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ELASTIC CONSTANTS AND ANALYTIC BOND ORDER POTENTIAL FOR ATOMISTIC SIMULATIONS OF SIMPLE CUBIC TUNGSTEN TRIOXIDE

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Abstract: A set of elastic constants was calculated and a parametrization of the potential was derived for simple cubic tungsten trioxide based on an analytical bond-order scheme. It was shown that the obtained parametrization provided a good description of interatomic forces and such properties as the lattice constant, the bulk modulus and the elastic constants.

Keywords: tungsten trioxide, DFT, elastic constants, bond-order potential

1. Introduction

Tungsten trioxide (WO_3) is one of the exciting materials for electrochromic devices *e.g.*, large-area displays, windows with controlled light transmission and variable reflectance mirrors [1], showing also surprisingly interesting physical properties (refer to surface superconductivity at 91 K reported in sodium-doped tungsten trioxide [2]). The special case of tungsten oxide applications touches one-dimensional nanostructures that have been found attractive for solid-state gas sensors [3] due to their high surface-volume ratio as well as radial stress relaxation that prevents generation of dislocations due to lattices mismatch [4]. Tungsten oxide nanowires can be grown from tungsten substrates, heated in various mixtures of argon, hydrogen, and oxygen [5]. This aim can be achieved also by a technique based on the vapor-liquid-solid (VLS) mechanism in which nanowires grow from small liquefied gold catalyst particles [6].

It is important to understand the processes responsible for growth of tungsten oxide nanostructures as well as their mechanical properties from the technological point of view. This can be done on the atomic level with the help of molecular dynamics (MD), a tool which is widely used for the examination of growth processes, phase transition as well as material activity under ion bombardment. However, successful large-scale computer simulation studies require a reliable analytic potential describing the atomic interactions in systems. Recently, isotropic Born-Mayer interatomic potential has been used in order to describe the amorphous state of tungsten oxide [7]. However, this potential cannot properly reproduce the high directionality of the W-O bonds, and therefore it cannot be applied to the study of mechanical properties of tungsten oxide. Indeed, the simple cubic structure of tungsten trioxide resembles the ABO_3 perovskite structure with removed A atoms. The real structures of WO_3 are more complicated than simple cubic ones (that can be figured as a set of oxygen octahedral with a tungsten atom placed inside) due to distortion and tilting of the oxygen octahedra [8]. There are several phases of tungsten trioxide depending on the pressure and temperature *e.g.*, the monoclinic ($P2_1/n$) phase with eight formula units per cell exists at atmospheric pressure and room temperature [9] the crystallographic parameters and elastic constants of which are still studied.

In this paper elastic constants of a simple cubic structure of WO_3 are investigated by means of the first-principles method. It is worth noticing that the literature information concerning elastic constants of simple cubic tungsten oxide is limited to the bulk modulus (B) [9, 10]. The calculated set of elastic constants enabled us to derive a new potential parametrization in terms of an analytic bond-order scheme.

2. Methodology

In all the DFT calculations, the exchange-correlation functional was described in terms of the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA-PBE) [11]. The ultrasoft Vanderbild pseudopotentials [12] were developed for W and O with the following valence electron configurations of $5s^2 5p^6 5d^4 6s^2$, and $2s^2 2p^4$, respectively. The solutions of the Kohn-Sham equation were expanded on a basis of plane waves up to the kinetic energy cut-off 50 Ryd while the charge density was calculated up to the kinetic energy cut-off 200 Ryd. The properties of the basic compounds (lattice constant, magnetic moment and bulk modulus) were converged with the $12\times 12\times 12$ Monkhorst-Pack grid [13] of the Brillouin-zone. The Brillouin-zone integration was performed with the tetrahedron method [14]. The calculations were performed for a simple cubic structure of tungsten oxide composed of four *bcc* lattices: O (1/2,1/2,0), O (0,1/2,1/2), O (1/2,0,1/2), and W (1/2,1/2,1/2).

The analytic bond-order potential (ABOP) [15, 16] scheme has already been successfully applied to various systems – metallic [15, 17], covalent [16, 18, 19], molecular [20] and mixed ionic-covalent bonding [17, 20].

In the ABOP scheme, the cohesive energy is written as a sum over individual bond energies [15, 16]:

$$E = \sum_{i>j} f^c_{ij}(r_{ij}) \left(V^R_{ij}(r_{ij}) - \frac{b_{ij}+b_{ji}}{2} V^A_{ij}(r_{ij}) \right), \tag{1}$$

where

$$V^R_{ij}(r_{ij}) = \frac{D_0}{S-1} \exp\left(-\beta\sqrt{2S}(r-r_0) \right), \tag{2}$$

$$V_{ij}^{A}(r_{ij}) = \frac{SD_0}{S-1}\exp\Big(-\beta\sqrt{2/S}(r-r_0)\Big). \tag{3}$$

The parameters D_0, r_0, S and β describe the two-body part of the interatomic interaction – D_0 is the dimer bond energy, r_0 is the dimer bond distance, S is the Pauling plot slope, β can be determined from the dimer's ground state oscillation frequency. The cutoff function $f^c(r)$ restricts the interaction range to the first or second nearest neighbors:

$$f^c(r) = \begin{cases} 1 & r \le R_C - D_C, \\ \frac{1}{2} - \frac{1}{2}\sin\Big(\frac{\pi}{2}(r-R_C)/D_C\Big) & |r-R_C| \le D_C, \\ 0 & r \ge R_C - D_C, \end{cases} \tag{4}$$

where D_C and R_C are adjustable parameters. The many-body component of the interaction is represented by the bond-order factor:

$$b_{ij} = (1+\chi_{ij})^{-\frac{1}{2}}, \tag{5}$$

where

$$\chi_{ij} = \sum_{k(\neq i,j)} f_{ik}^{C}(r_{ik})g_{ik}(\Theta_{ijk})\exp\Big(2\mu_{ik}(r_{ij}-r_{ik})\Big), \tag{6}$$

in which the information about the angular dependence of the interaction is included in factor $g(\Theta)$:

$$g(\Theta) = \gamma\left(1+\frac{c^2}{d^2}-\frac{c^2}{d^2+(h+\cos\Theta)^2}\right). \tag{7}$$

In the above, the many-body component of the interatomic interaction is represented by the parameters μ, γ, c, d and h. All parameters depend on the atom type in the compound which is monitored by indices i, j and k.

The parameter optimization strategy was composed of two stages. First, the two-body parameters D_0, r_0, S and β were fitted against the dissociation curve of the dimer calculated using the Gaussian code. Then, the remaining parameters μ, γ, c, d and h, determining the many-body component of the interatomic interaction were fitted against the lattice constants, bulk modulus and elastic constants calculated using the plane-wave-pseudopotential Quantum-Espresso code [21] within the density-functional theory (DFT) framework. In order to fit the many-body component of the interaction, we developed a program which enabled us to perform optimization of the parameters using either direct force matching [22] or fitting against a data set containing lattice constants, bulk modulus and elastic constants for a number of crystal structures. The hybrid approach, combining the direct force matching and fitting against the elastic properties is also possible.

3. Results and discussion

The parameters D_0, r_0, S and β, responsible for the two-body part of the W-O interaction, were derived by fitting against the W-O dimer dissociation curve which is presented in Figure 1. The remaining parameters μ, γ, c, d and h, describing the many-body component of the W-O interaction in the crystal structure were derived by fitting against the data set containing the lattice constant a_0, bulk modulus B and a set of elastic constants c_{11}, c_{12} and c_{44}, obtained from the DFT calculations. The complete derived parametrization of the W-O interaction in the ABOP scheme framework

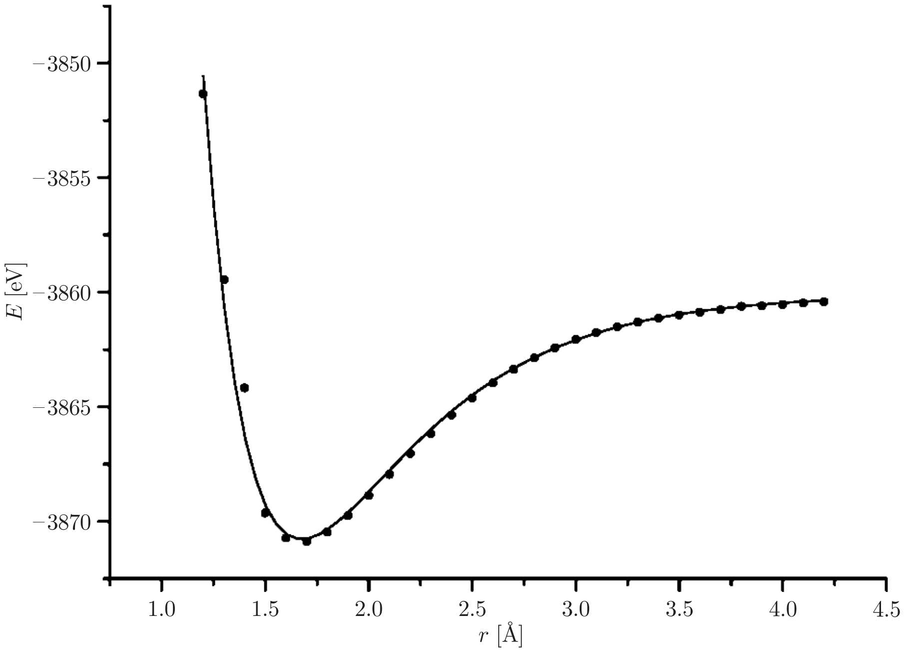

Figure 1. Calculated dissociation curve of the W-O dimer (circles). The solid line represents the fit using the ABOP energy expression (Equation (1))

is presented in Table 1 along with the W-W and O-O interaction parametrization adopted from the literature [17]. In the simple cubic structure of WO_3, the distance between the nearest oxygen atoms and also the distance between the nearest tungsten atoms are larger than the respective cutoff parameters R_C. Therefore, in the case of this structure, only the parameters characterizing the W-O interaction were fitted. The derived parametrization of the analytical bond order potential for simple cubic tungsten trioxide is presented in Table 1, along with the literature values of the W-W and W-O parameters [17].

Table 1. Parameter sets for W-W, O-O interactions [17] and the parametrization for the W-O interaction derived in this work

	W-W [17]	O-O [17]	W-O (this work)
R [Å]	2.0	2.2	3.0
D [Å]	0.3	0.1	0.1
D_0 [eV]	5.04687	5.166	10.7
S	2.18175	1.38634	2.29976
β [Å^{-1}]	1.33479	2.309	1.79755
r_0 [Å]	2.35724	1.20752	1.676
γ	0.00368724	0.82594	0.200703
c	2.44628	0.03560	4.00019
d	0.254415	0.04649	0.999532
h	−0.18195	0.45055	0.800301
μ [Å^{-1}]	1.29936	0	4.0

In order to asses to what extent the obtained parametrization reproduced the interatomic forces thus making the analytical potential suitable for atomistic MD simulations, a series of random deformations of the crystal lattice was generated by varying the atomic positions by 0–10% of the lattice constant length, and the forces acting on atoms were calculated using the DFT approach and using the analytical potential. The results for a few cases are illustrated in Figure 2. The simple cubic tungsten trioxide properties calculated using the DFT approach are collected in Table 2 along with their counterparts calculated using the analytical potential parameterized with the parameters derived in this work. These include the lattice constant, the bulk modulus and a set of elastic constants. It may be concluded that the obtained parametrization reproduced well the interatomic forces and elastic properties of the studied system. A generalization of the ABOP scheme for a larger set of real structures of tungsten oxide may be potentially possible and needs further studies.

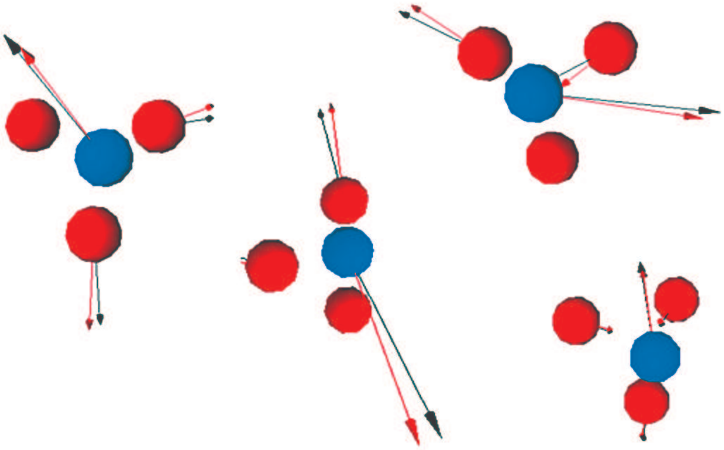

Figure 2. Interatomic forces for a few randomly generated deformations of the crystal lattice. The black arrows represent the forces calculated from the DFT approach. The red arrows represent the forces calculated from the ABOP scheme, using the parametrization derived in this work

Table 2. Properties of simple cubic WO_3, calculated from the DFT approach and obtained using the derived parametrization of the ABOP

	DFT [10]	DFT (this work)	ABOP (this work)
a_0 [Å]	3.82	3.6	3.698
B [GPa]	224	228.0	225.795
c_{11} [GPa]		337.3	334.485
c_{12} [GPa]		173.3	171.449
c_{44} [GPa]		2.6	2.603

4. Conclusions

The lattice constant, the bulk modulus and a set of elastic constants for simple cubic tungsten trioxide were calculated using the DFT approach and the data was used to derive the parameterization of the analytical bond order potential suitable for large scale molecular dynamics simulations. In order to do this, a program was developed for fitting the many-body component of the potential against the DFT calculated properties, the DFT calculated interatomic forces or the available experimental data. It was shown that the obtained parameterization provided a reasonably good description of the interatomic interactions in the studied system.

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