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First-principles study of the Ni(1 1 1)($\sqrt{3} \times \sqrt{3}$)R30°–Pb surface

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Abstract

We apply first-principles calculations based on density function theory (DFT) within the generalized gradient approximation (GGA) to investigate Pb adsorption on and absorption in Ni(1 1 1)($\sqrt{3} \times \sqrt{3}$)R30° surface. The adsorption energy calculations show that the substituional surface alloy without stacking fault is preferred, followed by on-surface hollow site adsorption, and the stacking faulted surface alloy is the most unstable. This confirms earlier experiments. The rumpling amplitude is calculated to be 0.987 Å. It broadly agrees with previous theoretical results and observations by low-energy electron diffraction (LEED) and medium-energy ion scattering (MEIS), but is much larger than that obtained by low-energy ion scattering. The work-function change due to Pb adsorption is found to be 0.433 eV, indicating the charge transfer from the substrate to the adsorbate.

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Keywords: Density functional theory; Lead; Nickel; Surface alloy; Stacking fault

1. Introduction

For years it has been widely recognized that the growth of metals on metals in a controlled manner provides the opportunities for preparing ordered surface alloy [1–5]. It can even occur when the constituent elements are immiscible in the bulk. A common phenomenon is that the radii of deposited atoms are larger than that of substrate atoms to be replaced, leading to the substitutional surface alloy with rumpled surface and different layer spacings relative to the underlying substrate. In addition, most experiments show that the rumpling magnitude is less than the prediction from a simple hard-sphere model [6–10]. The reason is that substituting substrate atom with larger atoms may actually reduce the valence electron charge density and lowers the surface stress. Then the atoms would prefer to stay close with each other, resulting in reduced rumpling amplitude and contraction of the outermost layer spacing [4,11]. One example is the 0.33 ML Ni(1 1 1)($\sqrt{3} \times \sqrt{3}$)R30°–Pb surface alloy. By means of impact-collision ion scattering spectroscopy, the Pb/Ni substitutional surface alloy was suggested and the rumpling magnitude was found to be 0.2 Å [12]. Medium-energy ion scattering (MEIS) was also used to determine the structure of Ni(1 1 1)($\sqrt{3} \times \sqrt{3}$)R30°–Pb surface phase [13]. Results support the substitutional surface alloy in the outermost layer, but also show Pb atoms above the Ni plane with protruding 0.65 ± 0.15 Å, much larger than previous experiment. In order to explain the discrepancy, the structure of this surface alloy was studied by Quinn et al. [14] using the technique of tensor low-energy electron diffraction (LEED). It shows that the rumpling amplitude for this surface alloy is 0.73 ± 0.05 Å, which agrees well with the MEIS results. Although the difference of the rumpling amplitude exists in experiments for the Ni(1 1 1)($\sqrt{3} \times \sqrt{3}$)R30°–Pb surface phase, all of them are much less than 1.67 Å, expected from a simple hard-sphere model.

Recent studies of 0.33 ML ($\sqrt{3} \times \sqrt{3}$) R30° phase on FCC(1 1 1) face have attracted considerable attention. It is because that a surprising additional feature was

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observed in Cu(1 1 1)($\sqrt{3} \times \sqrt{3}$)R30°–Sb and Ag(1 1 1) ($\sqrt{3} \times \sqrt{3}$)R30°–Sb surfaces [15–17]. Atoms in the single-layer alloy are displaced laterally to occupy so-called HCP hollow sites above those in the second layer of the substrate, rather than the proper FCC hollow sites above the third-layer ones. So the alloy–substrate interface indeed has a stacking fault, which is confirmed by density function theory (DFT) calculations [18]. It was supposed that this surface stacking fault may be found for other (1 1 1) ($\sqrt{3} \times \sqrt{3}$)R30° metal alloy phases. As for Ni(1 1 1) ($\sqrt{3} \times \sqrt{3}$)R30°–Pb surface alloy, the stacking fault was clearly excluded by Tensor LEED and MEIS. To the best of our knowledge, no theoretical analysis on the stacking fault of Ni(1 1 1)($\sqrt{3} \times \sqrt{3}$) R30°–Pb surface alloy by first-principles calculations has been reported.

In this work, we have investigated the Pb adsorption on and absorption in Ni(1 1 1)($\sqrt{3} \times \sqrt{3}$) R30° surface using DFT on the generalized gradient approximation (GGA). The spin-polarization effect was also considered. This method has been proved for calculating both structural and electronic properties of medium-sized systems [19–23]. Total energy calculations show that the substitutional surface alloy without stacking fault is preferred and the Ni(1 1 1)($\sqrt{3} \times \sqrt{3}$) R30° surface alloy has no stacking fault. The optimized geometries and change of work-function were also presented and analyzed.

2. Calculation method

The calculations were performed using VASP package. The spin-polarization effect was also considered. The interaction between ions and electrons is described using the ultrasoft pseudopotentials introduced by Vanderbilt [24]. Computations were performed within GGA proposed by Perdew and Wang [25]. The influence of different k-point samplings and plane-wave cutoff energies was explored in a series of test calculations, which led to calculations performed with a $6 \times 6 \times 1$ k-point sampling and a cutoff energy of 350 eV. We used a five-layer slab of Ni, periodically repeated in a supercell geometry with six layers of vacuum between any two successive metal slabs. The bottom two layers of the slab are kept frozen, whereas all other atoms are allowed to relax. Adsorption is allowed on only one of the two exposed surfaces, and the electrostatic potential is adjusted accordingly. We considered ($\sqrt{3} \times \sqrt{3}$) R30° unit cell with one Pb adsorbate, corresponding to the coverage of 0.33 ML. The calculated lattice constant for Ni is 3.515 Å, which is very close to the experimental value of 3.524 Å.

3. Results

3.1. Analysis of structure

For the Ni(1 1 1)($\sqrt{3} \times \sqrt{3}$) R30°–Pb system, we considered four different models: two high symmetry adsorption structures where Pb atoms occupy FCC hollow sites and HCP hollow sites, and two possible substitutional surface alloy models where Pb atoms substitute 1/3 Ni atoms in the outmost layer with and without stacking fault (see Fig. 1). In order to compare the stability of the surface-substitutional adsorption with that of the simple adsorption, it is necessary to define the adsorption energy per adatom [26]. For the simple adsorption structures, it is given as

$$E_{\text{ads}} = E_{\text{Pb/Ni-slab}} - E_{\text{Ni-slab}} - E_{\text{Pb-atom}},$$

where $E_{\text{Pb/Ni-slab}}$ and $E_{\text{Ni-slab}}$ are the total energy of Ni slab with and without Pb adsorption on the clean Ni surface, respectively, $E_{\text{Pb-atom}}$ is the energy of isolated Pb atom. In the case of Pb substitutional adsorption, the adsorption energy can be expressed as [26]

$$E^{\text{sub}}_{\text{ads}} = E^{\text{sub}}_{\text{Pb/Ni-slab}} - (E^{\text{vac}} + E_{\text{Pb-atom}}) + E^{\text{vac}}_{\text{f}}$$

and

$$E^{\text{vac}}_{\text{f}} = E^{\text{vac}} + E_{\text{Ni-bulk}} - E_{\text{Ni-slab}}.$$

Here $E^{\text{vac}}_{\text{f}}$ is the formation energy of surface vacancy, E^{vac} is the total energy per unit cell of the surface vacancy structure, $E_{\text{Ni-bulk}}$ is the bulk total energy per atom of FCC Ni.

Table 1 shows the main energetic and structural properties for Pb adsorption on Ni(1 1 1)($\sqrt{3} \times \sqrt{3}$) R30° surface. From the calculated adsorption energies, we see that the substitutional surface alloy without stacking fault (i.e. unfaulted alloy) is the most favorable, followed by the hollow site adsorption, with the stacking faulted surface alloy (i.e. faulted alloy) being the least stable. The energy difference between FCC and HCP hollow sites is found to be 58 meV, indicating that FCC hollow site is more stable. The unfaulted stack phase is 0.397 eV lower than the faulted stacking model, suggesting no stacking fault in the Ni(1 1 1)($\sqrt{3} \times \sqrt{3}$) R30°–Pb surface alloy. This trend of the stable adsorption site is consistent with experimental results [13,14]. The surface vacancy formation energy of Ni(1 1 1)($\sqrt{3} \times \sqrt{3}$) R30° model is 1.516 eV. The optimized surface structural parameters are also listed in Table 1. As for the most stable surface alloy, the rumpling amplitude is calculated to be 0.987 Å, agreeing well with previous theoretical results of 0.98 Å [11]. This value is slightly larger than that found by MEIS (0.65 ± 0.15 Å) [13] and LEED (0.73 ± 0.05 Å) [14], but large difference exists with 0.2 Å by low-energy ion scattering [12]. It shows that this smallest rumpling is probably inaccurate. In addition, both the observed and calculated rumpling magnitudes are much less than the prediction from hard-sphere model (1.67 Å). The bond lengths between Pb and first-layer Ni atoms (i.e. d_1), and between the Pb and second-layer Ni atoms (i.e. d_2), are 2.675 and 3.27 Å, respectively. The layer spacing of the Pb atoms relative to the outermost complete Ni layer, Z_{Pb}, is 2.96 Å, slightly larger than experiments. On the other hand, our calculations reproduce the observations in the layer spacings of Ni atoms for all possible adsorption sites. Compared with the ideal interlayer spacing of 2.029 Å for Ni(1 1 1) surface, the most stable surface alloy exhibits only