

# Molecular dynamics simulations for high-pressure induced B1–B2 transition in NaCl by Möbius pair potentials

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## Abstract

Based on the inversion pair potentials, the molecular dynamics simulations were performed to study the pressure-induced B1–B2 phase transition in NaCl crystal. Under a transition pressure close to the experimental value, it is found at the temperature of 600 K that there is a transformation from the six-fold coordinated B1 structure to the eight-fold coordinated B2 phase. But at the same temperature, the reversible transformation B2–B1 was presented under zero pressure by the same interionic potentials. These are in good agreement with the experimental observations. The atomistic mechanism of the phase transition was discussed in terms of the configurations under different pressures.

## 1. Introduction

The mechanism of transition from B1 (NaCl-structure) to B2 (CsCl-structure) of NaCl has been of great interest in the past decades. Mostly the mechanism can be explained by two models. The first model is often expressed as the Buerger mechanism [1], which uses a two-ion rhombohedral primitive cell ( $a = b = c$ ,  $\alpha = \beta = \gamma$ ) to take account of the phase transition. When the rhombohedral cell is compressed along its three-fold axes, the angle  $\alpha$  increases from  $60^\circ$  to  $90^\circ$  thus accomplishing the B1–B2 transition. The second one was proposed by Watanabe, Tokonami and Motimoto (WTM) in their study [2] on phase transition in CsCl. The B1–B2 transformation was considered as the process caused by the highly concerted intralayer rearrangement of atoms associated with interlayer translations. In terms of the two models, despite lots of calculations having been performed to show the atomistic picture of the phase transition, there is controversy arising from the previous molecular dynamics (MD) simulations. The MD calculations performed by Ruff *et al* [3] agreed with the WTM

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mechanism and disproved the Buerger model. Nga and Ong [4] used two different constant-pressure MD algorithms to indicate the equivalence of the two mechanisms. However, both of their calculated transition pressures were considerably in excess of the experimental observed transition pressure, so that Sims [5] suspected their conclusions would also apply at lower pressures, closer to the experimental transition pressures. All these MD simulations were based on the empirical interionic potentials. No *ab initio* interionic potential was used to study the B1–B2 phase transition. Then at the same temperature as that of Nga and Ong [4], we use the *ab initio* potentials derived by lattice inversion in our previous work [6, 7] to perform the MD calculations for the phase transition in NaCl. Since the inversion potentials are valid over a wide range of interionic separations and coordination environments, it is hoped that the stabilities of B1- and B2-NaCl crystals could be discussed under high and low pressures, and the temperature effect will be included. Then reasonable atomistic configurations could be presented to describe the phase transition in NaCl under the pressure closer to the experimental values. In terms of the Möbius pair potentials, the discrepancy between Buerger and WTM mechanisms could be explained by these MD calculations.

## 2. Computation details

In these MD simulations, we used the *ab initio* interionic potentials that were obtained from pseudopotential energy curves of NaCl in multiple virtual structures. By this scheme, without any prior potential function forms, the potential curves were directly inverted from the total-energy differences by Chen–Möbius lattice inversion. Since the multiple structures were involved, and the pseudopotential calculations were performed over a wide variation range of lattice constant, then the Möbius pair potentials are valid over a wide range of interionic separations and coordination numbers. Therefore, in our previous paper [6], despite no property of B2-NaCl being considered in the derivations of the potentials, both the static properties of B1- and B2-NaCl were well reproduced so as to be in good agreement with the experimental data. And the structural properties of NaCl clusters have also been reasonably described [7]. Thus it is believable that the Möbius pair potentials can be used to perform the MD simulations for the high-pressure induced phase transition in NaCl. The potentials can be expressed as follows:

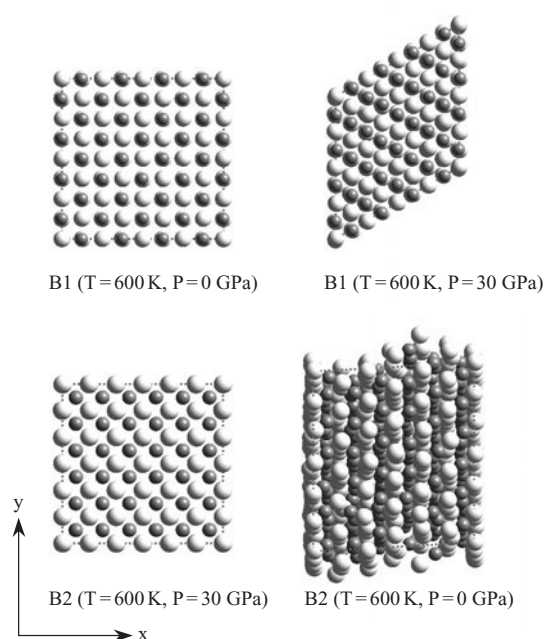
$$\phi_{++}(r) = \frac{q_+q_+}{4\pi\epsilon_0r}, \quad (1)$$

$$\phi_{--}(r) = \frac{q_-q_-}{4\pi\epsilon_0r} + D_{--} \left( \exp \left[ -\gamma_{--} \left( \frac{r}{R_{--}} - 1 \right) \right] - 2 \exp \left[ -\frac{\gamma_{--}}{2} \left( \frac{r}{R_{--}} - 1 \right) \right] \right), \quad (2)$$

$$\phi_{+-}(r) = \frac{q_+q_-}{4\pi\epsilon_0r} + D_{+-} \exp \left[ -\gamma_{+-} \left( \frac{r}{R_{+-}} - 1 \right) \right], \quad (3)$$

in which the short-range interaction of cation–cation is so small that the  $\text{Na}^+-\text{Na}^+$  potential can be described as a pure Coulomb interaction, and the short-range interactions of anion–anion and cation–anion are expressed in the forms of Morse and exponential repulsive (Exp.-Rep.) functions with the inverted potential parameters [6, 7], respectively.

In our MD simulations, the  $4 \times 4 \times 4$  periodic supercell was used, in which 512 ions with 256  $\text{Na}^+$  and 256  $\text{Cl}^-$  were arranged at the equilibrium atomic sites of the B1 structure to form the initial configurations. Then at the temperature of 600 K, which is same as that of the MD simulation in [4], this  $4 \times 4 \times 4$  B1-supercell was used to perform the MD calculations for the B1–B2 phase transition in NaCl. On the other hand, in order to demonstrate the B2–B1 transition under low pressure, a  $6 \times 6 \times 6$  B2-supercell with 432 ions was also used to perform



**Figure 1.** At the temperature of 600 K the stable configurations of the MD cell under 0 and 30 GPa, in which the structures marked with B1 and B2 indicate the initial configurations are of NaCl-type and CsCl-type, respectively.

the MD simulations at the same temperature. Here all MD calculations were performed for 30 000 time steps, where one time step was  $0.5 \times 10^{-15}$  s. A periodic boundary condition was applied and the Ewald summation technique [8] was used to cope with the Coulomb interaction. During the simulations, the constant-temperature and constant-pressure ensemble (NPT) was used to control both the temperature and pressure, and the extended system [9] with thermostat and barostat relation time of 0.1 ps was adopted. The temperature and pressure are controlled by the Nosé–Hoover [10] and Parrinello–Rahman algorithms [11], which allow both the shape and size of the MD cell to change, so that the internal stress of the system can match the external applied pressure. The calculation for the initial 10 000 time steps was used to stabilize the system, and the configurations after 10 000 time steps were used to show the physical quantities of interest to us.

Based on the MD simulations under 0 and 30 GPa, the structural stabilities of B1- and B2-NaCl may be presented at 600 K, respectively. However, the transition pressure could not be estimated only from the low- and high-pressure MD calculations. In order to reflect the properties around the transition pressure, the  $4 \times 4 \times 4$  B1-type supercell was also used to perform the MD simulations from 0 to 30 GPa, in which the pressure was applied in steps of 5 GPa, maintaining the temperature at 600 K. For each pressure, the calculations were performed for 20 000 time steps. It is hoped that the structural parameters of the MD cell under different pressures could be provided to show the details of phase transition.

### 3. Results and discussion

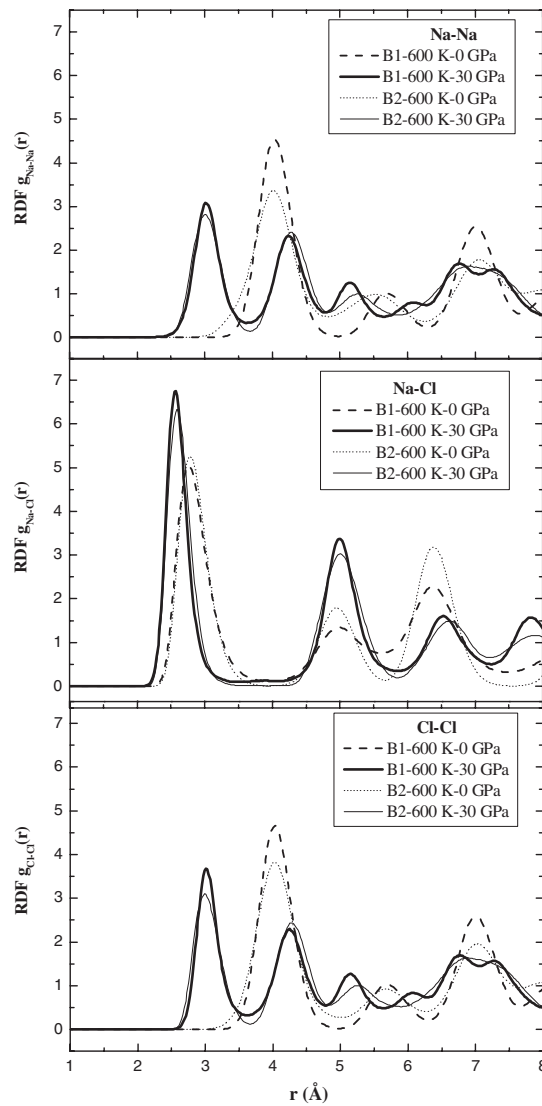
In terms of the MD simulations under 0 and 30 GPa, the stable configurations after 10 000 time steps are shown in figure 1 at the temperature of 600 K. In terms of these

configurations, it is shown that the B1 phase is stable for NaCl under zero pressure, and is unstable under high pressure. But for B2-NaCl, the reverse result was obtained, and the corresponding configurations indicate that the B2 structure is the high-pressure induced phase. This is in reasonable agreement with the experimental observations [12, 13], which indicate that the B1 and B2 configurations are separately stable under low and high pressures.

Although the configurations in figure 1 could not directly show that the B1  $\rightarrow$  B2 and B2  $\rightarrow$  B1 phase transitions have separately taken place under high and low pressures, the stable configurations indicate that there is an obvious structural transformation in B1-NaCl under high pressure, and for B2-NaCl under zero pressure, so that the B1- and B2-NaCl supercells are only kept relatively stable under low and high pressures, respectively. Their ions can be distinguished at their face-centred-cubic (fcc) and body-centred-cubic (bcc) atomic sites, respectively. In order to understand what structural changes have occurred to the B1- and B2-NaCl under 30 and 0 GPa, respectively, their radial distribution functions (RDFs) are separately compared with the RDFs of B1- and B2-NaCl at 0 and 30 GPa. The RDFs under 30 GPa indicate that the peak heights and positions of the distorted B1-NaCl are very close to those of B2-NaCl, and the difference of RDFs are very tiny between B1- and B2-NaCl supercells under zero pressure. Then the comparison clearly indicates the fact that the B1  $\rightarrow$  B2 phase transition has taken place for B1-NaCl under 30 GPa, which is very close to the experimental values [12], and at the same temperature 600 K the reverse transition B2  $\rightarrow$  B1 has also taken place for B2-NaCl under zero pressure. This is in good agreement with the experimental observations [13].

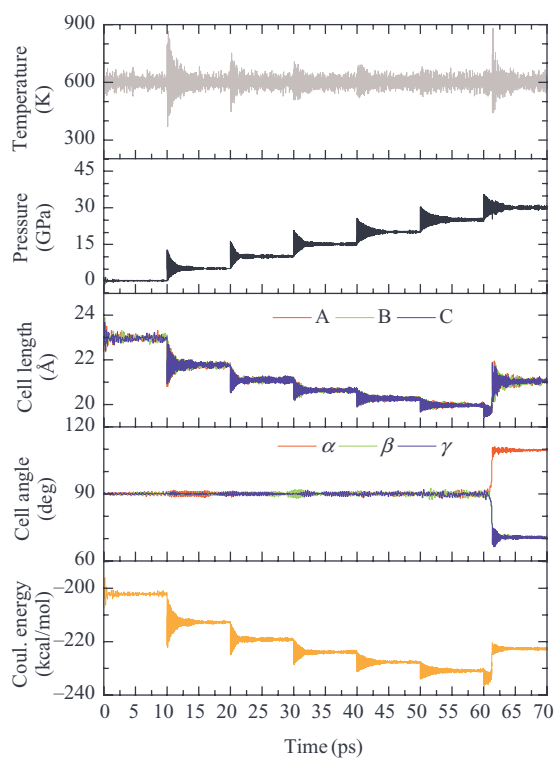
From 0 to 30 GPa, the temperature was controlled to be 600 K, as shown in figure 2. At the same time, the variations of cell parameters and Coulomb energy with the external pressure were also presented in figure 3, which indicates how the external pressure induced the structural changes in the MD cell. With increasing pressure, it can be seen that the cell lengths A, B and C all shrink at a similar magnitude before the phase transformation, the cell angles  $\alpha$ ,  $\beta$  and  $\gamma$  are almost kept as  $90^\circ$ , and the corresponding Coulomb energy was lowered by decreasing the first-nearest-neighbour distance, which may indicate that the coordination environment is almost kept unchanged so that there is no obvious change in Madelung constant, which is structure-dependent. When the pressure is set to 30 GPa, figure 3 shows there are abrupt changes in cell lengths and Coulomb energy, and the cell angles change from  $90^\circ$ ,  $90^\circ$  and  $90^\circ$  to  $109.5^\circ$ ,  $70.5^\circ$  and  $70.5^\circ$ , which indicate that there is a distinctive phase transition taking place when the external pressure changes from 25 to 30 GPa. In terms of the changes in the average first-nearest-neighbour distance  $d$  under the different external pressures, the variation of Madelung constant can be calculated from the Coulomb energy of figure 3 by the formula  $E_{\text{Coul}} = M \cdot q_+q_-/d$ , in which  $M$  is the Madelung constant,  $d$  is the average first-nearest-neighbour distance, and  $q_+$  and  $q_-$  are the ionic charges of cation and anion, respectively. The result in figure 4 clearly indicates that the Madelung constants are separately 1.74 and 1.76 before and after transition, consistent with the classic values of B1 and B2 structures from [14]. This shows that the B1  $\rightarrow$  B2 phase transition has taken place at pressure 30 GPa. In the meantime, the corresponding RDFs in figure 5 also reveal that the peaks with regard to the B1 structure have shifted to another structure from 25 to 30 GPa. Based on the RDFs in figure 2, the shifted peaks obviously indicate again that the new pressure-induced state is B2 phase. Then the B1  $\rightarrow$  B2 transition pressure was estimated as 30 GPa, which is very close to the experimental value [12, 13].

From the difference between the configurations before and after transition in figure 6, the transformation mechanism can be analysed as follows. First, the white rhombohedral cell transforms into the cubic cell, which is consistent with the Buerger mechanism [1, 5].

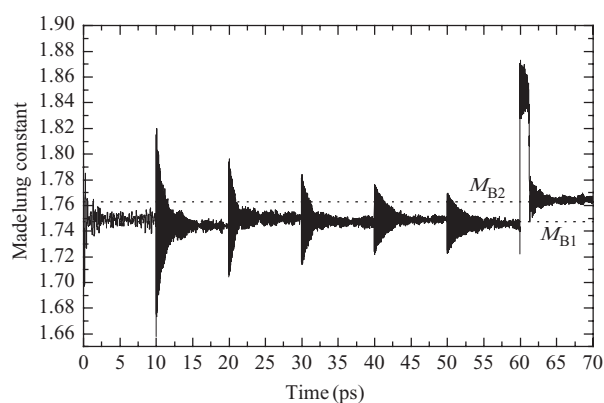


**Figure 2.** The Na–Na, Na–Cl and Cl–Cl pairs of RDFs under 0 and 30 GPa with respect to the configurations in figure 1.

Second, the grey orthorhombic repeat unit shows there is a concerted translation between every two adjacent (001) planes. This is in agreement with the WTM mechanism [2, 5]. Third, it is obvious that the crystal orientation relation  $[111]_{B1} || [111]_{B2}$  is retained before and after transition, this indicates that the MD cell is compressed along the [111] three-fold axis. Besides, the  $(001)_{B1}$  and  $(110)_{B1}$  planes are found to be parallel to the  $(011)_{B2}$  and  $(001)_{B2}$  planes, respectively. Then both the transition characters of Buerger and WTM mechanisms are presented by these MD simulations. Therefore, we finally may conclude that each of the Buerger and WTM mechanisms can only reflect one side of the phase transition. Actually the B1–B2 phase transition takes place with the characters of both Buerger and WTM models. The atomistic pictures in figure 6 could be used to explained the discrepancy between the two



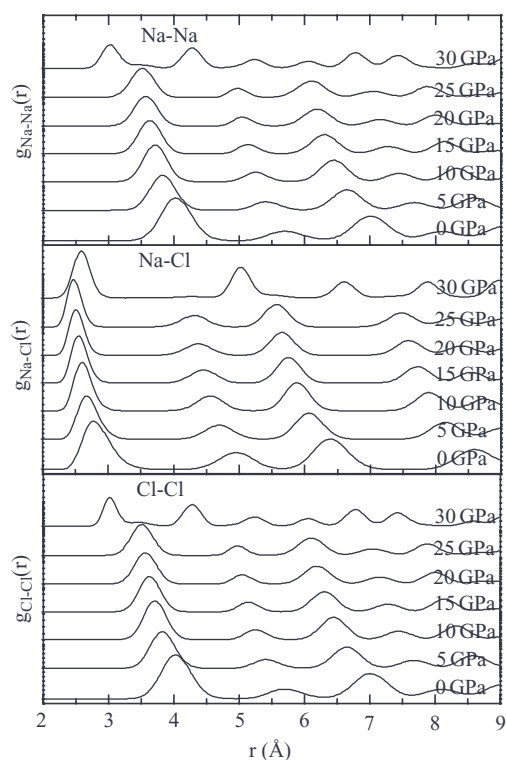
**Figure 3.** MD simulations for B1–B2 transition in NaCl. The first curve shows the fluctuation of the temperature around 600 K, and the changes in pressure are described by the second curve. In the meantime, the corresponding changes in cell lengths, angles and Coulombic energy are also displayed by the next three curves.



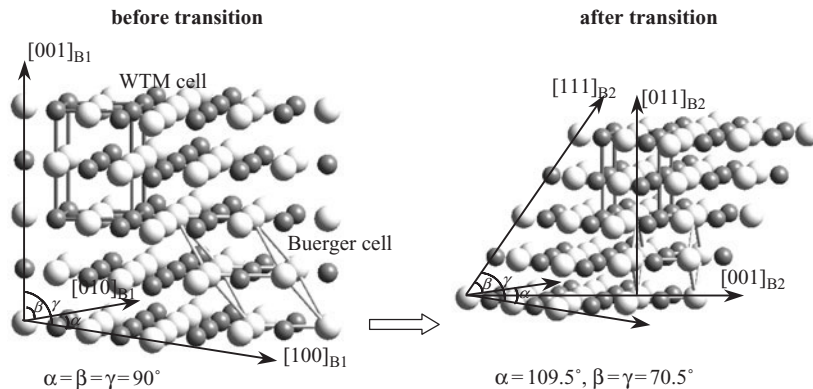
**Figure 4.** The calculated Madelung constants corresponding to the change of the external pressure in terms of the average first-nearest-neighbour distance.

mechanisms, and can be described as an overall model to interpret the B1–B2 high-pressure induced transition.

In the previous MD calculations [4], the B1–B2 transition occurs at a pressure many times the experimental values. This may reveal that the Born–Mayer–Huggins potentials [15] with



**Figure 5.** Variation of ion–ion pairwise RDFs under different pressures, which are shown on the right-hand side.



**Figure 6.** Microscopic mechanism of the B1–B2 structural transformation. The grey and white balls show the positions of cations and anions, respectively. The arrows indicate the crystallographic orientation relationships before and after phase transition.

Fumi–Tosi parameters could not accurately describe the B1–B2 transition for NaCl and RbBr, at least the transition pressure was obviously overestimated. In these MD simulations, at the same temperature, the transition pressure was estimated to be very close to the experimental results. And the relative stabilities of B1- and B2-NaCl crystals were also correctly described to be in reasonable agreement with the experimental observation. This may be attributed

to these potentials which were obtained to cover more interionic separations and coordination numbers.

#### 4. Conclusions

Based on the Möbius pair potentials, the MD calculations were performed to describe the B1–B2 phase transition. The results indicate the B1–B2 transition occurs under the pressure of 30 GPa, which is much closer to the experimental value than the previous MD simulations. And the relative stabilities under low and high pressures were also presented to be in reasonable agreement with the experimental observations. This indicates that the Möbius pair potentials are appropriate to describe the phase transition from B1 to B2 phase because of their validity over a wide range of interionic spacings and coordination environments.

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