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Gupta potential for alkaline earth metals: Calcium and strontium

Jie Fu [a,b], Chong Zhang [a,b,c], Jijun Zhao [a,b,*]

[a] Key Laboratory of Materials Modification by Laser, Ion and Electron Beams, Dalian University of Technology, Ministry of Education, Dalian 116024, China
[b] School of Materials Science and Engineering, Dalian University of Technology, Dalian 116024, China
[c] College of Advanced Science and Technology, Dalian University of Technology, Dalian 116024, China

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ABSTRACT

Empirical Gupta-type potentials have been developed for alkaline earth metals, Ca and Sr. The potential parameters were fitted according to the experimental lattice constants, cohesive energies and elastic constants. Compared to experiments and DFT calculations, our potentials can reproduce the bulk modulus, shear modulus, and sound speed very well. More importantly, our potentials can also describe phonon dispersion relationships of Ca and Sr solids correctly. Energy profiles for fcc–bcc transformation along the Bain deformation path has been calculated, which yields the correct energy difference between fcc and bcc phases. Our potentials are also applied to the low-coordination environments, i.e., vacancy formation energies and surface energies of low-index surfaces, and a qualitative agreement with experiment and previous theoretical results is obtained.

1. Introduction

Calcium (Ca) and strontium (Sr) are two typical alkaline earth elements located in the second column of the periodic table (group IIA). With nearly the same chemical behavior with alkali elements and closed-shell electronic configuration [Ar]4s^2, these two elements play an important role in a variety of compounds and processes. Calcium is the fifth-most-abundant element by mass in the Earth's crust and also one of the major components of the Earth's low mantle possibly in the form of perovskite [1]. The calcium solid is reactive and can be used to produce hydrogen that is safer than the alkali elements. It is easy for a Ca atom to lose its outer electrons and becomes a Ca^{2+} ion. Diffusion of Ca^{2+} ion in and out of the cytoplasm functions as a signal for many cellular processes, which are essential for living organisms. Strontium is a soft silver-white or yellowish metallic element that is highly chemically reactive. Many properties of strontium are similar to Ca. The primary usage of Sr is in the production of cathode ray tubes and Sr is also beneficial to bone growth in medicine research. Recently, the elements of Ca and Sr have been adsorbed on nanostructure to improve the feasibility of hydrogen storage [2].

Among the six elements of main group IIA (Be, Mg, Ca, Sr, Ba, Ra), only calcium and strontium crystals prefer face-center cubic (fcc) phase at ambient conditions. However, with the changes of temperature or pressure, they will transform into body-center cubic (bcc) phase or hexagonal close-packed (hcp) phase. Experimentally, Olijnyk and Holzapfel [3] found that Ca transforms from fcc to bcc at 19.5 GPa, while Sr undergoes an fcc-to-bcc transition at 3.5 GPa at room temperature.

During the past three decades, empirical potentials, from the pair-wise potentials (e.g., Lenard Jones, Morse) to many-body potentials, combined with molecular dynamics (MD) or Monte Carlo (MC) techniques, have been widely used in computational material science. Since the pair-wise potentials cannot reflect the effects from surrounding atoms, many-body potentials, such as Gupta potential [4], Glue potential [5], EAM (embedded-atom method) potential [6], EMT (effective-medium theory) potential [7], Finnis–Sinclair potential [8,9] become popular for description of metals and alloys.

Among these conventional many-body potentials, Gupta potential has almost fewest parameters and a very concise form, which is easily to be implemented in computer program and convenient to construct alloy potentials [4,10–12]. In 1981, Gupta potential [4] was originally proposed for calculating surface relaxation. Later, Tománek et al. [13] derived the potential form from tight-binding electronic structure theory and applied it to surface segregation in dilute alloys (Rh, Cu, and Au impurities on different Pt single-crystal surfaces). In 1993, Cleri and Rosato [10] extended Gupta potential to these common fcc (Ni, Cu, Rh, Pd, Ag, Ir, Pt, Au, Al, Pb) and hcp (Ti, Zr, Co, Cd, Zn, Mg) transition metals and their alloys (Cu$_3$Au, Ni$_3$Al) and successfully reproduced the fundamental bulk properties such as elastic modules and melting points. Afterwards, Gupta potential has been widely used in atomic simulation of elementary and binary metals [11,12,14–17].

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[*] Corresponding author at: Key Laboratory of Materials Modification by Laser, Ion and Electron Beams, Dalian University of Technology, Ministry of Education, Dalian 116024, China. Tel.: +86 411 84709748; fax: +86 411 84706100.

E-mail address: zhaojj@dlut.edu.cn (J. Zhao).

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Despite the importance of Ca and Sr in various fields, there have been only few versions of empirical potentials developed for Ca and Sr. Murrell et al. [18,19] obtained MM-type potentials for Ca and Sr to reproduce their physical properties of crystalline solid and examined the structural and dynamical aspects of solids, liquids, surfaces and clusters. Sheng et al. [20] fitted the "as-developed EAM potential" for more than fourteen elements including Ca and Sr. In addition, Dieterich et al. [21] constructed the Gupta potentials to simulate the alkaline earth clusters. However, the potential parameters were directly derived from interatomic interaction of dimers but cannot describe the corresponding bulk solids.

Here we fitted Gupta potentials for Ca and Sr from the fundamental physical properties of the fcc solids, including lattice constants, elastic constants, and cohesive energies. By comparing with available experimental data and density functional theory (DFT) calculations, our potentials are able to reproduce the sound velocity, phonon frequencies, Debye temperature and describe vacancy formation energy and surface energy of the fcc crystals of Ca and Sr to a satisfactory extent. The energy profiles along the path of fcc–bcc phase transition are also reasonably described.

2. Theoretical methods and potential parameters

Gupta potential [4] is based on the second-moment approximation of tight-binding theory, and includes an electronic band term (former) and a repulsive pair-wise term (latter) as:

$$E=\frac{U}{2}\sum_{i}\left(-\left(\sum_{j(\neq i)}\exp\left(-2q\left(\frac{r_{ij}}{r_0}-1\right)\right)\right)^{\frac{1}{2}}+\sum_{j(\neq i)}A\exp\left(-p\left(\frac{r_{ij}}{r_0}-1\right)\right)\right), \tag{1}$$

where U, q, A, p are empirical parameters; r_0 is the equilibrium first-neighbor distance in (fcc) solid; r_{ij} represents the distance between atom i and atom j.

In this work, we used General Utility Lattice Program (GULP) [22] to fit the potential parameters and to compute crystal properties of fcc phase Ca and Sr. The experimental lattice constant (a), cohesive energy (E_c) and elastic constants (C_{ij}) of Ca and Sr in the reference state (fcc phase) [23–26] were adopted as input. In brief, the potential fitting procedure was a least-square process, aiming to minimize the deviations of the observable and calculated parameters. GULP employed the Newton–Raphson algorithm to minimize the numerical first derivatives of the sum of square deviation.

Since some key properties of Ca and Sr solids are not available from previous experiments, we also carried out first-principles calculation on Ca and Sr crystals within the framework of density functional theory (DFT) and planewave pseudopotential technique, as implemented in the CASTEP (Cambridge Serial Total Energy Package) [27]. The interactions between ions and valence electrons were described by the ultrasoft pseudopotential [28]. The energy cutoff for plane-wave basis was set as 600 eV. Exchange–correlation interactions were described by the generalized-gradient approximation (GGA) [29] with the Perdew–Burke–Enzerhof (PBE) functional [30]. The mechanical properties of fcc solids of Ca and Sr were calculated with conventional 4-atoms unit cell and the Brillouin zone was sampled by a $10 \times 10 \times 10$ $\mathbf{k}$ point mesh. During the calculations of vacancy formation energy, we adopted a 256-atom supercell and Γ point. To calculate the surface energy, we used an eight-layer slab model with two middle layers fixed and an uniform separation 0.03 Å^{-1} of $\mathbf{k}$ points.

3. Results and discussion

Table 1 summarizes the Gupta potential parameters determined for Ca and Sr. Table 2 compares the essential physical properties of Ca and Sr solids obtained from experiments [24–26], the present Gupta potentials, DFT calculations, and previous MM potential [18]. As input parameter for fitting Gupta potential, the experimental lattice constant for the fcc solid of Ca is 5.58 Å [26], compared to 5.52 Å from our own DFT calculations and 5.59 Å by MM potential [18]. The cohesive energy for Ca is 1.84 eV per atom from experiment, Gupta or MM potentials, while DFT calculation yields a reasonable value of 1.88 eV/atom.

In addition, elastic constants C_{ij} of these two metals from Gupta potential also show excellent agreement with experimental data. As listed in Table 2, C_{11}, C_{12}, and C_{44} of Ca calculated with Gupta potential are 24.0 GPa, 15.2 GPa and 12.6 GPa, respectively, with maximum deviation of 1.4 GPa to experimental values. For comparison, the discrepancy of C_{ij} between MM potential [18] and experiment results can be as large as 10 GPa. Similar agreement is found for Sr solid and the difference between theoretical and experimental C_{ij} is less than 1.5 GPa.

To further assess the performance of Gupta potentials, we calculated bulk modulus, shear modulus, sound speed, and Debye temperature for fcc Ca and Sr and compared with the experimental results in Table 3. Here, the bulk modulus and shear modulus can be deduced from elastic constants of a crystal in its equilibrium state [26,31]. The bulk modulus of Ca solid obtained by Gupta potential is 18.2 GPa, only 0.1 GPa lower than the experimental value. For shear modulus, the calculated value from Gupta potential is 9.3 GPa, lying between the experimental one (9.8 GPa) and DFT value (8.4 GPa). In the case of Sr, the bulk modulus is overestimated by about 0.2 GPa (0.7 GPa) using Gupta potential compared with experimental (DFT) results. Meanwhile, the shear modulus of Sr solid calculated by Gupta potential is 6.2 GPa, which is also between the experimental (6.9 GPa) and DFT (5.7 GPa) values.

For a single crystal, its longitudinal and transverse sound velocities can be computed from the bulk modulus and shear modulus [26,31]. In this work, the longitudinal (transverse) sound speed of Ca was predicted as 4469 (2469) m/s, while the measured values are 4180 (2210) m/s [32]. As for Sr, the longitudinal (transverse) sound speed is 2811 (1550) m/s, which is overestimated by only c.a. 31 m/s as compared with experimental values of 2780 (1520) m/s [32]. The Debye temperatures of Ca are 274 K from Gupta potential and 230 K from experiment [26]. Similarly, the calculated Debye temperature of 158 K for Sr accords with experimental value of 147 K [26] rather well.

In addition to the fcc crystal at equilibrium state, we also investigated the energy–volume (E–V) relationships (which is also known as equation of states, EOS) of Ca and Sr solids from Gupta potential and DFT calculations. As displayed in Fig. 1, our Gupta potential is able to reproduce the DFT curves reasonably. The overall curvature of EOS can be quantified by the second derivative of $E(V)$ function at equilibrium, which are 2.79×10^3 eV/nm^6 from DFT and 2.82×10^3 eV/nm^6 from Gupta potential for Ca. Similarly, the second derivatives of E–V curve for Sr solid at equilibrium are 1.43×10^3 eV/nm^6 from DFT and 1.34×10^3 eV/nm^6 from Gupta potential, respectively.

Table 1
Parameters of Gupta potential for fcc phase Ca and Sr.

	U (eV)	A	p	q	r_0 (Å)
Ca	0.908225	0.092449	14.38749	1.257908	3.946
Sr	0.857226	0.095433	13.58451	1.251098	4.300