First-principles calculation of LaNi₅ surface

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Abstract. The spin-polarized, all-electron, ab initio calculations have been performed for the electronic structure of the surface of crystal LaNi₅ using the self-consistent cluster-embedding (SCCE) calculation method. The geometrical surface structure of crystal LaNi₅ and its electronic structure having the lowest ground-state energy are obtained, with the full relaxation of atomic positions along the direction perpendicular to the surface. On the surface of crystal LaNi₅, the La atom protruded, and the Ni atoms caved in, so the surface becomes uneven which increases the contacting area. The effective volume of the surface layer rises by 9%. The Fermi level of the LaNi₅ surface, which is contributed by mainly Ni 3d electrons, is much higher than that of body LaNi₅. The valence band is not fully filled. For the first two layers of LaNi₅ surface, there are 1.15 electrons transferred from La to Ni, and the two layers have small opposite spin magnetic moments which shows the paramagnet. All calculated results show that the properties of LaNi₅ surface are significantly different from that of body LaNi₅, but very similar to that of hydride LaNi₅H₇. So the geometrical surface structure of crystal LaNi₅ is in favor of the absorption of hydrogen.

1. Introduction

To use hydrogen as a major global energy carrier, there are several fundamental and technical problems to be solved. The largest challenge today may be to find hydrogen storage solutions. A hydrogen fuel cell car needs to store at least 4 kg hydrogen to match the range of a gasoline-powered car. Due to cost-expensive processes and geometric limitation, it is impossible to store this amount of hydrogen as liquid or gas at room temperature and atmospheric pressure. There has been more interest in storing hydrogen on solid state materials. However, it is a great challenge to meet the requirements for vehicular applications, which include: (1) Light, the weight percent of absorbed hydrogen to be 6.5% (the target of the United States Department of Energy). (2) Compact, hydrogen capacity per volume to be 62 kg m⁻³ (the mass density of liquid hydrogen is 70.8 kg m⁻³). (3) Fast, the rate of absorption/desorption to match the peak consumption of 1–3 g/s. (4) Safe and reversible, can be reversibly used at appropriate temperatures and pressures for several years (three or five years?). (5) Cheap. These are all important, but no metal hydride system has been found to meet all these demands.

The intermetallic compounds LaNi₅ is known to reversibly absorb and desorb gaseous hydrogen at appropriate temperatures and pressures [1, 2]. In tritium facilities, metal hydride technology has been used to store, purify, isotopically separate, pump, and compress hydrogen isotopes. One of the most important advantages of using hydride technology in tritium processes is the compact size of hydride equipment. This is due to the fact that the volumetric density of hydrogen in hydride is greater even than that of liquid hydrogen. Other benefits of using hydride technology for tritium handling applications are improved safety during storage of tritium in the hydride form at below atmospheric pressure [3-6].
Hydrogen is absorbed dissociatively. The cleavage of the hydrogen bond is endothermal to the extent of 4.45 eV/H₂. So there must be a strong exothermal interaction with the lattice as hydrogen enters to compensate for this energy. In order to understand the hydrogenation, first, we must know the electronic structure. As we know, there are seven calculations for crystal LaNi₅ [7-13] and two calculations for its hydride LaNi₅H₇ [8, 12]. The band structure calculations are not satisfactory because of the well localized 3d electrons in the valence band. Up to day, there is no report of calculated electronic structure of LaNi₅ surface, and no one has studied hydrogen absorption by LaNi₅ surface using the spin-polarized, all-electron, ab initio calculations. The interaction of hydrogen with LaNi₅ lattice has not been elucidated in any more than the most general terms; such as, for example, to assert that there is a strong La-H affinity in the LaNi₅ hydride, etc.

The self-consistent cluster-embedding (SCCE) calculation method is developed by the author based on the density functional theory, and is a first-principles method [14]. Unlike the band structure calculation and free-cluster calculation, the SCCE calculation uses a set of localized non-interacting electrons to describe systems. So the localized valence electrons in material can be better described by the localized wave functions obtained in the SCCE calculation. It has been successfully applied to crystals NiO, CoO, Ni, GaN, LaNi₅, LaNi₅H₇, hydrogen-decorated vacancies in Ni, and the Ga vacancy in GaN [15-23]. In addition, the computational effort of a SCCE calculation can scale quasi-linearly with the number of electrons, while the calculation precision is kept. This makes the electronic structure calculation of protein molecule a reality. The electronic structures of three proteins have been obtained by the first-principles, all-electron, ab initio calculations [18, 19, 21, 22].

LaNi₅ is not suitable for vehicular applications because it is expensive, weighty, and its weight percent of absorbed hydrogen is only 1.6%. But it will help us greatly in finding new hydrogen storage material if we can understand its hydrogenation.

In this paper, the geometrical structure as well as the electronic structure of LaNi₅ surface is obtained by first-principles, all electron, ab initio calculation using the SCCE method. This will enable us to calculate the hydrogen absorption on the surface of LaNi₅. In Sec. 2, we outline briefly the theoretical method. The results are presented in Sec. 3, and summarized in Sec. 4.

2. Theoretical model

The self-consistent cluster-embedding (SCCE) calculation method has been described in detail elsewhere (see references [14], [23] and website www.esprotein.org.cn), here we give only a brief overview for completeness.

In the density functional theory (DFT), Kohn and Sham assume that a non-interacting electron system has the same ground-state charge density as that of real interacting system [24, 25]. The energy functional of a system containing N electrons and M fixed nuclei can be written as (no relativistic effect is included; atomic units with the unit of energy being the Rydberg constant Ry= e² / 2a₀ =13.6049 eV are used: e² = 2, h = 1, and 2m_e = 1):

\[ E_{\rho} = T_{\rho} + E_{xc}, \]

where \( T_{\rho} \) is the kinetic energy of a non-interacting electron system, \( E_{xc} \) is the exchange-correlation energy. Each non-interacting electron can now be represented by a stationary state one-electron wave function \( \Phi_n^\sigma(r) \). The charge density \( \rho(r) \) and kinetic energy \( T_{\rho} \) of the non-interacting system are the sums of the electronic density and kinetic energy of each non-interacting electron, respectively:

\[ \rho(r) = \rho^\uparrow(r) + \rho^\downarrow(r) = \sum_{\text{occupied up}} |\Phi^\uparrow_n(r)|^2 + \sum_{\text{occupied down}} |\Phi^\downarrow_n(r)|^2 \]  

\[ T_{\rho} = \sum_{\text{occupied up}} \int \Phi^\uparrow_n(r)(-\nabla^2)\Phi^\uparrow_n(r) \, \mathrm{d}r + \sum_{\text{occupied down}} \int \Phi^\downarrow_n(r)(-\nabla^2)\Phi^\downarrow_n(r) \, \mathrm{d}r \]  

Using formulas (2) and (3), a single-electron Schrödinger equation, i.e., the well known Kohn-Sham
equation [25], is obtained by the variation of functional (1) with respect to \( \Phi_n^{\sigma}(r) \) under conservation rule \( \int \rho(r) dr = N \):

\[
\left\{ -\nabla^2 + 2 \sum_{i=1}^{M} \frac{Z_i}{|r-R_i|} + V_n^{\sigma}(r) \right\} \Phi_n^{\sigma}(r) = \varepsilon_n^{\sigma} \Phi_n^{\sigma}(r), \tag{4}
\]

where the exchange-correlation potential is

\[
V_n^{\sigma}(r) = \frac{\partial E_{xc}[\rho]}{\partial \rho^{\sigma}(r)}. \tag{5}
\]

The exact solution of Eq. (1) could be obtained if the following two conditions were satisfied: (i) \( E_{xc}[\rho] \) is exact. (ii) The trial one-electron wave functions \( \Phi_n^{\sigma}(r) \) are unconstrained in solving the Kohn-Sham equation (4) (required by the variational principle). Then we should obtain an uniquely exact set of \( \{ \Phi_n^{\sigma}(r) \} \) which corresponds to an uniquely correct \( \rho(r) \). The Kohn-Sham equation (4), with an exact \( V_n^{\sigma}(r) \) and a correct \( \rho(r) \), describes such a situation in which one electron (represented by an \( \Phi_n^{\sigma}(r) \)) moves under the average potentials of all other electrons and nuclei.

Because the potential produced by an electron \( \langle \Phi_n^{\sigma}(r) \rangle^2 \) does not act on itself, the single-electron Hamiltonian in equation (4) includes only the potentials produced by \( \rho^{\sigma}(r) = \rho(r) - \langle \Phi_n^{\sigma}(r) \rangle^2 \). This leads two results: (a) Different \( \Phi_n^{\sigma}(r) \) will correspond to different single-electron Hamiltonians in Kohn-Sham equation (4). (b) In general, the Hamiltonian acting on an \( \Phi_n^{\sigma}(r) \) has no symmetry of \( \rho(r) \). As an example, consider a perfect periodic crystal. Although its charge density \( \rho(r) \) is of lattice periodicity, in general, the single-electron Hamiltonian of Kohn-Sham equation (4) will have no lattice periodicity.

In practical calculation, however, the two conditions above cannot be satisfied. Two approximations are taken. (1) The exchange-correlation potential \( V_n^{\sigma}(r) \) is averaged over all one-electron states with spin \( \sigma \) (such as LDA). (2) Each \( \Phi_n^{\sigma}(r) \) is constrained to satisfy a certain boundary condition. Please note, the first approximation means that all \( \Phi_n^{\sigma}(r) \) in equation (4) now correspond to a same single-electron Hamiltonian which having the symmetry of \( \rho(r) \), and all \( \Phi_n^{\sigma}(r) \) are now constrained by this added symmetry. But this added constraint is not physically essential, and can be removed by boundary condition. The second approximation means that by choosing different boundary conditions, we can use different kinds of \( \{ \Phi_n^{\sigma}(r) \} \) to get approximate \( \rho(r) \). When one kind of \( \{ \Phi_n^{\sigma}(r) \} \) is chosen, it means that a kind of non-interacting electrons is used to describe the real system approximately. According to variational principle, the calculated energy will be close to the true ground-state energy, only if the trial one-electron wave functions \( \Phi_n^{\sigma}(r) \) describe real electrons well. For example, a set of Bloch functions can give a good description to quasi-free electrons, but can not do it for localized electrons. The latter can be best described by a set of localized one-electron wave functions.

Assume the first approximation has been taken, we discuss the second approximation. There are two kinds of non-interacting electrons, extended and localized. They satisfy different boundary conditions, and correspond to different calculation methods.
2.1 Extended non-interacting electron model

Each one-electron wave function $\Phi_n^\sigma(r)$ is constrained to spread over the whole region occupied by the system. Under this model, the equation (4), with periodic boundary condition, can be used to a perfect periodical crystal. The single-electron Hamiltonian with periodic boundary condition has the periodicity of $\rho(r)$, the Bloch theorem is valid and band structure calculation is performed. For a free cluster, equation (4) is solved with the natural finite boundary condition $\Phi_n^\sigma(r) \underset{r \to \infty}{\to} 0$, and the single-electron Hamiltonian has the point symmetry of the free cluster.

2.2 Localized non-interacting electron model

Each one-electron wave function $\Phi_n^\sigma(r)$ is constrained to distribute in a part of the region occupied by the system. Under this model, equation (4) is used for self-consistent cluster-embedding (SCCE) calculation [14]: The system is divided into $k$ embedded clusters, and all $N$ $\Phi_n^\sigma(r)$ are divided into $k$ groups. Because all $\Phi_n^\sigma(r)$ are localized, the $i$th embedded cluster has electronic density $\rho_i(r)$, and the rest of the system is treated as environment with electronic density $\rho_2(r)$ which has small overlap with $\rho_i(r)$. The $\Phi_n^\sigma(r)$ in the $i$th group satisfy the $i$th set of special boundary conditions:

$$\Phi_n^\sigma(r) \big|_{r \text{-in-the-core-regions-of-surrounding-atoms} = 0},$$  
(6)

$$\Phi_n^\sigma(r) \overset{r \text{-go-away-from-the-embedded-cluster}}{\to} 0,$$  
(7)

and localize in the $i$th embedded cluster. The physical reasons of boundary condition (6) were given in reference [14]. By calculating all $k$ embedded clusters one by one, we get a complete set of one-electron eigenfunctions of whole system which makes the total energy in formula (1) minimum [14]. For a periodic crystal, only one embedded cluster needs to be calculated self-consistently, while $\rho_2(r)$ is identical with the periodic extension of $\rho_1(r)$.

The optimum values of core radii of surrounding atoms are determined according to two criteria: (i) there is no collapse disaster; (ii) the number of cluster-electrons remaining in the surrounding core regions is the minimum. In general, the boundary condition (6) can be satisfied with high precision, and it is found that the results are not sensitive to the core radii if they are around the optimum values.

We refer readers to the Refs. [14], [23] and website www.esprotein.org.cn for further details concerning the SCCE calculation.

3. Calculation results of LaNi$_5$ surface

3.1 Calculation model

In order to get the geometrical surface structure of crystal LaNi$_5$, first, we calculate a neat surface of LaNi$_5$.

LaNi$_5$ crystallizes within the CaCu$_5$ structure with space group P6/mmm [26]. The primitive cell of crystal LaNi$_5$ contains 6 atoms (left side, Fig. 1): one La atom (atom 1), two Ni$_I$ atoms of the first type (atoms 2 and 3), and three Ni$_{II}$ atoms of the second type (atoms 4, 5 and 6). The lattice constants used in our calculation are $a_o=5.023 \AA$, $c_o=3.984 \AA$ [27, 28]. The initial embedded cluster (LaNi$_5$) is obtained by repeating the primitive cell twice along the $c$ direction (right side, Fig. 1). We call the atoms in the same level as one layer, such as the first layer containing atoms 1, 2 and 3. So a primitive cell has two layers, and the initial embedded cluster (LaNi$_5$) has six layers.
Assume only six layers near the surface are different from that of bulk crystal. So the surface of LaNi₅ is modeled by periodic extension of the embedded cluster (LaNi₅)₃ along the surface (Fig. 2, shaded part). Below them, from the seventh layer to the fourteenth layer, the calculated bulk electron charge density of crystal LaNi₅ [23] is used and is fixed during calculation.

The optimized Gaussian bases of Ni and La are the same as that used in the calculation of crystal LaNi₅ [23]: Ni --- 10s6p6d constructed from 16s10p7d, La --- 14s10p7d constructed from 20s16p11d, the total number of Gaussian bases of the embedded cluster (LaNi₅)₃ is 1107. There are 3311825 grid points used for numerical calculation of Vₓc. We use the von Barth and Hedin [29] form of the exchange-correlation potential, as parametrized by Rajagopal and co-workers [30]. The optimum values of core radii of surrounding La and Ni atoms are the same as that used in reference [23]: Rₖa=1.6861 a.u., Rₜₙ=0.7869 a.u. After convergence, the total number of cluster electrons remaining in the core regions of all surrounding atoms is less than 0.00073, which shows that the special boundary condition (6) is well satisfied.

After convergence, the force acted on each atom is calculated, and the atoms are moved along the direction perpendicular to the surface. Then, the electronic structure of the modified surface is recalculated by the SCCE method, and the atoms are moved again according to new results. This process is repeated. After 15 adjustments of atomic positions, the geometrical surface structure of crystal LaNi₅ having the lowest total energy is obtained.

Figure 1. The initial embedded cluster (LaNi₅)₃ (● represents Ni, ○ represents La)

Figure 2. Schematic diagram of the surface (centre is the embedded cluster)
3.2 Geometrical surface structure of crystal LaNi₅

The atomic coordinators of the embedded cluster (LaNi₅)₃ are shown in the table I. The results show that the La atoms of layer 1 and 2 protrude, the La atom of layer 3 caves in. While the Ni atoms of layers 1, 2 and 3 cave in, the Ni atoms of layers 4 and 6 protrude.

We are interested in the first and second layers. For the first layer, the surface becomes uneven which increases the contacting area. The effective volume between the first layer and the second layer rises by 9% compared with that of crystal LaNi₅. The experiments show that the volume of hydride LaNi₅H₇ is larger than that of LaNi₅ about 8%. So both characteristics of the LaNi₅ surface are in favor of the absorption of hydrogen.

| No. | x     | y     | z     | x₀    | y₀    | z₀    | Atom | Layer |
|-----|-------|-------|-------|-------|-------|-------|------|-------|
| 1   | 0.0000| 0.0000| 0.8583| 0.0000| 0.0000| 0.0000| La   | 1     |
| 2   | 4.7462| 2.7402|-0.0358| 4.7462| 2.7402| 0.0000| Ni   |       |
| 3   | 0.0000| 5.4804|-0.0358| 0.0000| 5.4804| 0.0000| Ni   |       |
| 4   | -2.3731| 4.1103|-3.9074| -2.3731| 4.1103| -3.7644| Ni   | 2     |
| 5   | 4.7462| 0.0000|-3.9074| 4.7462| 0.0000| -3.7644| Ni   |       |
| 6   | 2.3731| 4.1103|-3.9074| 2.3731| 4.1103| -3.7644| Ni   |       |
| 7   | 0.0000| 0.0000|-6.6705| 0.0000| 0.0000| -7.5288| La   | 3     |
| 8   | 4.7462| 2.7402|-7.6718| 4.7462| 2.7402| -7.5288| Ni   |       |
| 9   | 0.0000| 5.4804|-7.6718| 0.0000| 5.4804| -7.5288| Ni   |       |
| 10  | -2.3731| 4.1103|-11.0071| -2.3731| 4.1103| -11.2932| Ni   | 4     |
| 11  | 4.7462| 0.0000|-11.0071| 4.7462| 0.0000| -11.2932| Ni   |       |
| 12  | 2.3731| 4.1103|-11.0071| 2.3731| 4.1103| -11.2932| Ni   |       |
| 13  | 0.0000| 0.0000|-16.6025| 0.0000| 0.0000| -15.0576| La   | 5     |
| 14  | 4.7462| 2.7402|-15.0576| 4.7462| 2.7402| -15.0576| Ni   |       |
| 15  | 0.0000| 5.4804|-15.0576| 0.0000| 5.4804| -15.0576| Ni   |       |
| 16  | -2.3731| 4.1103|-18.7362| -2.3731| 4.1103| -18.8220| Ni   | 6     |
| 17  | 4.7462| 0.0000|-18.7362| 4.7462| 0.0000| -18.8220| Ni   |       |
| 18  | 2.3731| 4.1103|-18.7362| 2.3731| 4.1103| -18.8220| Ni   |       |

Table II. Eigenvalues and Mulliken populations of cluster (LaNi₅)₃ (spin up)

| State | Energy(eV) | x  | y  | z  | x₀ | y₀ | z₀ | La s | La p | La d | Ni s | Ni p | Ni d |
|-------|------------|----|----|----|----|----|----|------|------|------|------|------|------|------|
| 290   | -0.2601    | 0.0000| 0.0010| 0.0183| 0.0296| 0.0349| 0.9161|
| 291   | -0.2132    | 0.0000| 0.0004| 0.0297| 0.0472| 0.0405| 0.8822|
| 292   | -0.1826    | 0.0001| 0.0004| 0.0149| 0.0317| 0.0363| 0.9166|
| 293   | -0.1624    | 0.0000| 0.0002| 0.0041| 0.0056| 0.0186| 0.9714|
| 294   | -0.1249    | 0.0021| 0.0059| 0.0395| 0.0873| 0.0617| 0.8035|
| 295   | -0.0978    | 0.0000| 0.0003| 0.0067| 0.0232| 0.0205| 0.9493|
| 296   | -0.0175    | 0.0001| 0.0002| 0.0190| 0.0255| 0.0262| 0.9289|
|       |            |     |     |     |    |    |    |      |      |      |      |      |      |
| (E_F) | below are unoccupied states |     |     |     |    |    |    |      |      |      |      |      |      |
| 297   | 0.1451     | 0.0000| -0.0001| 0.0937| 0.0509| 0.0531| 0.8024|
| 298   | 0.2704     | 0.0000| 0.0006| 0.0565| 0.0187| 0.0601| 0.8641|
| 299   | 0.4018     | 0.0000| 0.0009| 0.1584| 0.0595| 0.0615| 0.7197|
| 300   | 0.4264     | 0.0012| 0.0523| 0.2612| 0.0292| 0.0757| 0.5804|

3.3 Electronic structure

Table II and III gives the eigenvalues and Mulliken populations of cluster (LaNi₅)₃ near the Fermi level. The Fermi energy E_F = -0.0175 eV, which is unusually high, and is about 5.1 eV higher than that of bulk LaNi₅. The valence band is from states 217 to 296 (spin up) and from state 217 to 295 (spin
down). It contains 85.2% of Ni 3d electrons, 7.2% of Ni 4s electrons, 3.9% of Ni 4p electrons and 3.0% of La 5d electrons. Below the valence band, there are La 5p electrons which belong to core electrons. Figure 3 shows the DOS of states 217 to 310. Each single level has been broadened by a Gaussian function with a FWHM of 1 eV (s electrons), 0.5 eV (p electrons) and 0.3 eV (d electrons), respectively.

**Table III.** Eigenvalues and Mulliken populations of cluster (LaNi$_5$)$_3$ (spin down)

| State | Energy(eV) | La s | La p | La d | Ni s | Ni p | Ni d |
|-------|------------|------|------|------|------|------|------|
| 290   | -0.1644    | 0.0000 | 0.0002 | 0.0298 | 0.0390 | 0.0380 | 0.8929 |
| 291   | -0.1351    | 0.0011 | 0.0022 | 0.0221 | 0.0447 | 0.0493 | 0.8806 |
| 292   | -0.1298    | 0.0000 | 0.0006 | 0.0077 | 0.0162 | 0.0292 | 0.9463 |
| 293   | -0.1009    | 0.0009 | 0.0037 | 0.0320 | 0.0589 | 0.0611 | 0.8434 |
| 294   | -0.0689    | 0.0002 | 0.0010 | 0.0204 | 0.0453 | 0.0282 | 0.9049 |
| 295   | -0.0237    | 0.0000 | 0.0001 | 0.0080 | 0.0230 | 0.0195 | 0.9495 |
| 296   | 0.0965     | 0.0000 | 0.0006 | 0.0431 | 0.0203 | 0.0220 | 0.9140 |
| 297   | 0.1751     | 0.0000 | -0.0002 | 0.1182 | 0.0621 | 0.0559 | 0.7640 |
| 298   | 0.3537     | 0.0000 | 0.0007 | 0.0635 | 0.0132 | 0.0583 | 0.8644 |
| 299   | 0.4315     | 0.0000 | 0.0009 | 0.1374 | 0.0475 | 0.0551 | 0.7591 |
| 300   | 0.4403     | 0.0011 | 0.0532 | 0.2620 | 0.0273 | 0.0761 | 0.5802 |

The table II and Fig. 3 show that the Fermi level of LaNi$_5$ surface falls in a rapidly decreasing potion of the Ni 3d bands which are not fully filled. This shows a metallic ground state. The DOS of Fermi level is large, and the contribution of La 5d electron is almost zero.

Compared with the calculated DOS of crystal LaNi$_5$ and its hydride LaNi$_5$H$_7$ [23], we find that there is marked difference between the DOS of crystal LaNi$_5$ and the Fig. 3, while the DOS of LaNi$_5$H$_7$ are very similar to the Fig. 3.

![DOS of La electrons](image)
Figure 3. Density of states of electrons of cluster \((\text{LaNi}_5)_3\). Units of DOS are states per electron-volt per \((\text{LaNi}_5)_3\) cell. In (a) and (b), dashed line: spin up electrons, solid line: spin down electrons.

(b) DOS of Ni electrons

(c) DOS of total electrons (spin up and spin down)
3.4 Charge transfer

Table IV gives the electron numbers of atoms calculated by Mulliken populations. Table IV shows that there is a charge transfer from atom La to atom Ni in the surface of LaNi₅. All La atoms lost electrons and are positively charged: La 1 atom of the first layer lost 1.11 electrons, La 7 atom of the third layer lost 1.25 electrons, and La 13 atom of the fifth layer lost 1.10 electrons. Most Ni atoms got electrons and are negatively charged. We are interested in the first layer and second layer: each Ni₁ atom of the first layer got about 0.5 electrons, and each Ni₂ atom of the second layer got about 0.2 electrons. Compared with the results of crystal LaNi₅ [23]: La atom lost 0.457 electrons, each Ni₁ atom got about 0.011 electrons, and each Ni₂ atom got about 0.145 electrons. For hydride LaNi₅H₇ [23]: La atom lost 1.16 electrons, each Ni atom lost about 0.05 electrons, and each H atom got about 0.20 electrons. So the charge transfer of the surface of LaNi₅ is larger than that of bulk, and is similar to that of hydride LaNi₅H₇ except for one thing: it is from La to Ni in the surface of LaNi₅, but is from La to H in hydride LaNi₅H₇.

Along the direction perpendicular to the surface, the first and second primitive cell got electrons, the third primitive cell lost electrons. So the electrons transfer from bulk to surface. A negatively charged surface is in favor of the absorption of hydrogen molecule which gets electrons and is dissociated to two H atoms.

Table IV. Electron number (Mulliken populations)

| No. | Atom | Electrons (spin up) | Electrons (spin down) | Total electrons | Magnetic moment (μₖ) | Magnetic moment/layer (μₖ) | Electrons/primitive cell |
|-----|------|---------------------|-----------------------|-----------------|----------------------|--------------------------|--------------------------|
| 1   | La   | 27.9434             | 27.9435               | 55.8870         | -0.0001              | -0.0203                  | 197.4782                 |
| 2   | Ni₁  | 14.2462             | 14.2562               | 28.5026         | -0.0101              | 0.0435                   | 1st layer                |
| 3   | Ni₁  | 14.2468             | 14.2568               | 28.5036         | -0.0100              | 0.0282                   | 1st primitive cell       |
| 4   | Ni₂  | 14.0861             | 14.0926               | 28.1787         | -0.0065              | 0.0567                   | 2nd layer                |
| 5   | Ni₂  | 14.0862             | 14.0929               | 28.1792         | -0.0067              | 0.0282                   | 2nd primitive cell       |
| 6   | Ni₂  | 14.1419             | 14.0853               | 28.2272         | 0.0567               | 0.0282                   | 3rd layer                |
| 7   | La   | 27.8714             | 27.8750               | 55.7464         | -0.0037              | 0.0282                   | 197.4116                 |
| 8   | Ni₁  | 14.0054             | 13.9896               | 27.9951         | 0.0158               | 0.3035                   | 3rd primitive cell       |
| 9   | Ni₁  | 14.0052             | 13.9891               | 27.9943         | 0.0161               | 0.2482                   | 4th layer                |
| 10  | Ni₂  | 14.1051             | 14.0188               | 28.1238         | 0.0863               | 0.2482                   | 4th primitive cell       |
| 11  | Ni₂  | 14.1063             | 14.0187               | 28.1250         | 0.0875               | 0.2482                   | 5th layer                |
| 12  | Ni₂  | 14.7782             | 14.6486               | 29.4268         | 0.1297               | 0.2482                   | 5th primitive cell       |
| 13  | La   | 27.9454             | 27.9541               | 55.8994         | -0.0087              | 0.2482                   | 6th layer                |
| 14  | Ni₁  | 13.9326             | 13.8022               | 27.7348         | 0.1303               | 0.2482                   | 6th primitive cell       |
| 15  | Ni₁  | 13.9307             | 13.8041               | 27.7348         | 0.1266               | 0.3968                   | 7th layer                |
| 16  | Ni₂  | 14.1319             | 14.1322               | 28.2640         | -0.0003              | 0.3968                   | 7th primitive cell       |
| 17  | Ni₂  | 14.1328             | 14.1329               | 28.2657         | -0.0001              | 0.3968                   | 8th layer                |
| 18  | Ni₂  | 14.3043             | 13.9071               | 28.2115         | 0.3972               | 0.3968                   | 8th primitive cell       |

3.5 Magnetic property

The Mulliken population analyses show 1.00 μₖ spin magnetic moment per cluster (LaNi₅)₃, almost all comes from Ni atoms. The spin magnetic moments of all layers are parallel except for the first layer. Different primitive cells have different spin magnetic moments. Closer to surface the primitive cell is, smaller the spin magnetic moment is. For the first primitive cell, its two layers have small opposite spin magnetic moments, and the spin magnetic moment of La atom is almost zero. This
primitive cell can be considered as paramagnet because of very small spin magnetic moment of 0.0232 \( \mu_B \).

The experimental data show that LaNi\(_5\) is a Pauli paramagnet [31, 32]. However, all previous calculations show LaNi\(_5\) as a weak ferromagnet: a primitive cell has spin magnetic moment of 1 \( \mu_B \) (self-consistent cluster-embedding calculation [23]), 1.33 \( \mu_B \) (band structure calculation [12]), 0.65 \( \mu_B \) (band structure calculation [7]), and 0.602 \( \mu_B \) (band structure calculation [13]), all conflict with the experimental data. The reason is not clear. Our results show that the surface of LaNi\(_5\) can be considered as paramagnet, may be an elucidation.

Previous calculations show that the hydride LaNi\(_5\)H\(_7\) is not a magnet. So like other properties, the magnetic property of the surface of LaNi\(_5\) is also similar to that of hydride LaNi\(_5\)H\(_7\).

3.6 Ionization potential and electron affinity

If the \( V_{xc}(r) \) in the equation (4) is considered to be correct, according to Slater and Janak [33-35], the absolute value of an eigenvalue is equal to the amount of energy required to remove an electron from the orbital, with the error being of the second order in the derivative of the total energy. The transition-state method [33-34] will reduce the error to the third order. Eigenvalue is usually lower than true ionization potential. In the SCCE calculation, because the surrounding charge density \( \rho_s(r) \) is fixed and the electron rearrangement in embedded-cluster (LaNi\(_5\)) is constrained by \( \rho_s(r) \), the ionization potential obtained by transition-state method is higher than the true value (the limitation of rearrangement raises the energy)[15]. We take the true ionization potential as the average of eigenvalue and the result of transition-state calculation.

The result of transition-state method gives about 0.9 eV of ionization potential, and about 1.0 eV of electron affinity for the surface of LaNi\(_5\). Some transition energies from occupied states to the lowest unoccupied state are calculated using the transition-state method. Compared with the eigenvalues, the obtained transition energies simply moved a small value as a whole. The relative distribution of transition energies is similar to that of eigenvalues, and has no essential effect on the density of states.

4. Summary

The spin-polarized, all-electron, \textit{ab initio} calculations have been performed for the electronic structure of the surface of crystal LaNi\(_5\) using the self-consistent cluster-embedding (SCCE) method. The geometrical surface structure of crystal LaNi\(_5\) and its electronic structure having the lowest ground-state energy are obtained, with the full relaxation of atomic positions along the direction perpendicular to the surface. On the surface of crystal LaNi\(_5\), the La atom protruded, and the Ni atoms caved in, so the surface becomes uneven which increases the contacting area. The effective volume of the surface layer rises by 9%. Both characteristics are in favor of the absorption of hydrogen. The Fermi energy of the LaNi\(_5\) surface is -0.01746 ev, which is unusually high, and is about 5.1 eV higher than that of bulk LaNi\(_5\). The Fermi level falls in a rapidly decreasing potion of the Ni 3d bands which are not fully filled. This shows a metallic ground state. The DOS of Fermi level is large, and is mainly contributed by Ni 3d electrons. The DOS of valence electrons of the surface of LaNi\(_5\) is different from that of bulk LaNi\(_5\), but similar to that of hydride LaNi\(_5\)H\(_7\). There is a charge transfer of 1.15 electrons from atom La to atom Ni in the first and second layers of the surface. The two layers have small opposite spin magnetic moments, so the spin magnetic moment of the first primitive cell is only 0.0232 \( \mu_B \), which show the paramagnet. Farther from the surface the primitive cell is, larger the spin magnetic moment is. For the surface of LaNi\(_5\), the ionization potential is about 0.9 eV, and the electron affinity is about 1.0 eV.

Table V shows the properties of the surface of LaNi\(_5\) and that of hydride LaNi\(_5\)H\(_7\) [23]. All calculated results show that although the properties of the surface of LaNi\(_5\) are significantly different
from that of body LaNi$_5$, they are very similar to that of hydride LaNi$_5$H$_7$, so the structure of the surface of LaNi$_5$ is in favor of the absorption of hydrogen.

**Table V.** Calculated results of LaNi$_5$ surface and hydride LaNi$_5$H$_7$

|                  | Spin magnetic moment ($\mu_B$) | Volume            | DOS of electron | Fermi energy (eV) | Ionization potential (eV) | Charge transfer |
|------------------|-------------------------------|-------------------|-----------------|-------------------|--------------------------|----------------|
| LaNi$_5$ surface | 0.023                         | Larger than LaNi$_5$ about 9% | Similar to LaNi$_5$H$_7$ | -0.01746 | $\approx$ 0.9 | 1.15 e La $\rightarrow$ Ni |
| Uppermost two layers |                  |                   |                 |                   |                          |                |
| Hydride LaNi$_5$H$_7$ | 0                              | Larger than LaNi$_5$ about 8% | Similar to LaNi$_5$ surface | +0.047  | $\approx$ 1.0 | 1.16 e La $\rightarrow$ H |

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