Computational Materials Science 114 (2016) 72–78

Contents lists available at ScienceDirect

Computational Materials Science

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

High-pressure phase diagram of gold from first-principles calculations: Converging to an isotropic atomic stacking order

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ARTICLE INFO

Article history:
Received 16 September 2015
Received in revised form 5 December 2015
Accepted 12 December 2015
Available online 29 December 2015

Keywords:
Phase diagram
High pressure and high temperature
Atomic stacking order

ABSTRACT

We reported the high pressure and temperature phase diagram of noble metal gold up to 500 GPa and 7000 K constructed from first-principles calculations. Using the unbiased multi-algorithm-collaborative (MAC) crystal structure prediction method, we discovered several metastable polymorphs of gold besides the previously known face-centered-cubic (fcc) structure. The phase boundaries of these polymorphs were located deliberately in the framework of quasi-harmonic approximation (QHA). The stability field of fcc-Au is almost identical to the experimental data. More importantly, we discovered and verified a new phase, the double hexagonal close-packed (dhcp) structure, before it transits to hcp under increasing compression. At room temperature, gold transforms from the fcc to the dhcp structure at 231.6 GPa, and at further compression it transits to the hcp structure at 447.8 GPa. From its elastic properties, an isotropy of atomic stacking order was observed in Au under increasing compression.

1. Introduction

As the noblest of all metals, gold has been widely used not only in daily life but also in industrial production throughout the whole history of human being, owing to its natural golden beauty, chemical inertness, high ductility, and crystal structure stability. In modern high-pressure science, gold is a popular pressure calibrator based on the well established equation of state (EOS) [1–3], due to its stable face-centered-cubic (fcc) structure and efficient X-ray scattering properties [4]. In order to discover its fundamental behaviors at extreme high-pressure conditions, researchers paid much attention to its high-pressure structural stability [2,4–11]. It is interestering that the recent studies [4,11] uncovered its structural instability at some conditions, e.g., extreme compression and heating. This places a natural constraint on the fcc-Au used as a popular pressure standard in the high-pressure experiments, such as the diamond anvil cell (DAC) experiment.

Although the two-stage light-gas gun and the laser-driven shock wave experiments did not show any solid–solid phase transition of gold along the Hugoniot state up to 580 GPa [12,13] and 10 TPa [14] respectively, both the DAC experiment by Dubrovinsky et al. [11] and theoretical calculations [4,7,10] by others discovered its structural phase transitions under extreme compression. Dubrovinsky et al. observed the fcc-hcp phase transition at 240 GPa in the X-ray diffraction experiments, however their *ab initio* calculations predicted the transition of fcc to the double hexagonal-close-packed (dhcp) at 250 GPa [11]. The earliest theoretical results indicated that Au transits from fcc to the hexagonal-close-packed (hcp) structure at 241 GPa [7], as was argued that it first transits from fcc to hcp at 151 GPa and then to the body-centered-cubic (bcc) structure at 400 GPa [10]. While, the different exchange–correlation functionls produced much different transition pressures for the fcc-hcp phase transition, 350 GPa for the local density approximation (LDA) and 410 GPa for the generalized gradient approximation (GGA) [1].

From the stacking sequence of Au atoms, recently Ishikawa et al. [4] discovered that Au transits from fcc to the ABCACB stacking at 390 GPa, to dhcp at 540 GPa, and then to hcp at 830 GPa by further compression, using the projector-augmented wave (PAW) method combined with the LDA. At the same time, they found that different methods alter the phase transition points considerably. Although, the phase diagram of Au was determined, the phase boundaries are far away from the experimental results (almost 350 GPa difference in pressure). Furthermore, the previous studies [1,4,7,11] started from several specific structures of Au, instead of the globally optimized stable structures. Some low-energy structures may be neglected for constructing the whole phase diagram of Au. This motivated us to have a detailed structure predictions for

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http://dx.doi.org/10.1016/j.commatsci.2015.12.009
0927-0256/

Au using the unbiased crystal structure search algorithm, and then construct its complete high pressure and high temperature phase diagram.

In this work, we performed detailed structure searches for metal Au using the multi-algorithm collaboration (MAC) crystal structure prediction technique [15]. The high pressure and temperature phase boundaries of the predicted low-energy structures were determined in the framework of the quasi-harmonic approximation (QHA). The rest of the paper is organized as follows. In Section 2, we describe the details about the crystal structure prediction and the method for constructing the whole phase diagram of Au. The results and discussion are presented in Section 3. Section 4 is a short summary of the conclusions.

2. Methodology

2.1. Structure prediction

In order to determine the low-energy structures of Au under high pressure, we searched its structures globally from 0 to 900 GPa with the interval of 50 GPa. The structure searches were preformed using the unbiased MAC crystal structure prediction technique implemented in our developed MUSE package [15]. The MAC technique has been applied to crystal structure predictions for several cases successfully [15–18]. In the MAC algorithm, we integrated several optimization algorithms organically to improve search efficiency and success rate, including the evolutionary algorithm, the simulated annealing algorithm, and the basin hopping algorithm. With the help of the competition mechanism introduced in all the evolutionary and variation operators, we realized the self-adaptive evolution of the crystal population and the choice of the operators. In the first generation, MUSE generates the random structures with symmetry constraints. This also largely shortens the optimization time for the first generation and increases the diversity of crystal population. The random structures are produced by choosing the space group numbers from 2 to 230 stochastically. At the same time, Wyckoff positions of all kinds of atoms were restricted to accord with the atom-number ratios of different space groups.

The structures were generated by MUSE and locally optimized by VASP package [19,20], and the evolution of the crystal population and the generation of the new crystal structures were governed by MUSE. We applied the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE) [21] and the electron–ion interaction described by the projector augmented wave (PAW) scheme [22,23]. The pseudopotential for Au has the valence electrons' configuration of $6s^15d^{10}$, which is the most recent version developed by VASP group. To achieve good convergences, the kinetic energy cutoff and the k-point grids spacing were chosen to be 500 eV and 0.03 $Å^{-1}$, respectively. The accuracies of the target pressure and the energy convergence for all optimizations are better than 0.1 GPa and 10^{-4} eV, respectively. The systems containing 2, 4, 6, and 8 atoms in the primitive cell were used in the structure searches for all pressures.

2.2. Gibbs free energy

After predicting several low-energy structures of Au, we calculated its phase diagram based on the quasi-harmonic approximation. The determinations of phase transition points obeyed the principle of lowest Gibbs free energy. In the framework of the QHA, the Helmholtz free energy of a crystal system is written as,

$$F(V,T) = E_{\text{static}}(V) + F_{\text{zp}}(V) + F_{\text{ph}}(V,T), \tag{1}$$

where $E_{\text{static}}(V)$ is the first-principles zero-temperature energy of a static lattice at volume V. In Eq. (1), the term F_{zp} is the zero-point motion energy of the lattice written as,

$$F_{\text{zp}}(V) = \frac{1}{2}\sum_{\mathbf{q},j}\hbar\omega_j(\mathbf{q},V), \tag{2}$$

where $\omega_j(\mathbf{q},V)$ is the phonon frequency of the jth mode of wave vector $\mathbf{q}$ in the first Brillouin zone (BZ).

The term $F_{\text{ph}}(V)$ in Eq. (1) is the phonon free energy due to lattice vibrations, and it can be calculated from,

$$F_{\text{ph}}(V,T) = k_BT\sum_{\mathbf{q},j}\ln\{1-\exp[-\hbar\omega_j(\mathbf{q},V)/k_BT]\}. \tag{3}$$

In the QHA, we calculated the static lattice energy at 0 K and neglected the dependences of the phonon vibration energy on temperature. The phonon vibrational frequencies of Au at various volume (pressure) was calculated using the finite displacement method [24] implemented in the PHONOPY code [25]. The force constants of the constructed supercells were calculated by the VASP package [19,20]. In order to compare the differenes between different exchange-corelation functionals, we adopted the GGA parameterized by PBE [21] and the local density approximation (LDA) parameterized by Perdew and Zunger [26] to calculate the exchange–correlation interactions between electrons, and the PAW scheme [22,23] to describe the electron–ion interactions. Others parameters are the same as those in the structure prediction calculations. The phonon vibrational frequencies of the low-energy structures of Au were calculated from 0 to 500 GPa with the pressure interval of 25 GPa. The high pressure phase boundary of Au was then automatically analyzed based on the quasi-harmonic approximation using our developed PHASEGO toolkit [27,28], which automates and simplifies the phase transition analysis and the phase boundary location and plot.

3. Results and discussions

3.1. Predicted structures

In our high-pressure structure searches for Au, besides the known fcc structure we also discovered several meta-stable structures, including the hexagonal-closed-package (hcp) structure, the double-hexagonal-closed-package (dhcp) structure, the body-centered-cubic (bcc) structure, the structures with the C2/m (12), I4/mmm (139) and Immm (71) symmetries, and so on. The hcp and dhcp structures have been reported previously [11,4]. The nanocrystal Au with the I4/mmm and Immm symmetries have recently been prepared successfully at ambient pressure and high temperature [29]. While, the ABCACB packing sequence of Au proposed theoretically in Ref. [4] was not reproduced in current searches, possibly because of the even number of atoms in our supercells. The energies of these polymorphs are comparable with that of ground-state fcc-Au.

3.2. Ground state properties

We derived the Helmholtz free energy of fcc-Au as a function of volume V and temperature T from Eq. (1). To deduce the thermodynamic properties, we fitted a Murnaghan EOS [30] to the calculated free energy versus volume data at each temperature. The reduced 300 K isothermal compressional curves are compared with experiments in Fig. 1a, in which we find a good agreement of the calculated PV curves with the experimental data [5,31].

The Hugoniot curve is one of the fundamental properties of materials, which reflects their responses to both pressure and