_0 : first pressure deviation of bulk modulus; V_0 : volume at ambient pressure.

B_0 (GPa)	B'_0	V_0 (\AA^3)	
24.2	4.71	44.83	297 K, Decker (Ref. 1)
25.9	4.54	44.72	300 K, Brown (Ref. 7)
34.1	4.71	40.00	0 K, LDA (this study)
24.2	4.72	45.65	0 K, GGA (this study)
24.0	4.95	44.96	300 K, AIMD (this study)

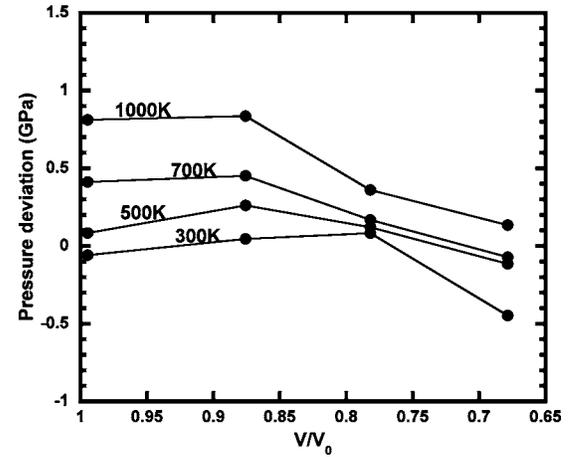


FIG. 2. Deviations of pressures of *B1*-type NaCl between the present calculations and the previous EOS. The solid circles denote the differences relative to the previous EOS (Ref. 7) for *B1*-type NaCl as a function of V/V_0 . Positive deviations correspond to the previous EOS predicting higher pressures than the present calculations using GGA method.

$$\Delta P(V_a \rightarrow V, 300) = 3B_{Ta} \frac{\left[1 - \left(\frac{V}{V_a}\right)^{1/3}\right]}{\left(\frac{V}{V_a}\right)^{2/3}} \exp\left\{\frac{3}{2}(B'_{Ta} - 1)\right\} \times \left[1 - \left(\frac{V}{V_a}\right)^{1/3}\right], \quad (3)$$

where B_{Ta} is the isothermal bulk modulus, and B'_{Ta} is $(\partial B_T / \partial P)_T$ at ambient temperature. Experiments on a wide range of materials have shown that the thermal pressure term P_{th} on the right hand side of Eq. (2) often takes a simple linear form, $P_{\text{th}} = \alpha B_T \Delta T$, when the temperature is higher than the Debye temperature.^{22,24} In general, αB_T is both temperature and volume dependent. When the temperature dependence of αB_T is negligible, Anderson *et al.*²⁴ yielded

$$P_{\text{th}}(V, 300 \rightarrow T) = \left[\alpha B_T(V_a) + \left(\frac{\partial B_T}{\partial T}\right)_V \ln \left(\frac{V_a}{V}\right) \right] (T - 300), \quad (4)$$

where $\alpha = (1/V)(\partial V / \partial T)_P$ is the volume thermal expansion coefficient, and $(\partial B_T / \partial T)_V$ is the temperature derivative of the isothermal bulk modulus at constant volume. Finally, Eq. (2) can be written as

TABLE II. Comparison of bulk modulus of *B2*-type NaCl at 0 K. The Birch–Murnaghan equation of state was used to calculate the bulk moduli of *B2*-type NaCl of this study.

B_0 (GPa)	B'_0	V_0 (\AA^3)	
26.6	5.2	41.35	Bukowinski and Aidun (Ref. 26)
24.4–35.6		39.65	Aprà <i>et al.</i> (Ref. 4)
25.6		40.54	Pendás (Ref. 27)
38.96	4.45	37.411	0 K, LDA (this study)
29.12	4.42	42.239	0 K, GGA (this study)

TABLE III. Comparison of transition pressure of NaCl.

P (GPa)	References
Experiments	
30	Bassett <i>et al.</i> (1968) (Ref. 9)
29.2	Piermarini and Block (1975) (Ref. 11)
29	Sato-Sorensen (1983) (Ref. 12)
26.8	Li and Jeanloz (1987) (Ref. 13)
30.6	Nishiyama <i>et al.</i> (2003) (Ref. 14)
Calculations	
27	Froyen and Cohen (Ref. 2)
11.4	Feldman <i>et al.</i> (Ref. 3)
28.9–39.2	Aprà <i>et al.</i> (Ref. 4)
22	Recio <i>et al.</i> (Ref. 5)
24.6–38.3	Sims <i>et al.</i> (Ref. 28)
27.2	Sims <i>et al.</i> (Ref. 29)
30	Zhang and Chen (Ref. 30)
25.0	GGA (this study)
26.5	LDA (this study)

$$\begin{aligned}
& P(V, T) - P(V_a, 300) \\
&= 3B_{Ta} \left[\frac{1 - \left(\frac{V}{V_a}\right)^{1/3}}{\left(\frac{V}{V_a}\right)^{2/3}} \right] \\
&\quad \times \exp \left\{ \frac{3}{2} (B'_{Ta} - 1) \left[1 - \left(\frac{V}{V_a}\right)^{1/3} \right] \right\} \\
&\quad + \left[\alpha B_T(V_a) + \left(\frac{\partial B_T}{\partial T} \right)_V \ln \left(\frac{V_a}{V} \right) \right] (T - 300). \quad (5)
\end{aligned}$$

This equation was used to fit the P - V - T data from AIMD calculated in this study. The fitting of thermoelastic parameters was performed by the least squares fit using the ORIGIN 7.5 software package. In the first step, parameters of isothermal compression (V_a , B_{Ta} , and B'_{Ta}) were determined using data at 300 K. Then, parameters of the thermal pressure due to the isochoric temperature change [$\alpha B_T(V_a)$ and $(\partial B_T / \partial T)_V$] were refined using data at high temperatures.

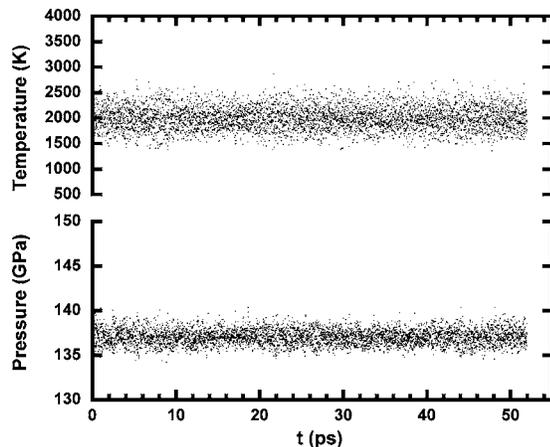


FIG. 3. Examples of temperature and pressure fluctuations of *ab initio* molecular dynamics simulation. The dots denote temperature and pressure values at 10 fs step. The volume was fixed during calculation. The cubic supercell containing 54 atoms ($3 \times 3 \times 3$) was used.

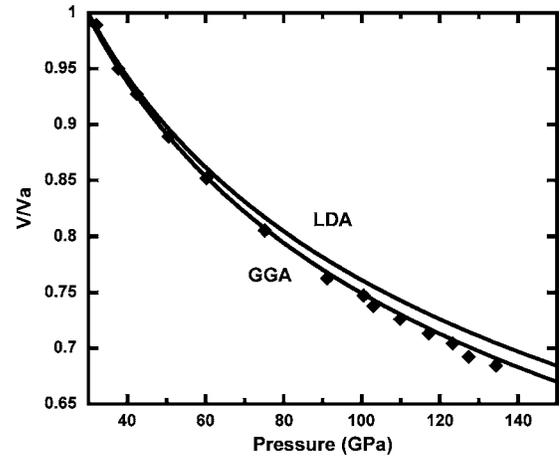


FIG. 4. Pressure-volume data for $B2$ -type NaCl at 300 K. The solid lines denote the volume changes calculated by the GGA and LDA methods. Solid diamonds denote the volumes from experimental study (Ref. 15). Volumes were normalized at 30 GPa.

IV. RESULTS AND DISCUSSION

In density-functional theory (DFT), one of two approximations to the exchange-correlation energy are usually used. One of them is the local density approximation (LDA), which has been used over the past 30 years. The other is the GGA, which includes several different functionals. We tested these two different approximations for the exchange-correlation functional, the LDA²⁵ and the GGA known as PW91.¹⁹ At first, we calculated the volume-pressure relationship of $B1$ -type NaCl at 0 K to assess both approximations. The primitive unit cell (eight atoms) at $6 \times 6 \times 6$ k -point grid was used to calculate the volumes and pressures. Figure 1 shows the comparison between our calculations and the experimental study. The calculated volumes of GGA are slightly larger than those observed by experiments. In contrast, LDA underestimated the volume significantly compared with experiments. The comparison of bulk moduli is shown in Table I. Our LDA calculation is inconsistent with the experimental observations. The calculated bulk modulus is much larger than those from experimental studies, and the

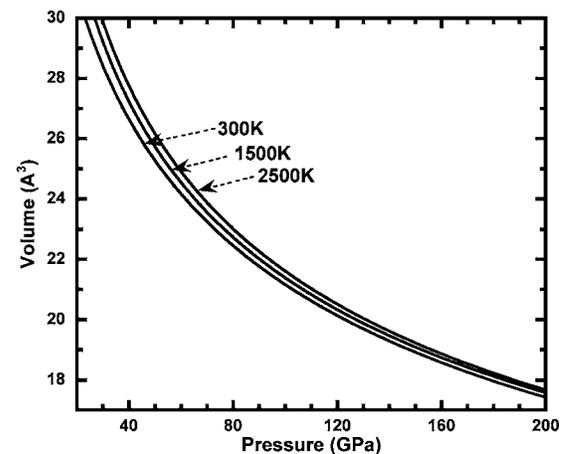


FIG. 5. Isothermal volume changes of $B2$ -type NaCl. The solid lines denote the calculated isotherms at temperatures of 300, 1500, 2500 K.

TABLE IV. Thermoelastic parameters of *B2*-type NaCl. The reference pressure, subscript *a*, is 30 GPa.

Parameter	
V_a (\AA^3)	27.70 ^a
B_{Ta} (GPa)	128.66
B'_{Ta}	4.374
$\alpha B_T(V_a)$ (GPa/K)	0.003 3
$(\partial B_T / \partial T)_V$ (GPa/K)	0.000 87

^aThe experimental data were used as the reference volume at 30 GPa (Ref. 15).

calculated volume at ambient pressures is lower than experimental values. In contrast, our GGA calculation is in good agreement with experiments. Therefore, we used GGA in our AIMD simulations to calculate the volume-pressure relation for NaCl.

An AIMD simulation for *B1*-type NaCl was also carried out at 300 K. We used a cubic supercell containing 64 atoms (equivalent to eight primitive unit cells), a plane-wave cutoff of 262.4 eV, and Γ point sampling. The calculated volume and bulk modulus from the AIMD simulations are in excellent agreement with experimental values (Table I). This fur-

ther indicates that the AIMD simulations using GGA is suitable to investigate the equation of state for NaCl.

Figure 2 shows the comparison between our calculations and experimental based *P-V-T* data⁷ at high temperatures. Pressure deviations are less than 1 GPa at pressures of 0–26 GPa, corresponding to the stability field of *B1*-type NaCl. As the deviation among previous equations of states (EOSs) based on the experimental data^{1,7} was ~ 0.5 GPa, our calculations using GGA are consistent with the EOSs for *B1*-type NaCl reported by previous studies.

Next, we calculated the volume-pressure relation of *B2*-type NaCl at 0 K using both LDA and GGA. A cubic supercell containing 16 atoms (equivalent to eight primitive unit cells) at $4 \times 4 \times 4$ *k*-point grid was used. Table II shows the comparison between our results and calculations from previous theoretical studies. Our calculations are in general agreement with those reported in previous studies. In our simulations, the bulk modulus from LDA calculations was larger than that from GGA calculations. This result is consistent with what we found for *B1*-type NaCl.

We also investigated the transition pressure from *B1* to *B2* type using both LDA and GGA at 0 K. The enthalpy was obtained directly in our calculations from

TABLE V. Pressure-temperature-volume table of *B2*-type NaCl from this study. Reference volume V_a is 27.70 \AA^3 from experimental study. (Ref. 25). Unit of pressure is given in GPa.

$1 - V/V_a$	300 K	500 K	1000 K	1500 K	2000 K	2500 K	3000 K
-0.14				21.23			
-0.12				22.50			
-0.10				23.93			
-0.08			23.91	25.53	27.14		
-0.06			25.68	27.31	28.93	30.55	
-0.04		26.02	27.66	29.29	30.92	32.56	
-0.02	27.56	28.22	29.86	31.50	33.14	34.78	
0.00	30.00	30.66	32.31	33.96	35.61	37.26	38.91
0.02	32.72	33.38	35.04	36.70	38.36	40.02	41.67
0.04	35.74	36.41	38.07	39.74	41.41	43.08	44.75
0.06	39.10	39.78	41.45	43.13	44.81	46.48	48.16
0.08	42.85	43.52	45.21	46.90	48.58	50.27	51.96
0.10	47.02	47.70	49.39	51.09	52.78	54.48	56.17
0.12	51.66	52.34	54.04	55.75	57.45	59.16	60.87
0.14	56.82	57.51	59.22	60.94	62.65	64.37	66.09
0.16	62.58	63.27	64.99	66.72	68.44	70.17	71.90
0.18	68.99	69.69	71.42	73.16	74.89	76.63	78.37
0.20	76.15	76.85	78.59	80.34	82.09	83.83	85.58
0.22	84.14	84.84	86.60	88.35	90.11	91.87	93.63
0.24	93.06	93.77	95.54	97.31	99.08	100.85	102.62
0.26	103.05	103.76	105.54	107.33	109.11	110.89	112.67
0.28	114.24	114.95	116.75	118.54	120.33	122.13	123.92
0.30	126.78	127.51	129.31	131.12	132.92	134.73	136.53
0.32	140.88	141.61	143.42	145.24	147.06	148.88	150.69
0.34	156.73	157.34	159.30	161.13	162.96	164.79	166.62
0.36	174.61	175.34	177.19	179.03	180.88	182.72	184.56
0.38	194.79	195.53	197.39	199.25	201.10	202.96	204.82
0.40	217.63	218.38	220.25	222.12	223.99	225.86	227.74
0.42	243.53	244.29	246.18	248.06	249.95	251.84	253.72
0.44	272.99	273.75	275.66	277.56	279.46	281.36	283.27
0.46	306.58	307.35	309.27	311.19	313.11	315.02	316.94
0.48	345.00	345.78	347.71	349.64	351.58	353.51	355.45

$$H = E + PV, \quad (6)$$

where E is the internal energy. Table III shows transition pressures between $B1$ - and $B2$ -type NaCl from our simulation and previous studies. The transition pressure from GGA is almost the same as that for LDA and is consistent with those from previous simulations (Table III). The experimentally reported transition pressures (27–31 GPa) are slightly higher than those from our simulations (25 GPa for GGA and 26.5 for LDA).

Figure 3 shows an example of pressure and temperature fluctuations in the AIMD simulation for $B2$ -type NaCl. The thermostatic temperature was 2000 K. After ~ 1 ps, this system reached an equilibrium state, and no displacement from the equilibrium state was observed up to 50 ps. Typical ranges of fluctuation for temperature and pressure were 500 K and 2 GPa at 2000 K, respectively. We tested the adequacy of the $3 \times 3 \times 3$ supercell by simulations with different system sizes, $2 \times 2 \times 2$ and $4 \times 4 \times 4$ supercells. The results from the $2 \times 2 \times 2$ supercell showed the large difference compared to the $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercells. For example, the thermal pressure from 300 to 2000 K for the $2 \times 2 \times 2$ supercell was 40% smaller than those for other supercells. In contrast, no significant discrepancy between the $3 \times 3 \times 3$ and the $4 \times 4 \times 4$ supercells was observed. This indicated that converged results could be obtained from the $3 \times 3 \times 3$ supercell simulation.

Next, we calculated the volume-pressure relation of $B2$ -type NaCl at 300 K using both LDA and GGA. A cubic $3 \times 3 \times 3$ supercell containing 54 atoms (equivalent to 27 primitive unit cells) at the Γ point grid was used. Figure 4 shows the volume-pressure relations of our calculations and experimental data from our previous study.¹⁵ The bulk modulus from LDA calculations is significantly larger than that from experimental data. In contrast, GGA calculations agree with experimental data. This also indicated that GGA is suitable for the investigation of the equation of state for $B2$ -type NaCl.

The P - V - T data of $B2$ -type NaCl were calculated in the ranges of 14–288 GPa and 300–2500 K using AIMD simulations by GGA (supplemental material³¹). Most of the data were calculated in the stability field of $B2$ -type NaCl to avoid uncertainty from being in a metastable state. Figure 5 shows the fitted isothermal compressibility curves at 300, 1500, and 2500 K. We fitted the P - V data of 300 K with the Vinet equation of state [Eq. (3)]. A least squares fit yielded an isothermal bulk modulus B_{Ta} and its pressure derivative B'_{Ta} of 128.66 GPa and 4.374, respectively, at the reference pressure of 30 GPa. It is known that GGA tends to predict volumes that are slightly too large. As the overestimated volume compared to experimental data¹⁵ is 0.66 \AA^3 at 30 GPa and 300 K, we simply reduced all the calculated volumes by this amount when fitting to the equation of state.

We used the thermal pressure equation of state [Eq. (5)] to analyze the P - V - T data. The results of the fit for our P - V - T data to Eq. (5) are listed in Table IV. $\alpha B_T(V_a)$ and $(\partial B_T / \partial T)_V$ were 0.0033 and 0.000 87, respectively. ΔP_{th} of $B2$ -type NaCl was insensitive to volume change because $(\partial B_T / \partial T)_V$ was very small. Table V lists the pressure at selected compressions and temperatures based on the equation

of state in this study. As $B1$ -type NaCl is the stable phase at the low pressure and low temperature region, data at this region are omitted. Moreover, the region above the melting temperature of NaCl is also omitted.

In conclusion AIMD simulations can be used to predict the temperature and volume dependence of pressure for the ionic crystal. Thus, in the absence of any accurate experimental data, our results may now enable the use of $B2$ -type NaCl as an *in situ* pressure standard for experimental studies at pressures and temperatures beyond the stability field of $B1$ -type NaCl.

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³¹See EPAPS Document No. E-JAPIAU-103-102802 for a table on the raw results of pressure-temperature volume relations by the AIMD calculations. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>).