Computational Materials Science 112 (2016) 75–79

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Gupta potentials for five HCP rare earth metals

Xiaojie Li, Jie Fu, Ying Qin *, Shengzhi Hao, Jijun Zhao *

Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education, Dalian 116024, China

ARTICLE INFO

Article history:
Received 22 July 2015
Received in revised form 6 October 2015
Accepted 11 October 2015
Available online 19 November 2015

Keywords:
Rare earth
Gupta potential
Elastic constants
Phonon dispersion

ABSTRACT

Empirical Gupta-type potentials based on the second-moment approximation of tight-binding model have been developed for five hexagonal-closed-packed (hcp) rare earth metals: Er, Dy, Gd, Tb, Lu. The potentials can reproduce experimental cohesive energies, lattice constants and elastic constants of Er, Dy, Gd, Tb and Lu. The calculated bulk moduli, shear moduli, sound velocities and Debye temperatures are in reasonable agreement with the measured values. Vacancy formation energies and surface energies of these metals are also calculated and compared with previous theoretical results. Our potentials are able to simulate the phonon dispersions of Tb, Er, Dy, Gd, and Lu solids and reproduce Tb's experimental data in detail. The present Gupta potentials would be useful for future simulations of elementary metals of Er, Dy, Gd, Tb, Lu and their alloys.

1. Introduction

Rare earth materials become known to the world by the discovery of ytterbite by Johan Gadolin in 1794. Rare earth metals were once scientifically precious, but now have commercial values with modern methods of separation and applications. With exotic optical, magnetic, electronic and chemical properties, rare earth elements play an important role in material science and industry, for example, improving the performance of steels and cast iron with a small amount of rare earth elements, working as catalysts in chemical engineering; their oxides being used as laser materials, superconductor materials and so on. Under ambient conditions, lutetium (Lu), gadolinium (Gd), terbium (Tb), erbium (Er), dysprosium (Dy) belong to hcp crystals. Lu is the hardest metal among rare earth solids and is mainly used for fundamental research. Gd shows stronger ferromagnetism at 273 K than iron and is widely used in medical science and industry [1]. Dy also shows ferromagnetism at low temperature [1]. Faraday rotator glass [2], which containing Tb, is widely used for manufacture rotator, isolator and circulator in laser technology. Er_2O_3 is used to make glazes.

The properties of rare earth elements and their compounds are interesting and technologically important. Atomistic simulation can help us to understand the underlying mechanism of their attractive performance. Since it is difficult for first-principles methods to deal with large scale systems containing more than thousands atoms [3], semiempirical or empirical methods which can deal with long time and large scale systems have attracted considerable attentions in the past three decades. The key point is to develop the reliable potential parameters that can describe the atomistic interactions simply and correctly. Pair-wise potentials (e.g. Lennard-Jones potential, Morse potential) own the simplest form but they are unable to describe the many-body effects in metals. Many-body potential, such as tight-binding (TB) potential [4,5], embedded atom method (EAM) potential [6], Finnis–Sinclair (FS) potential [7], Glue potential [8], have been developed and successfully applied to metals and alloys, including hcp metals [9–14].

With a concise form and almost fewest parameters, Gupta potential (or TB potential) [4] has drawn considerable attention among the current many-body empirical potentials. It was first proposed by Gupta [4] to calculate surface relaxation in 1981. Then, Tománek et al. [15] utilized this potential form to consider the electronic contribution and applied the potential to impurity segregation at metal surfaces in 1985. In 1993, Cleri and Rosato [5] developed the TB potentials for transition metals within second-moment approximation and reproduce the fundamental properties of some fcc (Ni, Cu, Pd, Rh, Ag, Ir, Pt, Au, Pb) and hcp (Ti, Zr, Co, Cd, Zn, Mg) metals. Since then, Gupta potential has been widely used in atomistic simulations of different elementary metals and binary alloys [16–29].

So far, several empirical potentials have been developed for rare earth metals. For instance, Hachiya and Ito [29] presented a hybridized nearly-free-electron-tight-binding-bond (NFE-TBB) potential for some rare earth metals and calculated the elastic constants, interatomic spacing and bulk modulus. Baskes and Johnson [9] fitted a modified embedded atom method (MEAM) potential and calculated the defect energies, structural energy and lattice constants for several hcp rare earth metals (Dy, Er, Gd, Tb). Our group has

* Corresponding authors.
E-mail addresses: qinying@dlut.edu.cn (Y. Qin), zhaojj@dlut.edu.cn (J. Zhao).

http://dx.doi.org/10.1016/j.commatsci.2015.10.014
0927-0256/

obtained the parameters of Gupta potential for two fcc rare earth metals: lanthanum and cerium [28]. However, within our knowledge, there is no Gupta potential fitted for hcp rare metals. In this work, we develop Gupta potentials for Er, Dy, Dd, Lu, Tb of the hcp phase, which are able to describe the physical properties (including lattice constants, cohesive energy, elastic modulus, sound velocity, Debye temperature, phonon dispersion, surface energy and vacancy formation energy) of Dy, Er, Gd, Tb and Lu solids reasonably well and would be useful for the future simulations of these rare earth metals and related materials.

2. Theoretical methods and potential parameters

Based on the second-moment approximation of tight-binding theory, the Gupta potential is introduced and the ion–ion interaction is described by an electronic band term and a repulsive term. The general form is given below and the detailed meanings of each term can be found in the original papers [4,5]:

$$E_C = \frac{U}{2}\sum_i \left(\sum_{j\neq i} A\exp\left(-p\left(\frac{r_{ij}}{r_0}-1\right)\right) - \left(\sum_{j(\neq i)} \exp\left(-2q\left(\frac{r_{ij}}{r_0}-1\right)\right)\right)^{\frac{1}{2}} \right) \quad (1)$$

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

In this work, the General Utility Lattice Program (GULP) [30] was used to fit the potential parameters and calculate some physics properties. In brief, the potential fitting procedure is aimed to minimize the average deviation between the experimental data and the calculated ones by adjusting four fitting parameters of the Gupta potential. GULP employs the Newton–Raphson algorithm to minimize the numerical first derivatives of the sum of square deviations. The experimental lattice constants (a, c), cohesive energy (E_c), elastic constants (C_{ij}) for these five hcp solids [31–33] were employed as inputs and the cutoff distance was chosen as 12 Å.

For hexagonal crystals, there are five independent elastic constants (C_{11}, C_{12}, C_{13}, C_{33} and C_{44}). The bulk modulus (B) and polycrystalline shear modulus (G) were computed using the Hill average scheme [34]

$$B_H = \frac{1}{2}(B_R + B_v)$$
$$G_H = \frac{1}{2}(G_R + G_v) \quad (2)$$

The Reuss (B_R and G_R) and Voigt (B_V and G_V) bounds are given as [35]:

$$B_R = \frac{c_{33}(c_{11}+c_{12}) - 2c_{13}^2}{c_{11}+c_{12}+2c_{33}-4c_{13}}$$
$$B_v = \frac{2(c_{11}+c_{12}) + 4c_{13} + c_{33}}{9} \quad (3)$$

and

$$G_R = \frac{5}{2}\frac{c_{44}c_{66}(c_{33}(c_{11}+c_{12}) - 2c_{13}^2)}{(c_{44}+c_{66})(c_{33}(c_{11}+c_{12}) - 2c_{13}^2) + 3B_v c_{44}c_{66}}$$
$$G_v = \frac{12c_{44} + 12c_{66} + c_{11} + c_{12} + 2c_{33} - 4c_{13}}{30} \quad (4)$$

respectively, where $c_{66} = c_{11} - c_{12}$ [36]. The longitudinal (v_L) and transversal (v_T) sound velocities can be calculated from the bulk modulus and shear modulus [37],

$$\rho v_L^2 = B + \frac{4}{3}G$$
$$\rho v_T^2 = G, \quad (5)$$

where ρ is the density. The Debye temperature is calculated from the following equation:

$$\Theta_D = \frac{h}{k_B}\left(\frac{3}{4\pi V}\right)^{1/3} v_m \quad (6)$$

where V is the average atomic volume, h is the Planck's constant, k_B is the Boltzmann's constant, and v_m is the average sound velocity determined from the following equation:

$$v_m^{-3} = \frac{1}{3}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right) \quad (7)$$

Table 1
Gupta potential parameters for Er, Gd, Tb, Lu and Dy.

	U (eV)	A	P	q	r_0 (Å)
Er	0.80496	0.016840	24.63088	0.453437	3.56
Gd	0.89719	0.017699	23.15789	0.333519	3.63
Tb	1.08718	0.038474	16.00164	0.496138	3.60
Lu	0.87562	0.015867	24.94317	0.292646	3.50
Dy	0.82070	0.029736	21.02317	0.516655	3.59

Table 2
Lattice constants (a, c), cohesive energy (E_C) and elastic constants (C_{ij}) of Er, Gd, Tb, Lu and Dy crystal from experiment [31–33], NFE-TBB model [29] and this work.

		a (Å)	c (Å)	E_C (eV)	C_{11} (GPa)	C_{12} (GPa)	C_{13} (GPa)	C_{33} (GPa)	C_{44} (GPa)
Er	Expt.	3.56	5.59	3.29	86.34	30.50	24.38	85.54	28.09
	Gupta	3.49	5.68	3.31	77.67	32.60	23.57	91.22	21.65
	NFE-TBB				82.35	27.02	25.38	89.31	23.51
Gd	Expt.	3.63	5.78	4.14	66.67	24.90	21.32	71.91	20.69
	Gupta	3.57	5.85	4.18	68.57	28.01	18.38	73.55	17.11
	NFE-TBB				70.86	24.48	18.78	74.73	18.26
Tb	Expt.	3.60	5.70	4.05	67.88	24.32	22.99	72.25	21.40
	Gupta	3.59	5.72	4.02	58.29	27.51	22.46	80.26	19.26
	NFE-TBB				72.51	25.47	19.26	75.62	18.63
Lu	Expt.	3.50	5.55	4.43	86.23	32.03	28.0	80.86	26.79
	Gupta	3.44	5.61	4.44	79.11	32.49	23.26	91.16	21.96
	NFE-TBB				86.72	27.77	25.24	100.36	30.11
Dy	Expt.	3.59	5.65	3.04	74.66	26.16	21.01	78.71	24.27
	Gupta	3.59	5.73	3.01	61.52	28.01	24.17	87.78	21.39
	NFE-TBB				69.63	16.64	29.08	110.97	29.49