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A simple descriptor for energetics at fcc-bcc metal interfaces

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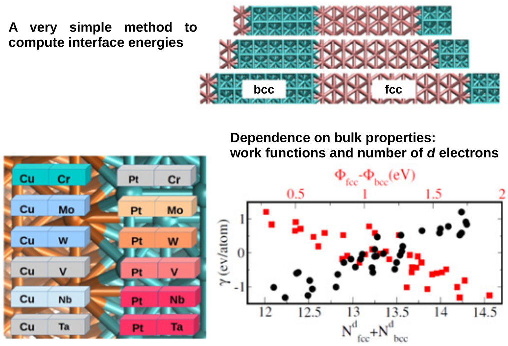
HIGHLIGHTS

- A simple, efficient method has been developed to calculate the interface energy and work of separation between materials from first principles. It overcomes the problem of differing periodicities between surfaces and bulk.
- By applying this to 36 fcc/bcc transition-metal interfaces, simple bulk descriptors for interface energies have been unveiled: the difference of work functions on the one hand, and the total number of *d* electrons per unit cell on the other.
- For the bcc metals, the interface energy was also found to follow the average energy of the unit-cell *d* electrons, which again is a descriptor based on bulk properties.

GRAPHICAL ABSTRACT



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ABSTRACT

We have developed a new and user-friendly interface energy calculation method that avoids problems deriving from numerical differences between bulk and slab calculations, such as the number of *k* points along the direction perpendicular to the interface. We have applied this to 36 bcc-fcc metal interfaces in the (100) orientation and found a clear dependence of the interface energy on the difference between the work functions of the two metals, on the one hand, and the total number of *d* electrons on the other. Greater mechanical deformations were observed in fcc crystals than in their bcc counterparts. For each bcc metal, the interface energy was found to follow the position of its *d* band, whereas the same was not observed for fcc.

1. Introduction

The study of metal-metal interfaces is crucial for many industrial processes and technological applications [1–3], including growth modes in thin films [4,5], catalysis [6], as well as many experimental techniques used in nanotechnology such as those involving metallic tips on metal surfaces [7]. Theoretical support in designing metallic interfaces is essential as it can provide information that is extremely difficult to extract experimentally. An example is given by interface energies, which determine the nucleation barrier and the shapes of precipitates [8–10], besides the stability and reliability of the whole system. These energies are not directly accessible experimentally.

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Thorough studies have been performed at the level of first-principles calculations on selected solid-solid interfaces, focusing on various aspects such as the film thickness [4], orientation [7], magnetoresistance [11], magnetic anisotropy [12] ferromagnetic moments [13], as well as electronic [14–17], mechanical [18–21], and thermodynamic [22–26] properties. Notwithstanding the detailed nature of these analyses, they were quite often mostly focused on a very few materials. What is currently still missing is, for instance, a systematic analysis and a rule of thumb as to how to “cherry pick” materials and match them, ensuring stability of their interface at the same time. In this work, therefore, we chose to follow a different approach. We focused on only one crystal orientation (100) and on one type of relative dislocation between the two metals, but we performed a systematic analysis spanning over 36 interfaces. These were obtained by combining 6 face-centred-cubic (fcc) crystals (Au, Ag, Cu, Ni, Pd, Pt) with 6 body-centred-cubic (bcc) crystals (Cr, Mo, W, Nb, V, Ta). Such an approach has allowed us to formulate a descriptor for interface energies based on very similar conditions for all systems.

In particular, we aimed to understand whether it is possible to predict trends in interface energetics on the basis of simple bulk properties. In previous work, on the basis of non-first-principles calculations [27], interface energies were found to depend on the balance between several quantities, including the number of *d* electrons per atom in the interface layers and in the bulk, the bandwidth of the interface layers and the bulk, the cohesive energies, the Fermi levels and the intra-atomic potentials. We show here, instead, that modern density functional theory (DFT) calculations make it possible to reveal much simpler relationships. In particular, we show that, for certain metal pairs, simply the difference between their work functions or the sum of the electrons in their *d* bands can provide a first hint on the stability of the interface. We anticipate that this will prove to be a very useful finding for the design of metallic multilayers and heterostructures for technological applications. Our work is particularly timely and relevant for interface layer selection and design in the context of high-throughput materials simulation and informatics, a research area which is gaining increasing traction at present.

2. Methods

The interface energy is the energy cost associated with the introduction of an interface. It can be interpreted as the surface “binding” energy density of the two components. It comprises two contributions, namely the chemical and electronic energy that originates from breaking and creating bonds to form an interface, and the elastic energy required to create the interface by matching the two lattices [28]. We mainly focus on the electronic component and neglect the elastic contribution, which goes beyond the scope of the present work. Within one of the most accurate methods to date [29], the interface energy γ can be calculated as:

$$\gamma = E'_{\text{fcc/bcc}} - E^{\text{bulk}}_{\text{fcc}} - E^{\text{bulk}}_{\text{bcc}}, \tag{1}$$

where

$$E'_{\text{fcc/bcc}} = E_{\text{fcc/bcc}} - \sigma_{\text{fcc}} - \sigma_{\text{bcc}}. \tag{2}$$

Here, $E_{\text{fcc/bcc}}$ is the total energy of the system, $E^{\text{bulk}}_{\text{x}}$ is the total energy of the crystal in the bulk state. The surface energies σ_{x} are calculated relative to the bulk crystal experiencing the same strain as in the interface (see Ref. [29] for details), via

$$\sigma_{\text{x}} = \left(E_{\text{x}} - E^{\text{bulk}}_{\text{x}}\right)/2. \tag{3}$$

Although this method has proven successful [29], it requires five separate calculations (one for the interface, two for the corresponding bulk materials and two for their free surfaces), which require particular care when defining the unit-cell dimensions and the corresponding strain in each of them. More importantly, it carries the intrinsic problem of performing algebraic operations between quantities that are calculated using different numbers of *k* points. In fact, the lattice periodicity is preserved in all three space directions in bulk crystals, but only in two directions at surfaces. Consequently, energies computed for bulk and slab calculations are not directly comparable for all thickness values and slow convergence of the calculated interface energy with respect to the number of layers can thereby arise. Slight variations of Eq. (1) have also been used [30], but these present the same problem.

We thus propose an alternative method, namely an extension of the Fiorentini procedure [31] that was originally developed to calculate surface energies, and which has been shown to provide accelerated convergence with respect to the number of layers in the system [32]. Surface energy is the energy needed to cleave a bulk crystal into two separate surfaces [4] and it can be expressed as

$$\sigma = \lim_{N\to\infty} \frac{1}{2}\left(E^{\text{slab}}_{N} - NE^{\text{bulk}}\right), \tag{4}$$

where E^{slab}_{N} is the total energy of an *N*-atom slab and E^{bulk} is the total energy of the bulk per atom. Within the Fiorentini method, E^{bulk} can be calculated as the slope in E^{slab}_{N} plotted against *N* and then used in Eq. (4). This is possible because the following linear relationship applies:

$$E^{\text{slab}}_{N} \approx 2\sigma + NE^{\text{bulk}}. \tag{5}$$

This method allows us to avoid problems deriving from calculating E^{slab}_{N} and E^{bulk} with a different number of *k* points. We note that, if one-atom unit cells are considered, *N* equals the number of layers.

By replacing the vacuum region with another metal, we have extended this scheme to the calculation of interface energies. In fact, in the same way that interface energies are the energies originating from breaking old bonds and creating new bonds in the interface, surface energies can likewise be interpreted as the energy involved in breaking the same old bonds and creating new “bonds” with the vacuum. Within such a scheme, we built, for each fcc-bcc interface, at least three structures which differ from each other by the number of layers on each side (see Fig. 1). After collecting the total energies of each structure, we extracted the slope *s* of the total energy of the fcc-bcc system $E_{N_{\text{x}}+N_{\text{y}}}$ versus the total number of layers $N_{\text{x}}+N_{\text{y}}$, where N_{x} and N_{y} are the number of layers on each side of the interface. The interface energy γ is then given by

$$\gamma = \left(E_{N_{\text{x}}+N_{\text{y}}} - (N_{\text{x}}+N_{\text{y}}) * s\right)/2, \tag{6}$$

where $E_{N_x+N_y}$ and $N_x + N_y$ must be taken from the same structure. As for surface energies, this method avoids problems arising due to numerical differences between bulk and slab calculations for interface energies. In addition, it only requires two simple calculations (although it is recommendable to perform at least one more to make sure the slope is evaluated in the linear regime). The work of separation *W* (the energy needed to separate the interface into two free surfaces) is given by [1,33]

$$W = \sigma_{\text{fcc}} + \sigma_{\text{bcc}} - \gamma. \tag{7}$$

In order to calculate the necessary total energies, we carried out density functional theory (DFT) calculations by using the PWscf code