



## *Ab initio* based interionic potential for silver iodide

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### ABSTRACT

In this paper, a new interionic potential is derived for silver iodide (AgI) via the Chen–Möbius lattice inversion and *ab initio* calculation. The accuracy of the proposed potential is checked by comparing the molecular dynamics simulation results on the static properties, structural stability, disordered states, mean-squared displacement and phase transition of AgI with experimental data. The simulation results are consistent with experimental data and density functional theory (DFT) calculations, indicating that the proposed interionic potential is valid over a wide range of interionic separations and applicable for describing the major properties of AgI.

### 1. Introduction

Superionic conductors have attracted much attention because of their potential for applications in solid electrolytes [1–3], fast-response gas sensors [4,5], and photographic materials [6–9]. Among various superionic compounds, silver iodide (AgI) is well known due to its high ionic conductivity and stability. The ionic and electrical conductivities of AgI have been measured experimentally [10–15].  $\alpha$ -AgI, the high-temperature phase of AgI, displays a high ionic conductivity with weak dependence on temperature from 147 °C to 555 °C. However, the highly ionic conducting  $\alpha$ -AgI undergoes a phase transition into a normal ionic conducting  $\beta$ -AgI at 147 °C. In the low temperature  $\beta$  phase, the iodine ions form a hcp lattice while the silver ions are tetrahedrally bonded to each iodine and exhibit no self-diffusion. In the high temperature  $\alpha$  phase, the iodine ions form a bcc lattice and exhibit self-diffusion and high mobility. X-ray [16–18], neutron diffraction [19–21], and extended X-ray absorption fine structure [22–24] measurements are performed to determine the structure of AgI. To understand the mechanism of this phase transition, many correlative investigations from both experiments and theoretical calculations have been performed [25–27]. However, in order to obtain a deeper understanding of the nature of ionic motions and the phase transition, atomistic scale simulations are needed to provide the necessary microscopic perspective [28]. Density functional theory (DFT) calculations are typically used to study the static properties of small systems. Alternatively, molecular

dynamics (MD) simulations have been widely used to study the dynamic properties of larger systems. The structure factor of AgI, the diffusion constant of  $\text{Ag}^+$  and its temperature dependence are obtained from MD simulations and the results are consistent with experimental data [29–34]. However, reproducing the phase transition is still a challenging task for MD simulations and the accuracy of MD simulations directly depends on the accuracy of the potentials used. Although the  $\alpha = \beta$  phase transition of AgI is observed in MD simulations based on the potential developed by Rahman, Vashishta and Parrinello [32] (known as RVP potential), a robust potential which can capture both static (e.g., lattice constants, cohesive energy, and elastic constants) and dynamic (e.g., phase transition and ionic diffusion constant) characteristics of AgI is needed, which is currently missing. Recently, the lattice inversion (LI) method proposed by Chen [35] has been successfully applied to derive the short-range pairwise potential for alkali halides, solid oxides, metal alloys, and semiconductors [36–40]. On the basis of the information on the interatomic interactions from *ab initio* calculations, the potential form can be determined and its parameters can be evaluated. Therefore, the potentials derived by the LI method inherit the accuracy from *ab initio* calculations.

In the current work, the LI technique is employed to derive the interionic potential for AgI. The idea is to first construct several extended structures of AgI and perform the *ab initio* cohesive energy calculations. Then the short-range interactions are directly derived from a series of cohesive energy differences using the LI method. Next, the functional

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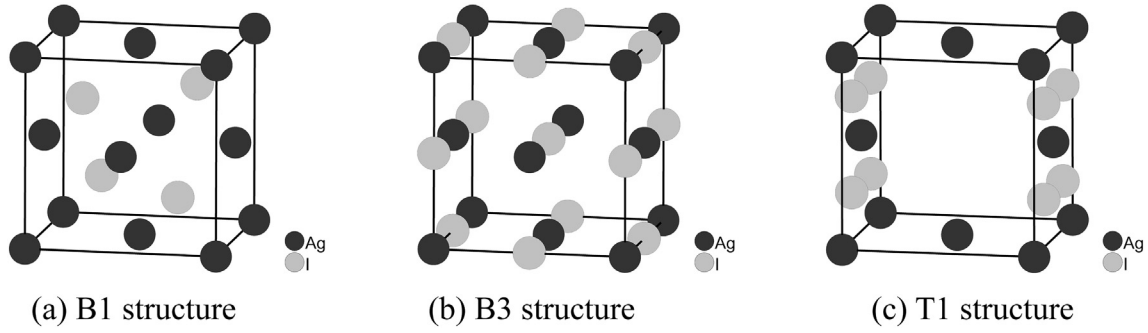


Fig. 1. Extended AgI structures used for the *ab initio* cohesive energy calculations.

form and its initial parameters are evaluated by fitting the inverted potential. Finally, the parameters are optimized with the training set from *ab initio* calculations. Furthermore, on the basis of the proposed potential, several applications are given for verification purpose. Static properties, structural stability, disordered states, mean-squared displacement and phase transition of AgI are discussed in detail.

## 2. Derivation of interionic potential of AgI

For the AgI system, the cohesive energy can be expressed as

$$E_{\text{coh}} = E_{\text{cou}} + E_{\text{Ag-I(SR)}} + E_{\text{I-I(SR)}} + E_{\text{Ag-Ag(SR)}}, \quad (1)$$

where  $E_{\text{cou}}$  is the long-range part (Coulomb energy) and  $E_{\text{SR}}$  is the short-range part. The long-range part is evaluated using the Ewald summation technique [41], while the short-range part is derived from an extended phase space including several virtual structures as shown in Fig. 1.

In this paper, the cohesive energies of B1-, B3- and T1-AgI are calculated by DFT with the Vienna *Ab initio* Simulation Package (VASP) [42–44]. The Perdew-Burke-Ernzerhof (PBE) [45] exchange-correlation functional is utilized based on the projector augmented wave (PAW) method [44]. The unit cells are optimized using a  $12 \times 12 \times 12$  Monkhorst-Pack k-points mesh and the cutoff energy for the plane wave basis set is 500 eV. The pseudopotentials with valence states of Ag (4s, 4p, 5s, 4d) and I (5s, 5p) are employed for more accuracy. All ionic positions are optimized with the conjugate gradient algorithm until the forces on each ion are  $< 0.01$  eV/Å. All the calculations are spin polarized. Fig. 2 depicts the calculated cohesive energies of the three extended phases as a function of the lattice constant.

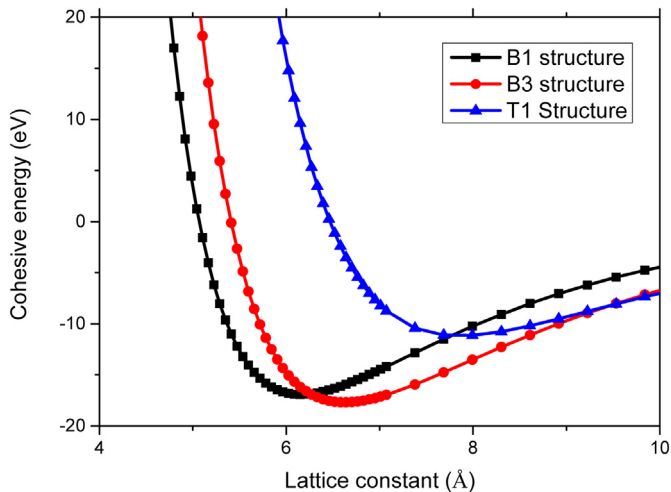


Fig. 2. Cohesive energies versus lattice constant in B1-, B3- and T1-AgI structures from the *ab initio* calculations.

### 2.1. Ag-I interionic potential

The cohesive energy  $E_{\text{coh}}^{\text{B1}}(a)$  of B1-type AgI for a lattice constant  $a$  can be written as in Eq. (2), which includes three kinds of ionic interactions,  $E_{\text{Ag-Ag}}^{\text{fcc}}(a)$ ,  $E_{\text{I-I}}^{\text{fcc}}(a)$ , and  $E_{\text{AgI}}^{\text{B1}}(a)$ ,

$$E_{\text{coh}}^{\text{B1}}(a) = E_{\text{Ag-Ag}}^{\text{fcc}}(a) + E_{\text{I-I}}^{\text{fcc}}(a) + E_{\text{Ag-I}}^{\text{B1}}(a), \quad (2)$$

where  $E_{\text{Ag-Ag}}^{\text{fcc}}(a)$  and  $E_{\text{I-I}}^{\text{fcc}}(a)$  are the contributions of uniform ions on the fcc (face-centered-cubic) sublattice, and  $E_{\text{Ag-I}}^{\text{B1}}(a)$  is the contribution of unlike ions.

Similarly, the cohesive energy  $E_{\text{coh}}^{\text{B3}}(a)$  of B3-type AgI for a lattice constant  $a$  can be written as Eq. (3).

$$E_{\text{coh}}^{\text{B3}}(a) = E_{\text{Ag-Ag}}^{\text{fcc}}(a) + E_{\text{I-I}}^{\text{fcc}}(a) + E_{\text{I-I}}^{\text{B3}}(a). \quad (3)$$

The cohesive energy combines both short-range and long-range interactions. Using Eqs. (2) and (3), the short-range Ag-I interaction difference between B1- and B3-AgI can be written as

$$\begin{aligned} \Delta E_{\text{Ag-I(SR)}}(a) &= E_{\text{Ag-I(SR)}}^{\text{B3}}(a) - E_{\text{Ag-I(SR)}}^{\text{B1}}(a) \\ &= (E_{\text{Ag-I(coh)}}^{\text{B3}}(a) - E_{\text{Ag-I(cou)}}^{\text{B3}}(a)) - (E_{\text{Ag-I(coh)}}^{\text{B1}}(a) - E_{\text{Ag-I(cou)}}^{\text{B1}}(a)), \\ &= (E_{\text{coh}}^{\text{B3}}(a) - E_{\text{cou}}^{\text{B3}}(a)) - (E_{\text{coh}}^{\text{B1}}(a) - E_{\text{cou}}^{\text{B1}}(a)) \end{aligned} \quad (4)$$

where  $E_{\text{coh}}^{\text{B3}}(a)$  and  $E_{\text{coh}}^{\text{B1}}(a)$  are determined from the *ab initio* calculation as shown in Fig. 2.  $E_{\text{cou}}^{\text{B3}}(a)$  and  $E_{\text{cou}}^{\text{B1}}(a)$  are evaluated by the Ewald summation technique with the value of charge,  $+0.6e$  for  $\text{Ag}^+$  and  $-0.6e$  for  $\text{I}^-$ , which is kept the same as in the RVP potential.

Based on Eq. (4), the short-range Ag-I interaction difference between B1- and B3-AgI is obtained as shown in Fig. 3(a).

For the mixed virtual lattice B3-B1, the relation between the cohesive energy difference  $\Delta E_{\text{Ag-I(SR)}}(a)$  and the interionic potential  $\phi_{\text{Ag-I}}$  is given by

$$\begin{aligned} \Delta E_{\text{Ag-I(SR)}}(a) &= E_{\text{Ag-I(SR)}}^{\text{B3}}(a) - E_{\text{Ag-I(SR)}}^{\text{B1}}(a) \\ &= \frac{1}{2} \sum_{i,j,k} \phi_{\text{Ag-I}}^{\text{SR}} \left( \sqrt{(i+k-1/2)^2 + (i+j-1/2)^2 + (i+k-1/2)^2} \frac{a}{2} \right) \\ &\quad - \frac{1}{2} \sum_{i,j,k} \phi_{\text{Ag-I}}^{\text{SR}} \left( \sqrt{(i+k-1)^2 + (i+j-1)^2 + (i+k-1)^2} \frac{a}{2} \right) \end{aligned} \quad (5)$$

From Eq. (5), the short-range Ag-I pair potential curve can be derived directly by Chen-Möbius LI techniques, as shown in Fig. 3(b). Morse function [46] is used to fit the curve. Combining both the short-range term and the Coulomb term, the total Ag-I pair potential is given by

$$\phi_{\text{Ag-I}} = D_{+-} (e^{-2\alpha_+ - (r-R_{+-})} - 2e^{-\alpha_+ - (r-R_{+-})}) + \frac{q_+ q_-}{4\pi\epsilon_0 r}, \quad (6)$$

where  $D_{+-}$ ,  $\alpha_{+-}$  and  $R_{+-}$  are the parameters of the Morse potential between cation and anion.

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