Characterization of the High-Pressure Structural Transition and Thermodynamic Properties in Sodium Chloride: A Computational Investigation on the Basis of the Density Functional Theory

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Using first-principles calculations, the elastic constants, the thermodynamic properties, and the structural phase transition between the B1 (rocksalt) and the B2 (cesium chloride) phases of NaCl are investigated by means of the pseudopotential plane-waves method. The calculations are performed within the generalized gradient approximation to density functional theory with the Perdew–Burke–Ernzerhof exchange-correlation functional. On the basis of the third-order Birch–Murnaghan equation of states, the transition pressure \( P_t \) between the B1 phase and the B2 phase of NaCl is determined. The calculated values are generally speaking in good agreement with experiments and with similar theoretical calculations. From the theoretical calculations, the shear modulus, Young’s modulus, rigidity modulus, and Poisson’s ratio of NaCl are derived. According to the quasi-harmonic Debye model, we estimated the Debye temperature of NaCl from the average sound velocity. Moreover, the pressure derivatives of elastic constants, \( \partial C_{ij}/\partial P \), \( \partial C_{ij}/\partial P \), \( \partial C_{ij}/\partial P \), \( \partial S_{ij}/\partial P \), \( \partial S_{ij}/\partial P \), and \( \partial S_{ij}/\partial P \), for NaCl crystal are investigated for the first time. This is a quantitative theoretical prediction of the elastic and thermodynamic properties of NaCl, and it still awaits experimental confirmation.

1. Introduction

With the rapid development of high-pressure techniques, there has been considerable interest in recent years in the investigations of the structural phase transition and high-pressure behavior in material because the knowledge of physical and chemical properties of material at high pressure is important for a variety of scientific and technological applications.1–7 For instance, the optical properties, the thermodynamic properties, and the equation of state (EOS) of mineral material at high pressure is essential in the investigations of the interior of the earth in geophysics and for the investigations of the evolutions of stars in astrophysics. NaCl is one of the most widely used nonmetallic mineral materials. It plays an important role in biology, chemistry, and several other scientific disciplines as well as being a material of obvious importance to many aspects of daily life.8 As a simple ionic crystal, investigating the physical properties of NaCl, such as its phase transformation and elastic properties, can provide valuable information for understanding the physical and chemical properties of more complex ionic crystals.

The mechanism of transition from rocksalt structure (the B1 phase) to cesium chloride structure (the B2 phase) of NaCl has been extensively investigated both experimentally and theoretically in the past decades.9–19 On the basis of X-ray diffraction investigations under high pressure, Bassett et al. observed that the phase transformation of NaCl from B1 to B2 phases at a pressure of \( \sim 30 \) GPa at room temperature.9 In order to elucidate the phase boundary between B1 and B2 phases of NaCl, Nishiyama et al. have developed experimental techniques and performed a series of X-ray diffraction experiments at temperatures between 1150 and 2000 K using a Kawai-type apparatus.8 Theoretically, several groups have made to interpret the high-pressure behavior and calculated the EOS of NaCl by using the ab initio model. Bukowinski et al. have carried out a first-principles calculation of the equation of state and charge distributions for the B1 and the B2 phases of NaCl.12 On the basis of the lattice theory of ionic solids and analytical functions for the volume dependence of the short-range force constant, Shanker et al. have discussed the equation of state and pressure derivatives of bulk modulus for NaCl crystal.13 However, comparing with the availability of precise experimental data, an adequate analysis of the complete physical origin of NaCl under pressure is still lacking, especially for the B2-type NaCl. Furthermore, the investigations of the elastic and thermodynamic properties of ionic crystals at high pressure has been described as an important area of research in solid state physics to investigate the essential features of interatomic binding forces at the phase transformation.

In this paper, we describe a systematical investigation of the high-pressure behavior and structural phase transition of NaCl by the first-principles quantum-mechanical calculations, which are very successful in predicting the phase stability and high-pressure equations of state for a wide class of crystals. The aim of the present work is twofold. On the one hand, it is to provide a reasonable interpretation about the structural phase transition between the B1 phase and the B2 phase of NaCl under high-pressure. On the other hand, it is to provide powerful guidelines for future experimental investigations and hope that such a investigation might contribute some further understanding of the thermodynamic properties of NaCl and its isomorphs.

This paper is organized as follows: In section 2, a brief description of the technical details and model in the theoretical
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The determination of the structural phase transition and thermodynamic properties is reported. The calculated pressure-dependent structural, elastic, and thermodynamic properties as well as the experimental and theoretical results for the high-pressure behavior of NaCl are discussed in section 3. Conclusions are summarized in section 4.

2. Method

The equation of state and elastic properties calculations are performed using the pseudopotential plane-wave method within the framework of the density functional theory and implemented through the Cambridge Serial Total Energy Package (CASTEP) program.\textsuperscript{20–24} This technique has become widely recognized as the method of choice for computational solid structural properties investigations.\textsuperscript{25–27} The thermodynamic properties for the B1 and B2 phases of NaCl are calculated by the quasi-harmonic Debye model.\textsuperscript{28} The exchange correlation energy is described in the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional.\textsuperscript{29} The Na (2s\textsuperscript{2} 2p\textsuperscript{6} 3s\textsuperscript{1}) and Cl (3s\textsuperscript{2} 3p\textsuperscript{5}) states are treated as valence electrons. Interactions of electrons with ion cores are presented by the norm conserving pseudopotential for all atoms. In all the high-precision calculations, the cutoff energy of the plane-wave basis set is 500 eV for both rocksalt and cesium chloride structures of NaCl. The special points sampling integration over the Brillouin zone are carried out using the Monkhorst–Pack method with a 20 × 20 × 20 special k-point mesh. The kinetic energy cutoff and mesh of k-points are optimized by performing self-consistent calculations. The self-consistent is considered to be converged when the total energy is 10\textsuperscript{-6} eV/atom. These parameters are sufficient in leading to well-converged total energy and elastic stiffness coefficients calculations.

3. Results and Discussion

3.1. Pressure-Induced Structural Phase Transition. In order to obtain a more general insight into the phase stability of NaCl, we have carried out calculations of the Gibbs free energy $G$ for the two involved phases. In general, the Gibbs free energy $G$ can be expressed as\textsuperscript{30}

$$ G = E + PV - TS $$

where $E$ is the internal energy, $S$ is the vibrational entropy, and $P$ and $V$ are the pressure and volume. Since the theoretical calculations are performed at $T = 0$ K, the Gibbs free energy $G$ becomes equal to the enthalpy $H$

$$ H = E + PV $$

Under compression, the calculation shows that NaCl will undergo a structural phase transition from the B1 phase to the B2 phase by increasing the pressure (see Figure 1). According to the third-order Birch–Murnaghan equation of states\textsuperscript{30}

$$ P = \frac{3}{2}B_0\left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right] + \frac{3}{4}(B'_0 - 4) \times \left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right] $$

we calculated the total energy of the two-ion primitive cell of NaCl in both the B1 structure and the B2 structure as a function of pressure from 0 to 70 GPa. The transition pressure $P_t$ for the structural phase transitions is determined by the usual condition of equal enthalpies in the both phases, i.e., $H_{B1}(P_t) = H_{B2}(P_t)$. The variations of the enthalpy versus the pressure of the primitive cell of NaCl are presented in Figure 2. As can be seen from Figure 2, the intersection of the two enthalpy curves implies that the B1–B2 phase transition in NaCl occurs at 29.73 GPa. This result is in good agreement with experimental data and theoretical work.\textsuperscript{8,10,11,17} The comparisons of the transition pressure $P_t$ between the our theoretical values and previous investigations are shown in Table 1.

3.2. Structural Properties. The structural properties are very important for understanding the solid properties from a microscopic point of view. The reason is that the structural properties can provide highly detailed information about the essential features of interatomic binding forces in solids. Using the first-principles calculations, we have calculated the structural properties for both the B1-type and the B2-type NaCl. The calculated lattice constant $a$, the primitive cell volume $V_0$, the bulk modulus $B_0$, the first pressure derivative of bulk modulus $B'_0$, and the

<table>
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<th>$P_t$ (GPa)</th>
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<tr>
<td>28.20</td>
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<tr>
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<td>Piermarini et al. (1975) (ref 15)</td>
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<td>29.73</td>
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<td>25.00</td>
<td>Ono et al. (2008) (ref 11)</td>
</tr>
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<td>31.00</td>
<td>Galamba et al. (2007) (ref 10)</td>
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<td>28.90–39.20</td>
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Figure 1. The two structures of NaCl.

Figure 2. Enthalpy of NaCl in both the B1 and B2 structures. The phase transition appears at 29.73 GPa.
second pressure derivative of bulk modulus $B_0''$ for $B1$ and $B2$ phases are listed in Table 2, together with the available experimental, and theoretical work for comparison. From Table 2, we can see that the calculated lattice constant $a$ and primitive cell volume $V_0$ agree well with the experimental data. The overestimation of lattice constant $a$ parameter is 0.12% for $B1$ phase and 0.92% for $B2$ phase, and the primitive cell volume $V_0$ parameter is 3%. However, the calculated first pressure derivative of bulk modulus 4.03 of $B2$-type NaCl is smaller than the experimental value 5.20 obtained by Bukowinski et al., but it is in good agreement with the theoretical value 4.42 obtained by Ono et al. The good agreement between them shows the accuracy of the present electronic structure calculations.

### 3.3. Elastic Properties

For a cubic NaCl crystal, there are three independent elastic constants ($C_{11}, C_{12}, C_{44}$) which are believed to be related to the second-order change in the internal energy of a crystal under deformation. The mechanical stability criteria for a cubic crystal are given by:

\[ C_{11} > 0, \quad C_{44} > 0, \quad C_{11} > |C_{12}|, \quad (C_{11} + 2C_{12}) > 0 \]  

(4)

Hence, to investigate the stability of NaCl crystal, we have calculated the elastic constants under hydrostatic pressure by a direct method, i.e., ab initio stress–strain relations. In this method, the stress is calculated as a function of the strain with the internal coordinates optimized under each strain condition, and the elastic constants are the derivatives of the stress with respect to the strain. On the basis of the Hooke’s law, the elastic stiffness tensor $c_{ijkl}$ can be expressed as:

\[ c_{ijkl} = \left( \frac{\partial \sigma_{ij}(x)}{\partial \epsilon_{kl}(x)} \right)_X \]  

(5)

where $\sigma_{ij}$ and $\epsilon_{kl}$ are the applied stress and Eulerian strain tensors and $X$ and $x$ are the coordinates before and after the deformation. Under the hydrostatic pressure $P$, we have:

\[ c_{ijkl} = \left( \frac{1}{V(x)} \frac{\partial^2 E(x)}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \right)_X + \frac{P}{2} (\delta_{ij} \delta_{kl} - \delta_{il} \delta_{kj} - \delta_{ik} \delta_{jl}) \]  

(6)

where $\delta$ is the finite strain variable. For the case of isotropic stress, the three nonindependent elastic constants ($C_{11}, C_{12}, C_{44}$) of the isotropic aggregate can be transformed into the three independent elastic constants ($C_{11}, C_{12}, C_{44}$) as follows:

\[ c_{11} = C_{11}, \quad c_{12} = C_{12} + P, \quad c_{44} = C_{44} - \frac{P}{2} \]  

(7)

The adiabatic bulk modulus $B_s$ and the shear modulus $G$ of the NaCl can be expressed as a function of the three independent elastic constants, which are in the following forms:

\[ B_s = \frac{C_{11} + 2C_{12}}{3}, \quad G = \frac{C_{11} - C_{12} + 3C_{44}}{5} \]  

\[ G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})}, \quad G = \frac{G_V + G_R}{2} \]  

(8)

where $G_V$ is the Voigt shear modulus and $G_R$ is the Reuss shear modulus.

The elastic anisotropy of a crystal is the orientation dependence of the elastic modulus or sound velocities. Essentially, all known crystals are elastically anisotropic. A convenient method of describing the degree of elastic anisotropy for a cubic crystal has been defined as:

\[ A^* = \frac{3(A - 1)^2}{[3(A - 1)^2 + 25A]} \]  

(9)

where $A = 2C_{44}/(C_{11} - C_{12})$ is the usual anisotropy factor. Equation 9 is an important result of the present analysis because it represents the degree of elastic anisotropy for NaCl crystal. Generally, $A^*$ is zero for elastically isotropic crystal (i.e., $A = 1$). For an anisotropic crystal, $A^*$ is always positive and a single valued measure of the elastic anisotropy regardless of whether $A$ smaller or larger than 1. Further, it is shown that $A^*$ gives the relative magnitude of the actual elastic anisotropy possessed by the crystal. The anisotropic factors as calculated from the elastic constants of NaCl are given in Table 3. It can be seen from Table 3 that NaCl crystal is characterized by a profound anisotropy since the anisotropy factor $A < 1$ for both $B1$ phase and $B2$ phase, and the anisotropy factor $A = 0.583$ for $B1$ phase is larger than $A = 0.035$ for $B2$ phase. This means that the degree of elastic anisotropy for $B1$ phase is smaller that the $B2$ phase of the NaCl.
TABLE 3: Calculated Elastic Constants $C_{ij}$ (GPa), Anisotropic Factor A, Adiabatic Modulus $B_s$ (GPa), Voigt Shear Modulus $G_v$ (GPa), Reuss Shear Modulus $G_R$ (GPa), Shear Modulus $G$ (GPa), Young’s Modulus $E$ (GPa), Rigidmodulus $G$, (1/GPa), and Poisson’s Ratio $\nu$ for NaCl at Zero Pressure

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<tr>
<th></th>
<th>B1</th>
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<td>57.546</td>
<td>57.300$^{b, b}$</td>
<td>58.430$^{c, a}$</td>
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<td>$C_{44}$</td>
<td>13.315</td>
<td>13.300$^{e, e}$</td>
<td>13.310$^{e, e}$</td>
<td>13.730$^{e, e}$</td>
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<tr>
<td>A</td>
<td>0.583</td>
<td>0.035</td>
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<td>$A^*$</td>
<td>0.034</td>
<td>0.763</td>
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<td>$B_s$</td>
<td>27.117</td>
<td>27.934</td>
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<td>$G_v$</td>
<td>17.118</td>
<td>15.170</td>
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<td>$G_R$</td>
<td>15.977</td>
<td>2.039</td>
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<td>$G$</td>
<td>16.547</td>
<td>8.605</td>
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<tr>
<td>$E$</td>
<td>53.466</td>
<td>75.615</td>
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<tr>
<td>$\nu$</td>
<td>0.171</td>
<td>0.049</td>
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<td>$G_t$</td>
<td>22.822</td>
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$^a$ Reference 14, $^b$ Reference 39, $^c$ Reference 32, $^d$ Reference 40.

obtained elastic constants, we can see that $C_{11} - C_{12} > 0$ and $C_{11} + 2C_{12} > 0$. This implies that the both structures are elastically stable.

3.4. Thermodynamic Properties. To investigate the thermodynamic properties of NaCl, we apply the quasi-harmonic Debye model, in which the nonequilibrium Gibbs function $G^*(V,P,T)$ of NaCl can be written in the form of

$$G^*(V,P,T) = E(V) + PV + A_{V^B}(\Theta(V);T)$$

(11)

where $E(V)$ is the total energy per unit cell for NaCl, $PV$ corresponds to the constant hydrostatic pressure condition, and $A_{V^B}(\Theta(V);T)$ is the vibrational term, which can be written as

$$A_{V^B}(\Theta(V);T) = nKT\left(\frac{9\Theta}{8T} + 3\ln(1 - e^{-\Theta/T}) - D(\Theta/T)\right)$$

(12)

where $n$ is the number of atoms in the molecule, and the Debye integral $D(\Theta/T)$ is defined as

$$D(y) = \frac{3}{y^3} \int_0^y \frac{x^3}{e^x - 1} \, dx$$

(13)

One of the standard methods of calculating the Debye temperature, $\Theta$ in equation 12, is from elastic constant. It is related to an average sound velocity, since the vibrations of the solid are considered as elastic waves in Debye’s theory. For NaCl crystal, the Debye temperature can be estimated from the average sound velocity $\nu_m$ using the following equation

$$\Theta = \frac{h}{k_B}\left(\frac{3nN_A\rho}{4\pi M}\right)^{1/3} \nu_m$$

(14)

where $h$ is Planck’s constant, $k_B$ is Boltzmann’s constant, $N_A$ is Avogadro’s number, $M$ is the molecule mass, $\rho$ is the density, and the average sound velocity $\nu_m$ is approximately given by

$$\nu_m = \sqrt{3}\left(\frac{1}{V_p^3} + \frac{2}{V_S^3}\right)^{-1/3}$$

(15)

where $V_p$ and $V_S$ are the longitudinal and transverse elastic wave velocities, respectively, which can be obtained from Navier’s equation

$$V_p = \sqrt{\frac{3B_s + 4G}{3\rho}}, \quad V_S = \sqrt{\frac{G}{\rho}}$$

(16)

where $G$ is the shear modulus and $B_s$ is the adiabatic bulk modulus.

3.5. Pressure Dependence of Structural, Elastic, and Thermodynamic Properties. In order to investigate the pressure-dependence behaviors of the structural, elastic, and thermodynamic properties of NaCl, we concentrate our investigation to the pressure range below 70 GPa. In Figures 3–9, we present the dependence of elastic constants, shear modulus, Young’s modulus, and rigidity modulus on hydrostatic pressure. From Figures 3–5, we can note that $C_{11}$ and $C_{12}$ vary largely under the effect of pressure as compared with the variations in $C_{44}$. Both $C_{11}$ and $C_{12}$ increase monotonically with the pressure, whereas the $C_{44}$ decrease in the range of $P < P_t$ and increase rapidly in the range of $P > P_t$. It can be seen from Figure 6 that, in both $B1$ and $B2$ phases of NaCl, the adiabatic bulk modulus $B_s$ increase rapidly with increasing pressure. Furthermore, it is noted from Figure 6 that the adiabatic bulk modulus $B_s$ are found to show a linear variation with the pressure. From Figures 7–9, we can also observe that the pressure has an important influence on the shear modulus, Young’s modulus, and rigidity modulus.

In Figures 10–12, we have plotted the variation of the anisotropic factor and the Poisson’s ratio of NaCl crystal at different pressures. As shown in Figures 10 and 12, we find that both anisotropic factor $A$ and Poisson’s ratio $\nu$ in $B1$-type NaCl decrease with increasing pressure, while for $B2$-type NaCl, $A$ increases strongly with increasing pressure. From Figure 11, we can also find that the degree of elastic anisotropy $A^*$ in $B1$-type NaCl increases as the pressure increases and gradually tends to a linear increase at $P < P_t$. Meanwhile, in Figures 13 and 14, we have indicated the results of sound velocity, wave velocity, and Debye temperature for NaCl crystal. It is worth pointing out that the sound velocity, wave velocity, and Debye temperature increase as the pressure increase. From Figures 13 and 14, it is interesting to note that the increased tendency of average sound velocity $\nu_m$ and transverse sound velocity $\nu_s$, longitudinal sound velocity $\nu_p$, and Debye temperature $\Theta$ are, to some extent, similar. Some of the quantitative calculation results are listed in Tables 4 and 5.

Finally, we have also, for completeness, calculated the pressure derivatives of elastic constants, $\partial C_{ij}/\partial P$, $\partial C_{ij}/\partial P$, $\partial C_{44}/\partial P$, $\partial S_{ij}/\partial P$, $\partial S_{ij}/\partial P$, and $\partial S_{44}/\partial P$, for NaCl crystal. The theoretical results are presented in Table 6. Unfortunately, as far as we know, there are no experimental and theoretical data available related to the pressure derivative of elastic modulus of NaCl in the literature for our comparison. Consequently, our work is a first attempt in this direction and our results can serve as a prediction for future investigations.

3.6. Structural Properties of $B2$-Type NaCl at High Pressure. The investigation of NaCl crystal at high pressure is of considerable current interest, particularly in the case of elements. The knowledge of structural properties of NaCl at high pressure is important for high-pressure behavior inves-
For a long time, experiments to measure the structural properties of NaCl at high pressure remain a formidable challenge with existing measurement facilities. Furthermore, most of the theoretical work about the structural properties of NaCl is only performed at pressures below 70 GPa. We therefore think that it is worthwhile to perform a theoretical calculation for the structural properties of NaCl under high pressure in order to provide reference data for the experimentalists. Recently, it has become possible to compute with great accuracy an...
important number of electronic and structural parameters of solids from first-principles calculations.\textsuperscript{49–53} This kind of development in computer simulations has opened many interesting and exciting possibilities in condensed matter investigations. For example, it is now possible to explain and predict properties of solids which were previously inaccessible to experiments. In order to investigate the structural properties of B2-type NaCl under high pressure, we have carried out a theoretical investigation for the lattice constant $a$ and primitive cell volume $V_0$ up to 500 GPa. The first-principles calculations are performed within density-functional theory, using the pseudopotential method. The exchange correlation effects are treated with the generalized

Figure 9. Pressure dependence of rigidity modulus $G_r$ in both the $B1$ and $B2$ structures of NaCl: (a) omitting the phase transition; (b) considering the phase transition.

Figure 10. Pressure dependence of anisotropic factor $A$ in both the $B1$ and $B2$ structures of NaCl: (a) omitting the phase transition; (b) considering the phase transition.

Figure 11. Pressure dependence of the degree of elastic anisotropy $A^*$ in both the $B1$ and $B2$ structures of NaCl: (a) omitting the phase transition; (b) considering the phase transition.

Figure 12. Pressure dependence of Poisson's ratio $\nu$ in both the $B1$ and $B2$ structures of NaCl: (a) omitting the phase transition; (b) considering the phase transition.

Figure 13. Pressure dependence of average sound velocity $V_m$ and transverse wave velocity $V_S$ of NaCl.

Figure 14. Pressure dependence of longitudinal wave velocity $V_P$ and Debye temperature $\Theta$ of NaCl.
It is worth noting that the pressure dependence of the lattice modulus given by the gradient-corrected exchange-correlation functionals given by Perdew et al.\textsuperscript{29} are in good agreement with recent experimental and theoretical results published in the literature.\textsuperscript{1,13}

Using the pseudopotential plane-waves method based on the density functional theory, with the generalized gradient approximation, we have systematically investigated the structural, elastic, and thermodynamic properties of NaCl under high pressure. The obtained results might be interesting from the viewpoint of technological applications because, in addition to the traditional use of the elastic properties, the thermodynamic properties may have potential applications in material science. Furthermore, the accurate structural parameters of NaCl, which can be considered as a simple ionic crystal, are an important first step that helps to provide a complete interpretation of the essential features of interatomic binding forces in more complex ionic crystals. Significantly, the theoretical calculations clearly confirm that the structural phase transition between the B1 phase and the B2 phase of NaCl is 29.73 GPa. Another important conclusion of the present work is that the elastic properties sensitively depend on the pressure. The bulk modulus is found to show a linear variation with the pressure. These findings are of significant importance for a better understanding of the high-pressure behavior of NaCl crystal.
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4. Conclusions

From the above investigations, we have the following conclusions:

(i) The $B1-B2$ structural phase transition of NaCl has been investigated using the first-principles calculation. The calculated results show that the transition pressure $P_t$ for the structural phase transition from the $B1$ phase to the $B2$ phase is 29.73 GPa.

(ii) The structural parameters and thermodynamic properties for both the $B1$-type and the $B2$-type NaCl have been derived. The theoretical values are found to be in good agreement with the experimental findings.

(iii) The pressure dependence of the structural parameters and elastic properties is investigated. It is found that the pressure has an important influence on the structural parameters and a linear dependence of the bulk modulus versus applied pressure.

(iv) We have calculated the shear modulus, Young’s modulus, rigidity modulus, Poisson’s ratio, sound velocity, and Debye linear dependence of the bulk modulus versus applied pressure.

4. References and Notes


Figure 15. Pressure dependence of the primitive cell volume $V_0$ and lattice constant $a$ for $B2$-type NaCl at 300 K.

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