The equation of state of B2-type NaCl

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Abstract

The equation of state (EOS) of B2-type NaCl has been investigated to 270 GPa and 3000 K using the first-principles molecular dynamics method and high-pressure experiments in a diamond anvil cell. We used the high-pressure experimental data to determine the compressibility at room temperature, and used the generalized gradient approximation (GGA) and the projector augmented-wave method (PAW) in simulations to calculate the thermal pressure. A Vinet EOS fitted to the room temperature data yielded an isothermal bulk modulus of $B_{T0} = 39.25$ GPa and a pressure derivative of $B_{T0}' = 4.72$. The high-temperature data from the first-principles calculations were fitted to the thermal pressure EOS. The resulting calculated parameters of the thermal pressure, $aB_{T}(V_{0}, T)$ and $(\partial B_{T} / \partial T)_{V}$, were $3.28 \times 10^{-3}$ (GPa/K) and $4.3 \times 10^{-4}$ (GPa/K), respectively. A small volume dependence of the thermal pressure of B2-type NaCl was revealed from the analysis of our data. A significant temperature dependence of the calculated Grüneisen parameters was confirmed. This indicates that the conventional approach using the Mie-Grüneisen approximation is likely to have a significant uncertainty in determining the EOS for B2-type NaCl, and that an intrinsic anharmonicity should be considered to analyze the EOS.

1. Introduction

NaCl is an important alkali halide that is used as a pressure gauge in laboratory measurements of compression data [1-5]. It is one of the most widely used internal pressure standards in high-pressure diffraction experiments owing to the availability of a large body of experimental data. NaCl has a stable B1-type structure up to a pressure of ~30 GPa, and its phase transition into a B2-type structure has been confirmed [6]. Numerous attempts to investigate the EOS and thermoelastic properties have been carried out on B1-type NaCl. However, reliable data for the high-pressure B2-type NaCl phase are not available.

The bulk modulus of B2-type NaCl at room temperature has been repeatedly measured experimentally in previous studies [e.g., 3, 7]. In contrast, previous theoretical studies using first-
principles calculations have investigated the physical properties of NaCl, including its bulk modulus at 0 K [e.g., 8-10]. However, the uncertainty in first-principles calculations is non-negligible, because the discrepancy in the values of the bulk modulus and the zero-pressure volume from previous calculations is ~50 % and ~10 %, respectively [10]. We noticed that the scatter of the experimental bulk modulus values was much smaller than that obtained from calculations. This indicates that experiments are more accurate than first-principles calculations for determining the bulk modulus. It is likely that the experimental uncertainty is related to the differential stress in the sample and the credibility of the pressure standard. In the case of diamond anvil cell experiments, the differential stress is accumulated as the pressure increases because the diamond anvils apply a uniaxial compression in the sample chamber. Therefore, an annealing of the sample at each pressure increment is a good technique to reduce the differential stress of the sample. It is known that the influence of the pressure scale on the pressure-volume data is non-negligible. The ruby pressure scale [e.g., 11-13] has been frequently used in room temperature compression experiments. Recently, the ruby pressure scale has been re-evaluated by several groups [14-18]. For example, Mao et al.’s ruby pressure scale [13] underestimates pressure and misleads investigations into the elastic properties of materials. Typical underestimates of the pressure were 5~10 % at pressures above 100 GPa. Therefore, we have to consider a correction to the ruby pressure scale for the pressure-volume data set of B2-type NaCl. The available pressure-volume data at high temperatures from experiments is limited for B2-type NaCl [4]. Recently, the first-principle molecular dynamics method has been used to calculate the thermoelastic properties of materials under extreme high-pressure and high-temperature conditions. 

In this study, we used density functional theory to investigate the thermal pressure of B2-type NaCl. We also used the experimental data to determine the room temperature EOS of B2-type NaCl. The combination of the first-principles calculations and the high-pressure experiments led us to determine a reliable EOS for B2-type NaCl over a wide range of pressures and temperatures.

2. Methods

The first-principles calculations carried out in this study were based on density functional theory using the VASP package [19]. We used the generalized gradient approximation (GGA) [20] for the exchange-correlation functional. The electronic wave functions were expanded in a plane-wave basis set with a cut-off energy of 900 eV, and the electron-ion interactions were described using by the projector augmented wave (PAW) method [21, 22]. The core radii used were 2.20 a.u. for Na and 1.50 a.u. for Cl, respectively. We used a 54-atom supercell with Γ-point Brillouin zone sampling, and a time step of 1 fs for the first-principles molecular dynamics simulation at constant volume. Simulations were run in the constant NVT ensemble with the Nosé thermostat [23] for 5-10 ps after equilibration. The computation time required to reach equilibrium varied between configurations, and depended on the starting atomic positions, velocity, temperature, and pressure. Details of our methodology have been given elsewhere [10, 24].

The high-pressure experiments were performed at synchrotron beam lines of the BL13A, Photon Factory, Japan [25] and the BL10XU, SPring-8, Japan [26]. Powdered NaCl (purity = 99.99%) was mixed with gold (purity = 99.5%) and was ground to a fine powder, and formed into a small pellet with a thickness of ~10 μm using a hand press. Rhenium gaskets were pre-indentated to a thickness of 50 μm and then had a hole drilled in the centre of the indentation. The sample pellet was embedded in periclase (MgO), which was used as the pressure-transmitting medium. The embedded sample was then loaded into the diamond anvil cell. Gold was used as the internal pressure calibrant. The samples were heated from both sides to release the differential stress accumulated during the compression using an infrared laser. The laser beam was carefully scanned to heat the entire sample. The annealing temperature was estimated to about 1,500-2,000 K from the visual color of the sample emission. At the end of the heating period, the laser power was gradually decreased without invoking a temperature quench, because such a quench could lead to a significant differential stress occurring in the sample chamber. After annealing, the X-ray diffraction data of the sample were collected on an imaging plate. The observed intensity on the imaging plates was integrated as a function of 2θ to obtain conventional,
one-dimensional diffraction profiles. The pressure was determined from the observed unit cell volume of gold using the revised EOS of Takemura [27]. The EOS parameters for B2-type NaCl at room temperature were obtained using a least-squares fit to the pressure-volume data of the Vinet EOS [28]. Details of experimental methods used have been described elsewhere [29, 30].

3. Results and discussion

The EOS of a solid can be described in a general form as a functional relationship between the pressure, volume, and temperature as

\[ P_{\text{total}}(V, T) = P_{s}(V, 300) + P_{th}(V, T), \]

where \( P_{\text{total}}(V, T) \) represents the total pressure at volume \( V \) and temperature \( T \). The terms \( P_{s}(V, 300) \) and \( P_{th}(V, T) \) represent the static pressure at volume \( V \) and 300 K, and the thermal pressure at volume \( V \) and temperature \( T \), respectively. We determined the thermoelastic parameters for B2-type NaCl at ambient temperature (300 K) using the Vinet EOS [28]. The Birch-Murnaghan EOS is frequently used to analyze pressure-volume data for solids. However, the Birch-Murnaghan EOS does not accurately represent the pressure-volume data of most solids under very high compression. We used the Vinet EOS, as very high compression data (0.7 > \( V/V_0 \)) was estimated in our work. The Vinet EOS is given by the following expression

\[ P_{s} = 3B_{T0}\left(\frac{V}{V_0}\right)^{\frac{3}{2}}\left[1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right] \exp \left\{ \frac{3}{2}(B_{T0}' - 1) \left[1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right] \right\}, \]

where \( B_{T0} \) is the isothermal bulk modulus at 300 K, \( V_0 \) is the zero-pressure volume, \( V \) is the high-pressure volume, and \( B_{T0}' \) is the pressure derivative of \( B_{T0} \). The thermal pressure EOS was used to evaluate the thermal pressure, \( P_{th} \) [31]. The thermal pressure of the thermal pressure EOS can be written as follows

\[ P_{th} = \alpha B_{T}(V_0, T) + \left(\frac{\partial B_{T}}{\partial T}\right)_V \ln \left(\frac{V_0}{V}\right) (T - T_0), \]

The fitting parameters of the Vinet EOS combined with the thermal pressure EOS are \( V_0, B_{T0}, B_{T0}', \alpha B_{T}(V_0, T), \) and \( \left(\frac{\partial B_{T}}{\partial T}\right)_V \). The value of \( T_0 \) is 300 K. The thermal expansivity at ambient conditions can be calculated from \( \alpha_0 = (\alpha B_{T}(V_0, T))/B_{T0} \).

| Table 1. Comparison of the compressibility of B2-type NaCl at 300 K. |
|---------------------|-------------------|------------------|
|                    | \( B_{T0} \) (GPa) | \( B_{T0}' \)   | \( V_0 \) (Å³) |
| Experiment\(^a\)   | 26.86             | 5.25            | 41.35          |
| Classical MD\(^b\)| 28.45             | 5.16            | 41.11          |
| Experiment\(^c\)   | 31.25             | 4.98            | 40.59          |
| This study\(^d\)   | 39.26             | 4.72            | 39.28          |

The Vinet equation of state was used to calculate the parameters. Key: \( B_{T0} \): isothermal bulk modulus at 0 GPa and 300 K, \( B_{T0}' \): first pressure derivation of the bulk modulus, \( V_0 \): volume at 0 GPa and 300 K. \(^aFei\) et al. [4]. \(^bUeda\) et al. [32]. \(^cOno\) et al. [3] using Anderson et al.’s gold pressure scale [33]. \(^d\) data from high-pressure experiments [3] and the revised ruby scale [18] were used.

A least squares fit of the experimental data [3] at 300 K yields \( V_0 = 39.28 \text{ Å}^3, B_{T0} = 39.26 \text{ GPa}, \) and \( B_{T0}' = 4.72 \) using the gold pressure scale. We used Takemura’s gold scale [27] corrected using the
revised ruby scale of Dorogokupets and Oganov [18]. The EOS for gold applied in our study had \( B_{T0} = 166.5 \text{ GPa} \), and \( B_{T0}' = 5.907 \). Table 1 shows a comparison of the compressibility obtained from previous studies and that from our results. A difference in all the parameters is confirmed. When we used Anderson et al.’s gold scale [33] to calculate the parameters from our experimental data, the values of parameters were in general agreement with those reported by previous studies [4, 32]. Therefore, this discrepancy is due to the difference in the ruby pressure scale. Most of the older EOS studies used a diamond anvil cell at room temperature, and so were influenced by the old ruby scale of Mao et al. [12, 13] or related works, which underestimated the actual pressure. In contrast, the more recent reliable ruby scale was used in our study. Consequently, the value of our bulk modulus was larger, and the values of our pressure derivative and zero-pressure volume are smaller than those obtained in previous studies. It should be noted that the zero-pressure volumes of several B2-type alkali halides, which have been reported by previous studies [34], are smaller than that of B2-type NaCl.

Some EOSs (i.e., Murnaghan EOS [35], Birch-Murnaghan EOS [36], Vinet EOS [28], Natural strain EOS [37], and Parametric EOS [38]) have been proposed to analyze pressure-volume data for solids. To assess the influence of different EOSs, we calculated the parameters from our pressure-volume data using different EOSs. The difference in parameters is significant. As B2-type NaCl is unstable at pressures lower than 30 GPa, the uncertainty of parameters at ambient pressure is non-negligible. For example, the value of the bulk modulus using the Birch-Murnaghan EOS is larger, and the value of the pressure derivative is smaller than those using the Vinet EOS. These changes in the parameters are in agreement with those reported in previous study [4]. In general, the Vinet EOS gives a better representation of the data over a large compression range. Therefore, we used the Vinet EOS to calculate the parameters.

The results of the fit of our \( P-V-T \) data to the thermal pressure EOS are summarized in Table 2. Figure 1 shows the \( P-V-T \) data from both the experiments and calculations carried out in our study. The values of \( \alpha_{BT(V_0,T)} \) and \( (\partial B_T / \partial T)_V \) were 0.0033 and 0.00043, respectively. The thermal pressure, \( \Delta P_{th} \), of B2-type NaCl was not sensitive to changes in volume, because the values of \( (\partial B_T / \partial T)_V \) was very small. This result is in general agreement with previous studies [4, 10, 32].

| Parameter | Value |
|-----------|-------|
| \( V_0 \) (Å\(^3\)) | 39.28(2.24) |
| \( B_{T0} \) (GPa) | 39.26(13.77) |
| \( B_{T0}' \) | 4.72(50) |
| \( \alpha_{BT(V_0,T)} \) (GPa/K) | 0.00328(7) |
| \( (\partial B_T / \partial T)_V \) (GPa/K) | 0.00043(11) |

The Vinet equation of state was used to calculate the parameters of B2-type NaCl. Key: \( B_0 \): isothermal bulk modulus at 0 GPa and 300 K, \( B_{T0}' \): first pressure derivation of the bulk modulus, \( V_0 \): volume at 0 GPa and 300 K. The terms \( \alpha_{BT(V_0,T)} \) and \( (\partial B_T / \partial T)_V \) are parameters of the thermal pressure.
Figure 1. Pressure-volume data for B2-type NaCl. The circles and diamonds denote the volumes from experiments at 300 K and first-principle calculations at temperatures from 300 to 3000 K. The dashed lines denote the calculated isotherms at temperatures of 300, 500, 1000, 2000, and 3000 K.

Figure 2. Anharmonic effects on the Grüneisen parameter. The solid circles denote the calculated Grüneisen parameter at 300 and 3000 K using first-principles molecular dynamics calculations. The solid lines denote the linear fit using the least square method.
The Mie-Grüneisen-Debye EOS has been frequently used in previous studies on the EOS of solids. The Mie-Grüneisen approximation is valid, if the quasiharmonic term is dominant in the thermal pressure. However, it is known that the anharmonic term, which is not included in the Mie-Grüneisen approximation, is non-negligible at high temperatures. Therefore, we assessed the effect of the anharmonicity on the EOS for B2-type NaCl. The effective Grüneisen parameter can be written as follows

$$\gamma_{\text{eff}}(V,T) = \gamma_{qh}(V) - a(V,T),$$

where $\gamma_{qh}(V)$ and $a(V,T)$ are the quasiharmonic Grüneisen parameter and the intrinsic anharmonicity term, respectively. If the anharmonicity is negligible, then the effective Grüneisen parameter does not change at high temperatures. Therefore, we calculated the effective Grüneisen parameter at different volumes and temperatures. Figure 2 shows the temperature dependence of the effective Grüneisen parameter due to the intrinsic anharmonic effects. A difference in the effective Grüneisen parameter at different temperatures was confirmed. Our calculations indicate that the classical quasiharmonic approximation has a significant uncertainty in the determination of the EOS for B2-type NaCl. Most of the previous experimental studies on the EOS of solids have not considered the influence of anharmonicity, and the Grüneisen parameter has been assumed to be a function of volume only. As the error in the experimental data was considerable, detailed analyses could not be performed. In our study, the combination of high-pressure experiments with first-principles calculations has led to the uncovering of a temperature dependence of the Grüneisen parameter due to the anharmonicity of B2-type NaCl at high temperatures.

Acknowledgments
This work made use of the super computer system of JAMSTEC and of the computer systems of the Earthquake Information Center of the Earthquake Research Institute. The synchrotron radiation experiments were performed at the PF, KEK (Proposal No. 2003G187) and at the SPring-8, JASRI (Proposal No. 2003A0013). This work was partially supported by Grant-in-Aid for Scientific Research from JSPS and the Earthquake Research Institute cooperative research program, Japan.

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