



Detailed first-principles studies on surface energy and work function of hexagonal metals



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ABSTRACT

The surface energies and work functions for ten kinds of Miller-indices surfaces of hexagonal metals, Be, Mg, Tc, Re, Ru, and Os are calculated by means of the density functional theory (DFT) method. The results show that the metals belonging to the same group have a very similar rule in work functions and surface energies. The work functions of (0001), (01 $\bar{1}$ 1), and (10 $\bar{1}$ 0) surfaces are generally larger than the work functions of (11 $\bar{2}$ 1), (11 $\bar{2}$ 2), (11 $\bar{2}$ 3), and (31 $\bar{4}$ 0) surfaces. In contrast to work functions, there is more regularity in the crystallographic orientation dependence of surface energies. However, for the metals belonging to different groups, there are always some differences in the exact order of orientation dependence. It is also shown that the work functions and surface energies of the main group metals decrease as they go from top to the bottom in the same group of periodic table, while for the transition metals, they do not always obey this rule.

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1. Introduction

Surface energy and work function are very important parameters that can determine various properties of materials, such as the Young's modulus for mechanical behaviors [1–3], the surface morphology of metals and alloys [4], and the zero charge potential of electrode surface [5]. These parameters can also help to understand many surface phenomena, for example, underpotential deposition (UPD) [6], surface segregation [7,8] and dealloying [9], metal dissolution or corrosion [10], and the formation of grain boundaries [11].

Surface energy, defined as the amount of energy required to divide an infinite crystal into two parts, is a very fundamental parameter of materials surface. Work function is defined as the minimum energy needed to remove an electron from the bulk of a material through surface to a point outside the material. Research works on surface energy and work function have been reported in many publications [5,12,13]. These studies have deeply promoted the development of materials science.

In experimental aspect, there have been numerous reports about the surface energies and work functions of metals, especially in the mid of last century. Since the end of the last century, theoretical calculations based on density functional theory (DFT) [14–22] have become a very widely accepted and useful tool to understand the surface energy and work function properties of materials. A roughly inverse proportional relationship between surface energy and work function was found by Wang et al. [23] through the analysis of their DFT results. Singh et al. [24] studied some BCC and FCC metals,

as well as Ti(0001), by first-principles calculation. Kokko et al. [19] reported their first-principles results on the (100), (110) and (111) surfaces of lithium.

Although the surface energies and work functions for most of the cubic metals have been calculated and reported so far, the situation for hexagonal metals is still far from satisfactory. Tang et al. [25] reported a detailed first-principles study on the surface energy of magnesium. Vitos et al. [26] calculated the surface energies of two kinds of low-index surfaces for a few hexagonal metals. In addition to a bit of data for (10 $\bar{1}$ 0) surface, the work function calculations of hexagonal metals were mostly done for (0001) surface only [18,27–30], reports on the other hexagonal surfaces are hardly touched yet.

In this work, we focus on calculation of the surface energies and work functions of six typical hexagonal metals for their (0001), (10 $\bar{1}$ 0), (01 $\bar{1}$ 1), (01 $\bar{1}$ 2), (01 $\bar{1}$ 3), (11 $\bar{2}$ 1), (11 $\bar{2}$ 2), (11 $\bar{2}$ 3), (21 $\bar{3}$ 0), and (31 $\bar{4}$ 0) surfaces. In some experimental work, some scientists [31–34] have reported the existence of (0001), (10 $\bar{1}$ 0), (01 $\bar{1}$ 1), (01 $\bar{1}$ 2), and (11 $\bar{2}$ k) surface in hexagonal crystals. But their work functions and surface energies are seldom studied theoretically. All the calculations are made with first-principles method within the framework of density-functional theory. The calculated surfaces are represented by periodic slab models, separated by 1.6 nm vacuum space to avoid successive repeat slab interactions. The results obtained by the present study are expected to provide a valuable database reference for the surface science.

2. Calculation method

The calculations are performed via the Vienna Ab initio Simulation Package (VASP) [35] with periodic boundary condition using the

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projector augmented wave (PAW) method [36,37]. The local density approximation (LDA) and Perdew–Burke–Ernzerh (PBE) [38] generalized gradient approximation (GGA) are both adopted for comparison.

The surfaces are modeled by 12 layer slabs for (0001) and (10 $\bar{1}$ 0) surfaces, 16 layer slabs for (01 $\bar{1}$ 1), (01 $\bar{1}$ 2), and (01 $\bar{1}$ 3) surfaces, 22 layers for (11 $\bar{2}$ 1), (11 $\bar{2}$ 2), and (11 $\bar{2}$ 3), and 30 layers for (21 $\bar{3}$ 0) and (31 $\bar{4}$ 0) surfaces to obtain the converged results, which is similar to the work of Wang et al. [23], Tang et al. [25], Skriver et al. [25] and Perdew et al. [38]. The Gamma centered grids are used for k-space integration, and the k-point meshes are adjusted depending on the size of the surface models. The energy cutoff is set to be 400 eV. For the structural relaxation, the convergence criterion of self-consistent calculations is 10⁻⁶ eV and a force criterion of 0.03 eV/Å between two consecutive steps is adopted for ionic relaxations. The surface unit cells are p(1 × 1) with the vacuum thickness set to be 1.6 nm. Spin polarization is taken into account through all the calculations to decrease some unexpected errors. The electron occupancies with a smearing width of 0.1 eV is taken. During relaxation, all the atoms in the slab models are allowed to relax. The details of our calculations are listed in Table 1. It gives almost all of the information about the calculations of Mg calculated with PBE functional. As for the other metals' calculations, the parameter settings are very similar.

The calculated lattice constants are listed in Table 2, compared with experimental values [39]. The results calculated with PBE functional show very good agreement with the experimental results. The results calculated with LDA approximation are a little bad, but still show good agreement with the experimental results. The calculated values of c/a ratio are similar for two approximations.

2.1. Slab models

Six hexagonal elemental metals are studied, including Be, Mg, Tc, Re, Ru, and Os. For each metal, the slab models of (0001), (10 $\bar{1}$ 0), (01 $\bar{1}$ 1), (01 $\bar{1}$ 2), (01 $\bar{1}$ 3), (11 $\bar{2}$ 1), (11 $\bar{2}$ 2), (11 $\bar{2}$ 3), (21 $\bar{3}$ 0), and (31 $\bar{4}$ 0) crystal orientations are built and calculated. Our created slab models are presented in Fig. 1. Although the surface models used in this work are the p(1 × 1) slab structure, Fig. 1 shows the p(3 × 2) models of the slabs in order to illustrate the periodic structures of these models.

In view of the surface configurations in this study there are rarely seen in other works, some more detailed explanations of these model buildings are supplied in Figs. 2 to 5. Fig. 2 takes the model of Mg (01 $\bar{1}$ 1) as an example to illustrate the structural periodicity of these models. Fig. 2(a) is a configuration of (3 × 2) super cell of the (01 $\bar{1}$ 1) slab model used in this calculation, Fig. 2(b) is a slab structure cut directly from the metal bulk. It is seen that the atomic arrangements in Fig. 2(a) and (b) by the two different methods are the same, which confirms that the models used in this work are strict for their periodicity. Fig. 3 gives a simple explanation of the (01 $\bar{1}$ 1) surface slab model, which is very similar to the slab models of (01 $\bar{1}$ 2) and (01 $\bar{1}$ 3) surfaces.

Table 1
The calculation details of Mg.

| Surface orientation | Atom layers | Slab thickness (Å) | K mesh | K points | Energy cutoff (eV) | Vacuum thickness (Å) | Energy convergence criteria (eV) | Force convergence criteria (eV/Å) |
|---------------------|-------------|--------------------|---------|----------|--------------------|----------------------|----------------------------------|-----------------------------------|
| (0001) | 12 | 44.48 | 14*14*1 | 57 | 400 | 16 | 10 ⁻⁶ | 0.03 |
| (10 $\bar{1}$ 0) | 12 | 30.75 | 10*6*1 | 24 | | | | |
| (01 $\bar{1}$ 1) | 16 | 33.49 | 10*6*1 | 32 | | | | |
| (01 $\bar{1}$ 2) | 16 | 30.49 | 10*4*1 | 18 | | | | |
| (01 $\bar{1}$ 3) | 16 | 26.49 | 8*3*1 | 13 | | | | |
| (11 $\bar{2}$ 1) | 22 | 32.02 | 6*5*1 | 16 | | | | |
| (11 $\bar{2}$ 2) | 22 | 29.59 | 6*5*1 | 12 | | | | |
| (11 $\bar{2}$ 3) | 22 | 28.31 | 5*4*1 | 11 | | | | |
| (21 $\bar{3}$ 0) | 30 | 29.93 | 5*3*1 | 6 | | | | |
| (31 $\bar{4}$ 0) | 30 | 26.99 | 5*2*1 | 6 | | | | |

Table 2
The comparison of the calculated crystal lattices with experimental values.

| Potential | Metal | Lattice constant | | | Error to experiment value [39] | | |
|-----------------|-------|------------------|-------|-------|--------------------------------|--------|----------|
| | | a (Å) | c (Å) | c/a | Δa (%) | Δc (%) | Δc/a (%) |
| PAW-PBE | Be | 2.264 | 3.567 | 1.575 | -0.96 | -0.47 | 0.45 |
| | Mg | 3.191 | 5.187 | 1.626 | -0.56 | 0.46 | 0.12 |
| | Tc | 2.746 | 4.395 | 1.601 | 0.40 | 0.15 | -0.19 |
| | Re | 2.774 | 4.481 | 1.615 | 0.47 | 0.56 | 0.06 |
| | Ru | 2.715 | 4.279 | 1.576 | 0.33 | -0.07 | -0.38 |
| | Os | 2.759 | 4.355 | 1.578 | 0.91 | 0.88 | -0.06 |
| PAW-LDA | Be | 2.232 | 3.524 | 1.579 | -2.36 | -1.67 | 0.70 |
| | Mg | 3.124 | 5.078 | 1.625 | -2.65 | -2.55 | 0.06 |
| | Tc | 2.707 | 4.327 | 1.598 | -1.02 | -1.39 | -0.37 |
| | Re | 2.741 | 4.422 | 1.613 | -0.72 | -0.76 | -0.06 |
| | Ru | 2.673 | 4.216 | 1.577 | -1.21 | -1.54 | -0.31 |
| | Os | 2.725 | 4.304 | 1.579 | -0.33 | -0.30 | 0 |
| Experiment [39] | Be | 2.286 | 3.584 | 1.568 | 0 | | |
| | Mg | 3.209 | 5.211 | 1.624 | | | |
| | Tc | 2.735 | 4.388 | 1.604 | | | |
| | Re | 2.761 | 4.456 | 1.614 | | | |
| | Ru | 2.706 | 4.282 | 1.582 | | | |
| | Os | 2.734 | 4.317 | 1.579 | | | |

Fig. 3(a) is a perspective view of 2 × 2 × 1 Mg cell. Where, the four index coordinate system of hexagonal close-packed crystals is indicated by the blue lines, the (01 $\bar{1}$ 1) plane and the [2110] direction are also labeled in this figure. Fig. 3(b) is the projective view of Fig. 3(a) along the [2110] direction; the two oblique lines indicate the (01 $\bar{1}$ 1) plane. Fig. 3(c) is the 2 × 2 view of Fig. 3(b) in order to give a better view of the atomic arrangement along the vertical direction of (01 $\bar{1}$ 1) plane. Fig. 3(d) rotates an anticlockwise angle from Fig. 3(c). Fig. 3(e) is the slab model of (01 $\bar{1}$ 1) surface built in this work. It is seen that the atomic positions in Fig. 3(e) are in strict conformity with the labeled area in Fig. 3(d).

Figs. 4 and 5 are very similar to Fig. 3. Fig. 4 presents a simple explanation of the slab model of (11 $\bar{2}$ 1) surface, which is very similar to the ones of (11 $\bar{2}$ 2) and (11 $\bar{2}$ 3) surfaces. Fig. 5 is for the slab model of (21 $\bar{3}$ 0) surface, it is very similar to (31 $\bar{4}$ 0) surface. As for the slab models of (0001) and (10 $\bar{1}$ 0) surfaces, they are very easy to build. There is no need to give too many explanations for them.

2.2. Surface energy and work function

The surface energy is the work required to form a unit area of surface. It is defined as follows:

$$\sigma = \frac{1}{2S} (E_{\text{slab}}^N - N * E_{\text{bulk}}) \quad (1)$$

where E_{slab}^N is the total energy of the slab, E_{bulk} is the per atom energy of the bulk metal, N is the total number of atoms in the slab, S is the surface

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