# The influence of hydrogen adsorption on magnetic properties of Ni/Cu(001) surface *)

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Ni/Cu(001) is known as a unique system showing the spin-reorientation transition from an in-plane to out-of-plane magnetization direction when the Ni-overlayer thickness is increased. We investigate different relaxed multilayer structures with a hydrogen adlayer using the full-potential linearized augmented plane-wave method. The relaxed geometries, determined by total energy and atomic force calculations, show that H-monolayer strongly influences the interlayer distance between the Ni-surface and sub-surface layers yielding the outward relaxation of Ni-layer at H/Ni interface. Furthermore, large decrease of local magnetic moments at the top surface area is found for the surface covered by H. The magneto-crystalline anisotropy energies are calculated for fully relaxed H/Ni-films. The spin-reorientation transition critical thickness of 4 ML is found in good quantitative agreement with the experiment.

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## 1 Introduction

Ultrathin ferromagnetic films grown on nonmagnetic substrate show peculiar magnetic behavior [1]. One of the unique phenomena which is observed in the ultrathin Ni films on Cu(001) substrate is the spin-direction-reorientation transition (SRT) from an in-plane to out-of-plane magnetization direction when the Ni-overlayer thickness is increased [2–4]. It is very important for the spintronic magnetic device applications and its microscopic understanding attracted recently both experimental and theoretical [5, 6] interest. The gas adsorption on magnetic film provides the way to monitor the surface magnetic properties resulting in strong influence on the SRT critical thickness $d_c$. For Ni/Cu(001) films, the hydrogen adsorption is observed to reduce $d_c$ by $\approx 4$ monolayers (ML) from its value of $\approx 11$ ML for the vacuum/Ni/Cu-films [3, 4].

The key quantity which drives the SRT in ultrathin magnetic films is the magneto-crystalline anisotropy energy (MAE). It determines the preferred film magnetization orientation by minimizing the free energy of the system. For the

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free-standing Ni/Cu(001) films, the $d_c$ is found to be determined [5, 6] by competition of the uniaxial MAE due to the tetragonal distortion of Ni-films (so-called "volume" MAE) and the surface MAE. The adsorption of gas produces non-trivial changes in geometrical structure as well as magnetic properties of Ni films [7, 8] influencing both volume and surface MAE, and results in change of the SRT critical thickness.

In recent years it has become possible to make use of *ab initio* density functional theory to predict the MAE in ultra-thin films [9]. From theoretical and computational point of view, the MAE calculations are extremely difficult due to the very high energy resolution in the range of few $\mu$eV which is required. For the H/Ni/Cu(001) films, the problem becomes even more complex due to the need of accurate account of structural relaxation. It requires to use the most accurate total energy full-potential linearized augmented plane wave method (FP-LAPW) [7] in order to take simultaneously into account the equilibrium geometrical and magnetic structures.

## 2 Method and results of calculations

The experiments show that $H_2$ adsorbs dissociatively on Ni(001) surface in fourfold hollow sites [10]. Therefore, as a structural model for *ab-initio* calculations we use free-standing Ni-films (H/Ni$_d$/H, $d$ = 1–11) and Ni-films on Cu-substrate (H/Ni$_d$/Cu$_7$/Ni$_d$/H, $d$ = 1–6) with ordered $p(1\times1)$H adsorbate overlayer as shown in Fig. 1.

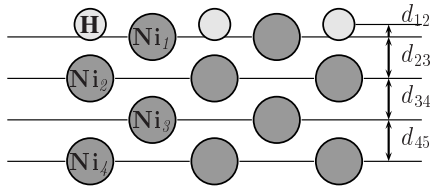


Fig. 1. Surface layers of H/Ni$_n$/Cu(100) system.

The in-plane experimental lattice constant of Cu $a_{\mathrm{Cu}} = 3.615$ Å [11] is used and remains unchanged in the calculations. All interlayer spacings $d_{ij}$ (see Fig. 1) are relaxed to the equilibrium values. In order to determine the equilibrium slab geometry we employ the FP-LAPW method in FLAIR implementation (unpublished improved and rewritten version of the original FLAPW codes [7]). The scalar-relativistic atomic-force technique is employed for the total energy minimization. Here, the Perdew and Wang [12] approximation for exchange-correlation potential is used with the plane wave energy cutoff $E_{\mathrm{cut}}$ of 13 Ry, and the 28 special $k$-points in the 1/8th irreducible part of 2-dimensional Brillouin zone (2D BZ) are used for the BZ integrations. The convergence better than $1 \times 10^{-6}$ e/(a.u.)$^3$ is achieved

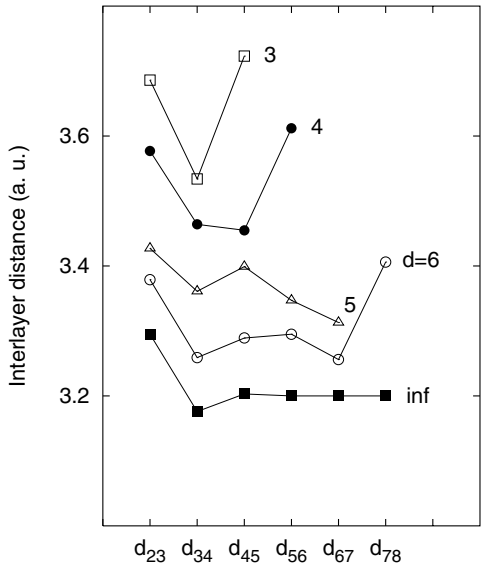


Fig. 2. Relaxation of interlayer distances for $H/Ni_n/Cu(001)$ for $n = 3$–6 and for $n = \infty$. For clarity, the data sets are shifted by 0.1 a.u. Lines serve as guide to the eye.

for charge/spin densities, and better than 0.2 mRy/a.u. for the atomic force acting on individual atom.

The relaxed interlayer distances for different free-standing films ($H/Ni_n/Cu_7/Ni_n/H$, $n = 3$–6) are shown in Fig. 2 and compared with the relaxation of tetragonal $p(1\times1)$H Ni(100) surface. Clearly, we can distinguish the outward relaxation of top Ni layer as well as the strong influence of Ni/Cu interface on inter-layer distances in the close vicinity of the interface. The relaxation of Ni/Cu subsurface is different only for 5 ML Ni. The deeper interlayer distances (thicker film) approach the bulk value.

The equilibrium values of inter-layer distances for two model systems: eleven-layer tetragonal Ni-film covered with H and seven-layer Cu-film with overlayer of six Ni layers covered with H are shown in Table 1. Both interfaces (H/Ni, Ni/Cu) strongly influence the interlayer distances in the overlayer slab. Note that the calcu-

Table 1. Interlayer distances in a.u..

| | $HNi_{11}H$ | $HNi_6Cu_7Ni_6H$ |
|---|---|---|
| $d_{12}$ | 0.63 | 0.60 |
| $d_{23}$ | 3.30 | 3.28 |
| $d_{34}$ | 3.18 | 3.16 |
| $d_{45}$ | 3.20 | 3.19 |

lated bond length $d_{\mathrm{H–Ni}}$ of 3.48 a.u. is slightly shorter than the bond length for the bulk nickel hydride (3.52 a.u.). The outward relaxation of top Ni-layer is found, the H-ML influences strongly only the interlayer distance between the Ni-surface and Ni-subsurface layer. Below the interface, the interlayer distances oscillate around the bulk value for strained tetragonal Ni bulk ($d_\perp = 3.20$ a.u.). The electron screening in the metal is responsible for fast damping of these oscillations.

Table 2. Magnetic moments in $\mu_{\mathbf{B}}$.

| | $HNi_{11}H$ | $HNi_6Cu_7Ni_6H$ |
|---|---|---|
| $Ni_1$ | 0.238 | 0.239 |
| $Ni_2$ | 0.593 | 0.588 |
| $Ni_3$ | 0.640 | 0.636 |
| $Ni_4$ | 0.633 | 0.633 |

The layer-resolved spin magnetic moments $M_{\mathrm{s}}$ for these systems are shown in Table 2. These values correspond to the magnetic moments in the Ni "muffin-tin" spheres ($R_{\mathrm{MT}} = 2.2$ a.u.). It is seen that there is strong reduction of the spin magnetization for the top Ni-layer due to the interaction with the H-adlayer. The strong hybridization of the H $s$ state with the filled majority Ni $d$ band changes the band structure and the surface density of states (SDOS) leading to the decrease of spin-majority and increase of the spin-minority SDOS. Away from the interface, the spin magnetic moments are slowly converging to their bulk values. The layer-resolved magnetic moments for different $H/Ni_n/Cu_7$-films ($n$ = 3–6) on Cu-substrate are shown in Fig. 3. We note that for very thin $H/Ni_n/Cu_7$-films with $n = 1, 2$ the Ni-local moments disappear and the system becomes non-magnetic. With the increase of the Ni-film thickness, the local Ni $M_{\mathrm{s}}$ of 0.24 $\mu_{\mathrm{B}}$ is formed at the Ni-interface and then increases away from the H/Ni interface. When approaching the Ni/Cu interface, the Ni-atom magnetic moments start to decrease again and become $\approx$ 0.45 $\mu_{\mathrm{B}}$ for Ni/Cu interface layer (depending of the Ni-film thickness).

The anisotropic energy density of a tetragonal ferromagnetic film is written as [13]:

$$\frac{E}{V} = -K_1^{\mathrm{v}} m_z^2 - K_2^{\mathrm{v}} m_z^4 - K_3^{\mathrm{v}} m_x^2 m_y^2 - \frac{2}{d}(K_1^{\mathrm{s}} m_z^2 + K_2^{\mathrm{s}} m_z^4 + K_3^{\mathrm{s}} m_x^2 m_y^2)\,,$$

where $K^{\mathrm{v}}$ terms are 2nd and 4th order volume-type anisotropy constants, $K^{\mathrm{s}}$ terms are surface/interface-type 2nd and 4th order anisotropy constants, $m_{x,y,z}$ are magnetization cosines with respect to the crystal axes, and $d$ is the thickness of magnetic film. We assume that the 4th order terms in Eq. (1) are significantly smaller than 2nd-order uniaxial anisotropy constant $K_1^{\mathrm{v}}$, and neglect them. The MAE then can be characterized by the difference in the total energy when magnetization is oriented along [100] (in-plane, $\parallel$) and [001] (out-of-plane, $\perp$) axes (MAE = $E[100] - E[001]$).

We use the relativistic version [14] of the FP-LAPW method to solve self-consistently the Kohn–Sham–Dirac equations with spin-orbit coupling included to

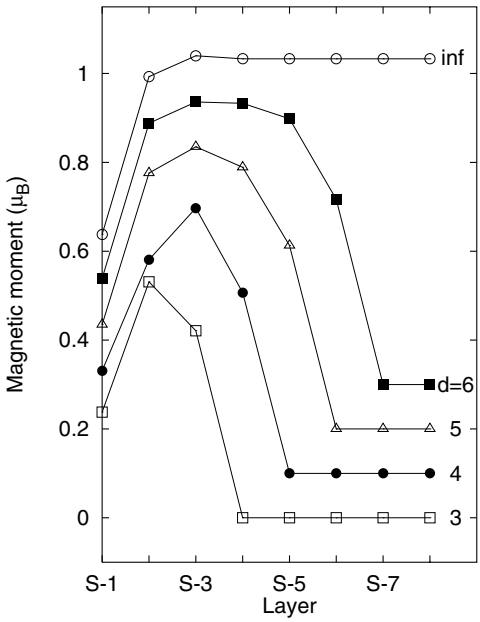


Fig. 3. Layer-resolved magnetic moments of H/Ni$_n$/Cu(001) for $n$ =3–6 and for $n = \infty$. For clarity, the data sets are shifted by $0.1(n-1)\mu_B$. Layers are labeled S, S-1, ... , starting with the surface layer S. Lines serve as guide to the eye.

obtain the ground state charge and spin densities for the magnetization directed along [001]-axis. The fully optimized interlayer distances as discussed above are used for free-standing Ni-films and Ni-films on Cu-substrate with H-adlayer. The MAE is obtained by applying the force theorem to the spin-axis rotation [15]: from the self-consistent ground state charge and spin density obtained for the [001] spin axis, the calculation of the band structure for [100] spin axis orientation is performed, and difference of the single particle eigenvalue sums is then taken to be the MAE. For the MAE calculations the $k$-points mesh equivalent to 6400 $k$-points in the full 2D BZ is used guaranteeing the MAE convergence better than 10 $\mu$eV.

The MAE as a function of the Ni-film thickness for the H/Ni$_d$/H films with $d$ = 3, 5, 7, 9 ML is shown in Fig. 4. For $d = 3$ we found small and negative MAE (–0.02 meV) keeping the Ni-film magnetization in [100] plane. It becomes positive for $d = 5$ (0.432 meV) resulting in the out-of-plane magnetization switching. The MAE is positive with further increase of $d$ and shows pronounced oscillations. The linear interpolation MAE $= dK_V + 2K_I$ yields the estimates for the "volume" $K_V = 0.106$ meV/atom and "interface" $K_I = -0.127$ meV/atom MAE contributions. The calculated "volume" MAE agrees well with $K_V = 0.0835$ meV/atom calculated for free-standing unrelaxed Ni-films without H-adlayer [6] and extrapolated to $T = 0$ K experimental value of 0.072 meV/atom [16]. The H/Ni "interface" $K_I$ is calculated to be substantially smaller than vacuum/Ni "surface"

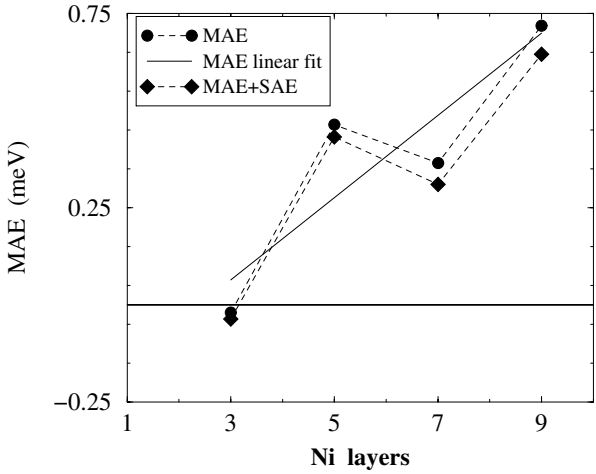


Fig. 4. The MAE (circles) and MAE+SAE (diamonds) for the fully relaxed H/Ni$_d$/H films as a function of the film thickness $d$ (in ML).

$K_S = -0.447$ meV/atom [6] for free-standing Ni-films and extrapolated to $T = 0$ K experimental value of $-0.7$ meV/atom [3]. We note that for the very thin Ni-films considered here, validity of the linear fit for the MAE and its separation into "volume" and "surface" contributions is *not well justified* due to the strong dependence of the Ni-film magnetic properties on the thickness of the film, especially in the presence of the H-adlayer.

In order to estimate the critical thickness $d_c$ for SRT, we take into account the shape anisotropy energy (SAE) due to the magnetic dipole interaction, which provides additional in-plane anisotropy. This anisotropy is estimated using the relation SAE $= -2\pi M^2$ to the spin magnetization density $M$ (in CGS units). It yields for the SAE the values of $-0.016$ meV, $-0.032$ meV, $-0.055$ meV, and $-0.073$ meV corresponding respectively to the H/Ni$_d$/H films with $d = 3, 5, 7, 9$ layers (which are consistent with experimentally derived SAE/Ni atom of $-0.0075$ meV [3]). This additional negative SAE slightly shifts the MAE in Fig. 4 downwards yielding $d_c = 4$.

Indeed, the H/Ni$_d$/H model is a way too simple to describe quantitatively the SRT in Ni/Cu layers with H-adlayer. As it was already mentioned in Refs. [3, 5], the Ni/Cu interface can play an important role. In order to evaluate the influence of Ni/Cu interface on SRT, we perform the calculations for H/Ni$_d$/Cu$_5$/Ni$_d$/H ($d = 3$, 4) films, where the 5 Cu layers play a role of the substrate. The use of 5 ML of Cu layers instead of 7 ML allows to reduce computational effort without producing any significant impact on the magnetic properties and the MAE of H/Ni/Cu-films, since they originate from Ni magnetic film and not from the Cu non-magnetic substrate, and the relaxed Cu-interlayer distance below the Ni-interface is found to be very close to its bulk value of 3.427 a.u. For $d = 3$ we found negative MAE of $-0.192$ meV and SAE of $-0.036$ meV keeping the Ni-film magnetization in [100]

plane. Already for $d = 4$ the MAE becomes positive, 0.543 meV, while the SAE is small and negative, $-0.052$ meV. Again as in the case of free-standing $H/Ni_d/H$ films we get the SRT critical thickness $d_c = 4$.

To summarize, we found that hydrogen adsorption for the Ni films on Cu substrate yields the reduction of the SRT critical thickness. The calculated $d_c = 4$ for both $H/Ni_d/H$ and $H/Ni_d/Cu_5/Ni_d/H$ films agrees well with the experimental $d_c$ of 7 ML [3]. We show that the MAE has strong and oscillatory dependence on the Ni-film thickness which deviates substantially from the linear fit. We attribute the decrease of the $d_c$ due to the H adsorption to strong reduction of the magnitude for the Ni "surface" MAE contribution. In turn, this is caused by strong decrease of the exchange splitting at the H/Ni interface due to the strong hybridization of the H s-state with the Ni-bands.

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