Atomic calculation of elastic constants for fcc metals: *ab-initio* and semiempirical approach

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Abstract

We demonstrate a quality of *ab initio* pseudopotential and semiempirical embedding atom method potential for three monoatomic fcc metals: copper, nickel and aluminium. The potentials are tested by computing basic equilibrium bulk properties, namely equilibrium lattice constant, bulk modulus and three second-order elastic constants. Two different approximations for *ab initio* calculation are used. The obtained results have proved that tests of potential ability to reproduce the bulk properties are necessary for further computer modelling of more complex phenomena in metals such as defects or alternative structure phases.

Key words: simulation, fcc metal, elastic constant, pseudopotential, semi-empirical potential

1. Introduction

Despite the great progress in experimental manipulation and observation at atomic level these techniques have still many limitations. Contemporary progress in high-end computing offers the ability to examine many details at nanoscopic level. Today, we believe that the most precise results are obtained from computational experiments, which are based on pure principles (*ab initio* techniques) and use only numerical approximations. Calculations based on such principles have become one of the biggest consumers of time on high performance computers around the world. For this in some cases we should use compromises that go beyond *ab initio* techniques but work with first principles accuracy. The compromises are based on fitting parameters determined from experimental or *ab initio* results. There is no doubt that numerical computing paves the way for modern technologies on nanoscale techniques (including *ab initio*). The accuracy of computed results mainly depends on the quality of used parameters. Therefore the aim of this paper is to present the evidence that well-parametrized numerical experiment is able to describe a variety of bulk properties.

2. Methodology

Mechanical properties of a perfect solid can be characterized by the elasticity tensor. The tensor contains 81 elements but these could be reduced due to symmetry. For cubic symmetry the tensor is reduced to three second-order independent elements assigned as C_{11}, C_{12} and C_{44} [1]. In this work we focused on investigation of bulk modulus, tetragonal shear constant and elastic constants C_{11} and C_{12}.

If we choose the strain

$$\varepsilon = (\gamma_1, \gamma_1, \gamma_1, 0, 0, 0)\,, \tag{1}$$

where γ_1 is component of strain ε, the bulk modulus B can be computed in volume non-conserving way as

$$B = V_0 \cdot \frac{\mathrm{d}^2 U}{\mathrm{d}V^2}, \tag{2}$$

where V_0 is volume per atom, V is volume, U is total energy.

Then tetragonal shear constant C' after applied strain

$$\varepsilon = (-\gamma_2/2, -\gamma_2/2, 2\gamma_2, 0, 0, 0) \tag{3}$$

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*Corresponding author: tel.: 0421 02 60291636; fax: 0421 02 65427427; e-mail address: kociskova@yahoo.com is calculated in volume conserving way due to following formula

$$C' = V_0 \cdot \frac{\mathrm{d}^2 U}{\mathrm{d}V^2}. \quad (4)$$

Using these definitions of B and C' we can calculate following elastic constants:

$$C_{11} = (3B + 4C')/3, \quad (5)$$

$$C_{12} = (3B - 2C')/3. \quad (6)$$

The atomic interaction in a solid is described by many-body potential. Our calculations were performed in the framework of Density Functional Theory (DFT) as well as Embedded Atom Method (EAM).

In *ab-initio* simulation, the bonding is represented by solving the non-relativistic quantum-mechanical Schrodinger equation for an interacting many-electron system. The quantum-mechanical calculations are performed within total energy pseudopotential method in which the only required input is the atomic number of given atom type and some fundamental constants. The only approximations in this method are DFT approximations, an exchange and correlation energy of valence electrons known as Local Density Approximation (LDA) and General Gradient Approximation (GGA). In this project we used ABINIT computational code. In the case of LDA, Teter-Pade parametrization of exchange and correlation energy of valence electron was applied and the tested scattering properties of ion cores are represented by Goedecker, Teter and Huetter (LDA1) or Fritz-Haber Institute LDA (LDA2) pseudopotentials. For GGA we considered Perdew-Burke-Ernzerhof functional [10] to approximate an exchange and correlation energy together with Fritz-Haber Institute GGA pseudopotential (GGA1) and OPIUM generated pseudopotential (GGA2). The Kohn-Sham wave functions are expanded in plane waves with a kinetic energy cut up to 70 Ha. The sampling of the Brillouin zone was accomplished by an 8 × 8 × 8 Monkhorst-Pack scheme and we use the highest amount of k-points.

Semiempirical EAM calculations were based on potentials developed by Mishin and co-workers [8, 9]. For this potential, each atom in a solid is viewed as an impurity embedded in a host comprising all other atoms [11]. The energy for an n-atom system then can be written as

$$E = \sum_{i=1}^{n} E_i, \quad (7)$$

Table 1. Structure and elastic properties of fcc copper computed by DFT technique

Copper					
	This work *ab-initio* results			*Ab-initio*^{a}	Experiment
	LDA1	GGA1	GGA2		
a (A)	3.599	3.711	3.695	3.610	3.62^{b}
B (GPa)	158.0	117.0	113.0	153.0–190.0	138.3^{c}
C' (GPa)	37.0	37.0	38.0	25.0–27.2	23.8^{c}
C_{11} (GPa)	207.0	166.0	164.0	193.0	170.0^{c}
C_{12} (GPa)	133.0	92.1	87.0	133.0	122.5^{c}

[a] [5], [b] [6], [c] [7]

Table 2. Structure and elastic properties of fcc nickel computed by DFT technique

Nickel					
	This work *ab-initio* results				Experiment
	LDA1	LDA2	GGA1	GGA2	
a (A)	3.422	3.520	3.643	3.622	3.52^{a}
B (GPa)	200.0	191.0	141.0	137.0	181.0^{b}
C' (GPa)	68.0	45.0	64.4	49.0	55.5^{b}
C_{11} (GPa)	290.0	249.0	226.0	203.0	262.0^{b}
C_{12} (GPa)	154.0	161.0	98.0	105.0	151.0^{b}

[a] [6], [b] [7]

Table 3. Structure and elastic properties of fcc aluminium computed by DFT technique

Aluminium			
	This work *ab-initio* results		Experiment
	LDA1	GGA1	
a (A)	3.991	4.048	4.05[a]
B (GPa)	81.4	76.7	79.0[b]
C' (GPa)	20.0	22.0	23.0[b]
C_{11} (GPa)	107.0	105.3	108.0[b]
C_{12} (GPa)	68.0	62.4	62.0[b]

[a] [6], [b] [7]

where the energy of single *i*-th atom is given by:

$$E_i = \frac{1}{2} \sum_{j(j \neq i)} \Phi(r_{i,j}) + F(\rho_i). \tag{8}$$

Here, r_{ij} is the scalar distance between atoms i and j, $\Phi(r_{ij})$ is a pairwise interaction potential, and ρ_i is the density at *i*-th atomic site due to all neighbours (located within a sphere of radius r_{cutoff}):

$$\rho_i = \sum_{j(j \neq i)} \rho(r_{i,j}). \tag{9}$$

The embedding function $F(\rho_i)$ can be interpreted as the energy arising from embedding *i*-th atom in an electron gas of density ρ_i [12]. For simulation, 27 supercells were used with total number of 4320 atoms of copper in combination with Born-von Karman periodic border condition. Both techniques were applied on pure fcc metals. The equilibrium lattice constant and bulk modulus were determined by calculating the energy per supercell as a function of lattice parameter. The data points were fitted by Birch fitting procedure [13] in case of *ab initio* results and EAM data were fitted by a quadratic polynomial using least-squares method. Elastic constants C', C_{11} and C_{12} were computed due to deformation which they perform. The results are shown in Tables 1 to 4.

3. Discussion

In the framework of both simulation tests first step includes calculation of equilibrium lattice constant of solid as a function of total energy. There is observed a well-known fact in *ab initio* concept concerning underestimation or overestimation of lattice constant depending on type of used approximation (LDA or GGA). This work confirmed this fact in most of our calculated results. As mentioned earlier, in order to fit the gained data we used non-harmonic Birch fitting functions because using harmonic polynomial fit for calculated *ab initio* data significantly shifted the value of equilibrium lattice constant toward incorrect value. An important dependence came out of computing bulk modulus and C' for the same number of *k*-points. In order to sample the reciprocal space of given structure we used 512 *k*-points. It has been shown that this experiment requires the same number of *k*-points for calculation of lattice constant as for calculation of C'. When ignoring this phenomenon, we have found senseless metastable phases of structure under investigation. In term of computing power and time, consummation is rising with complexity of solid's valence band. For example, Ni and Cu required Ecut of 60.00 and 70.00 Hartree because of *d*-electrons in the valence sphere.

The EAM potential used in this study was constructed on large set of experimental and *ab initio* database [17]. The accuracy of computed results depends on quality of embedding functions and on its ability to threat electron density in local coordination [14]. The computed lattice constant, bulk modulus, C', C_{11} and C_{12} for copper are in a very good agree-

Table 4. Results of EAM calculation for considered fcc metal

	EAM results								
	Aluminium			Copper			Nickel		
	This work	EAM[a]	Exp.	This work	EAM[d]	Exp.	This work	EAM[a]	Exp.
a (A)	4.05	4.05	4.05[b]	3.615	3.615	3.62[b]	3.52	3.52	3.52[b]
B (GPa)	77.0	79.0	79.0[c]	137.0	138.3	138.3[c]	184.0	181.0	181.0[c]
C' (GPa)	16.6	26.1	23.0[c]	23.7	23.7	23.8[c]	32.67	49.5	55.5[c]
C_{11} (GPa)	98.5	114.0	108.0[c]	168.6	169.9	170[c]	228.0	247.0	262.0[c]
C_{12} (GPa)	66.0	61.6	62.0[c]	121.2	122.6	122.5[c]	163.0	148.0	151.0[c]

[a] [8], [b] [6], [c] [7], [d] [9]

ment with experimental results. It has been proved that EAM deals with transition metals with nearly filled or nearly empty *d* bands quite well [15]. Elastic constants C', C_{11} and C_{12} of nickel display small deviation comparing to other EAM and experimental results. This implies the motivation in further improving of database and parametrization of used nickel EAM potential. The deviation in C' for aluminium poses the same trend in development of EAM potential but it is necessary to mention that aluminium is a metal which has anomalous elastic behaviour [16] because of its directional bonding. Results of this computer experiment strongly support the concept of EAM and *ab initio* DFT combination as a promising tool for describing the solid's properties at nanoscopic level.

4. Conclusion

We have studied the second order elastic constant for fcc metals. The results showed that experiments based on EAM potential give reliable results. Computed values of lattice parameter and elastic constants for tested metals give very good agreement with experimental data. Insufficient parametrization EAM potential for aluminium and nickel caused small deviation in elastic constant C'. Calculations based on *ab initio* technique in combination with both approximations (LDA and GGA) pose under- and overestimated lattice parameter. The value of elastic constant is over- and underestimated related to experimental result. The effect is well observed and is in good agreement with results of other studies. However, good results in comparison with experiment may be regarded as demonstration that the resulting error in elastic constants C', C_{11} and C_{12} is not serious. Despite the fact that an *ab initio* approach needs much more computation power and time, its rigorous application, accuracy and consistent prediction for real system are indisputable. The technique based on EAM is less consuming in computation and one could not deny the qualitative accuracy of such method applied to metallic materials.

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References

[1] MEHL, M. J.—KLEIN, B. M.—PAPACONSTANTOPOULOS, D. A.: Intermetallic Compounds: Principles and Practice. Eds.: Westbook, J. H., Fleischer, R. L. London, John Wiley and Sons 1995.

[2] ENGEBRETSEN, L.: Electronic structure calculations of the elastic properties of alkali hydrides. [Master's thesis]. Stockholm, School of Engineering Physics, Royal Institute of Technology KTH 1995.

[3] DEYIRMENJIAN, V. B. et al.: Phys. Rev. B, *52*, 1995, p. 15191.

[4] DAW, M. S.—BASKES, M. I..: Phys. Rev. B, *33*, 1986, p. 7983.

[5] WANG, L. G.—SOB, M.: Phys. Rev. B, *66*, 2002, p. 184105.

[6] KITTEL, CH.: Introduction to Solid State Physics. New York, John Wiley and Sons 1976.

[7] SIMONS, G.—WANG, H.: Single Crystal Elastic Constants and Calculated Aggregate Properties. Cambridge, MA, MIT Press 1977.

[8] MISHIN, Y.—FARKAS, D.—MEHL, M. J.—PAPACONSTANTOPOULOS, D. A.: Phys. Rev. B, *59*, 1999, p. 3393.

[9] MISHIN, Y. et al.: Phys. Rev. B, *63*, 2001, p. 224106.

[10] PERDEW, J. P.—BURKE, K.—ERNZENHOF, M.: Phys. Rev. Lett., *77*, 1996, p. 3865.

[11] DAW, M. S.—BASKES, M. I.: Phys. Rev. B, *33*, 1986, p. 7983.

[12] DAW, M. S.—BASKES, M. I.: Phys. Rev. B, *50*, 1983, p. 1285.

[13] BIRCH, F.: J. Geophys. Res., *83*, 1978, p. 1257.

[14] BALLO, P.—SLUGEŇ, V.—DEGMOVA, J.: Phys. Rev. B, *72*, 2005, p. 064118.

[15] CHANTASIRIWAN, S.—MILSTEIN, F.: Phys. Rev. B, *53*, 1996, p. 14080.

[16] OGATA, S. et al.: Phys. Rev. B, *70*, 2004, p. 104104.

[17] BALLO, P.—SLUGEŇ, V.: Computational Material Science, *33*, 2005, p. 491.