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Contribution of van der Waals forces to the plasticity of magnesium

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ABSTRACT

The accurate determination of stacking fault energies (SFE) and associated restoring forces is important for understanding plastic deformation, especially the dislocation emission and motion in metals. In this work, we use density-functional theory (DFT) calculations to, systematically study the all-dimension relaxed atomic models of Mg crystal slip, with a special focus on the "subslip modes" in prismatic and pyramidal slip systems. We find that slip systems with large interplanar distances are readily activated, which agrees well with experimental observations. Inclusion of the ubiquitous van der Waals (vdW) interactions results in lower generalized stacking fault energy curves. Remarkably, the unstable SFE value of pyramidal-II system is strongly reduced by up to 69 mJ/m^2, and the related restoring stress is lowered by 0.74 GPa after taking into account the vdW energy. Our calculations indicate significant effect of vdW forces on the plasticity of Mg.

1. Introduction

Magnesium (Mg) and its alloys have found extensive applications in automobile, aircraft, and electronic components, due to their high strength, lightweight, and good electric properties [1,2]. However, their broader applications in modern industry are severely limited by their low tensile strength and poor plasticity [3–5]. Typically, the plastic deformation in Mg is primarily carried out by five slip systems on basal, prismatic and pyramidal planes. Facilitating cross slip from basal plane to prismatic and pyramidal planes has been shown as a promising method to enhance the plasticity of hcp metals. Unlike the basal plane in Fig. 1a, the interplanar distances are not identical in prismatic and pyramidal planes, leading to two slip systems (named as type "I" and type "II") along the same $<11\bar{2}0>$ direction (Fig. 1b and c). Although such "subslip phenomenon" generally exists in hcp metals [6], it was often neglected in previous studies. As such, one would cast doubt on the sufficiency of slip systems normally defined in hcp crystals, raising a question on the most preferable slip route for Mg. In addition, due to the anisotropic deformation behavior and the lack of easy-slip systems in hcp metals, deformation mechanisms of Mg and its alloys are known to be more complicated than their face-centered and body-centered cubic counterparts [7–9].

The stacking fault energy (SFE) is a key parameter for understanding the deformation mechanism of metals. The SFE value represents the energy associated with interrupting the normal stacking sequence of a crystal plane, and significantly affects the mobility of dislocations. To interpret the mobility of dislocations, the generalized stacking fault energy (GSFE) curve is often calculated, which involves both stable and unstable SFEs. Obviously, an accurate GSFE curve is important, both for determining the energy barrier between two adjacent planes in a slip system, and for calculating the restoring force described in the famous Peierls-Nabarro model for dislocations [10,11]. However, there is a large scatter in the SFE data obtained from experiments. For example, the SFE values for pure Mg range from 50 to 280 mJ/m^2 [12–14]. The large discrepancy in determining the SFE values reflects the difficulty in finding the correct slip modes and resulting deformation mechanisms in Mg.

Density-functional theory (DFT) calculations are widely used to calculate the SFE and GSFE curves. For example, Smith [15] has used generalized gradient approximation (GGA) method to study four different basal plane stable SFEs, and the unstable SFEs on basal, prismatic, and pyramidal planes. He found that the unstable SFE of

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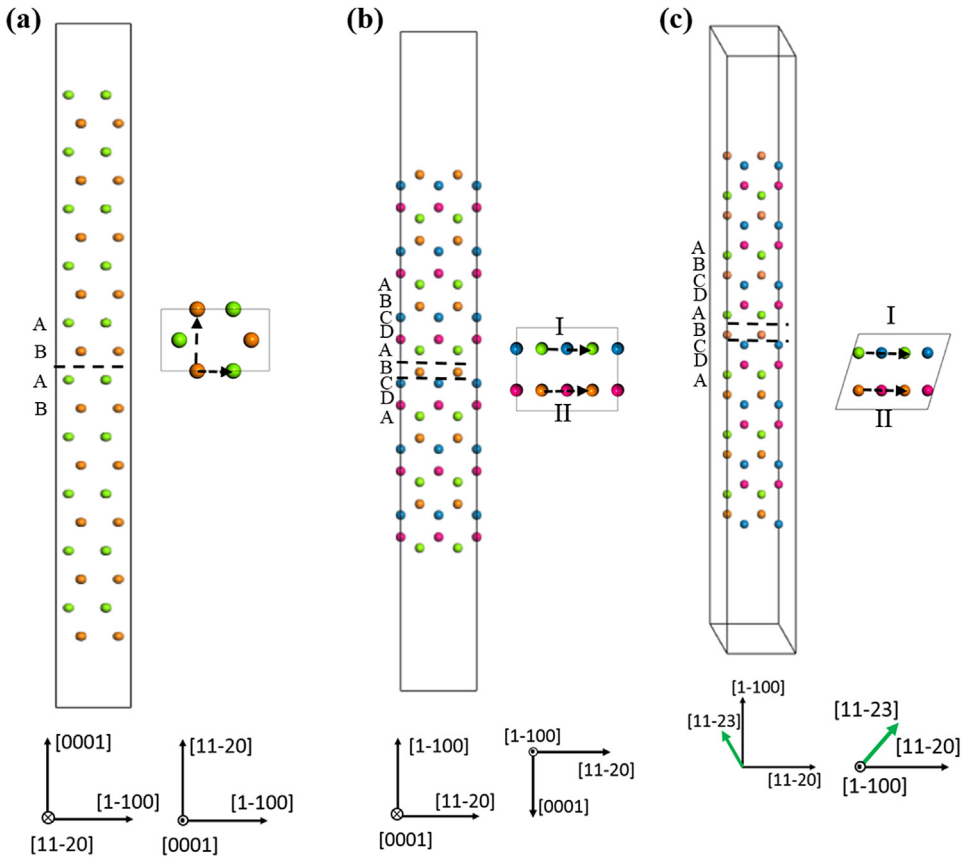

Fig. 1. The slab supercells used to calculate the GSFE of magnesium for basal plane (a), prismatic plane (b), and pyramidal plane (c). In plot (a), the dotted line in the side view represents the slip plane, and the arrows in the top view denote the $<1\bar{1}00>$ and $<11\bar{2}0>$ slip directions. In plots (b) and (c), there exist two slip planes in the prismatic and pyramidal planes due to the difference in interplanar distances. Slip along AB layer with a large distance is named as "I", slip along BC layer with a small distance is named as "II". The arrows in the top views indicate the two slip modes.

the pyramidal plane is 30% greater than that on the prismatic plane, and the SFE results from GGA are consistently lower than those from the local-density approximation (LDA) method. Also using the GGA method, Wen *et al.* [16] systematically calculated the GSFE surface of basal planes and non-basal planes, concluding that slip occurs primarily on basal plane for pure Mg. These DFT calculations provide insights into the underlying deformation mechanisms of Mg. However, it is known that the standard DFT functionals, including both LDA and GGA, cannot capture the long-range van der Waals (vdW) interactions for nonhomogeneous electron densities [17,18]. This may lead to serious errors in the prediction of the structure, stability, and function of materials [19–22]. A recent work has clearly demonstrated that the inclusion of vdW interactions is necessary for obtaining reasonable structures observed from experiments for noble metals and alkali metal [23]. In addition, vdW forces are found to make considerable contribution to the stability and cohesive properties, such as cohesive energies and bulk moduli, of metals [24]. Notably, many previous studies have focused on the role of vdW interactions in *alkaline-earth metal clusters* [25–28]. A consensus from all these studies is that the vdW interactions play a critical role in alkaline-earth metal clusters, including Mg, and the inclusion of the vdW in the calculation yields better agreement with available experimental data. For example, the vdW interactions can significantly reduce the binding energy of Mg dimer from 3.28 to 1.39 kcal/mol, making it much closer to the experimental data (1.21 kcal/mol) [25]. Although the effects of vdW forces have been reported in bulk metals such as Cu, Al, Ag, and Au [29], their contributions to mechanical properties of Mg bulk have yet to be explored. Therefore, one would expect the vdW forces to affect the SFE values and GSFE curves. However, no previous studies have considered the role of vdW forces in metal plasticity.

In this contribution, we systematically study the slip modes and plasticity of hcp Mg by including the vdW effects in the DFT calculation. We find that the inclusion of vdW interactions consistently results in lower SFE values than those from the standard GGA-PBE functional. In particular, vdW interactions are found to contribute more to unstable SFEs than to stable ones, due to the different degree of charge density distributions in the two systems. We also find that the slip along a plane with a larger interplanar distance is easier to be activated in prismatic and pyramidal planes, which is consistent with experimental findings. Our results would help with understanding the cross slip from basal plane to non-basal planes, and the resulting plastic deformation mechanism in hcp metals.

2. Computation approach

All calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [30]. The interaction between the valence electrons and ionic cores was described by the projector augmented wave (PAW) method [31]. The standard Perdew–Burke–Ernzerhof (PBE) form of the GGA [32] was used as the exchange-correlation functional throughout the paper. A vdW-inclusive approach named optB88-vdW [29,33] was employed to account for dispersion interactions in our calculations. The optB88-