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 spin-reorientation transition critical thickness of 4 ML is found in good quantitative agreement with the experiment.

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I. INTRODUCTION

Ultrathin ferromagnetic films grown on nonmagnetic substrate show peculiar magnetic behavior. 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. It is very important for the spintronic magnetic device applications and its microscopic understanding attracted recently both experimental and theoretical 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. For Ni/Cu(001) films, the hydrogen adsorption is observed to reduce the critical thickness by ≈ 4 monolayers (ML) from its value of ≈ 11 ML for the vacuum/Ni/Cu-films.

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 free-standing Ni/Cu(001) films, the d_{c} is found to be determined 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 a gas produces non-trivial changes in geometrical structure as well as magnetic properties of Ni films 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. 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 µeV 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 us to use the most accurate total energy full-potential linearized augmented plane wave method (FP-LAPW) in order to account simultaneously on equilibrium geometrical and magnetic structures.

II. METHOD AND RESULTS OF CALCULATIONS

The experiments show that H_{2} adsorbs dissociatively on Ni(001) surface in fourfold hollow sites. Therefore, as a structural model for ab-initio calculations we use free-standing Ni-films (H/Ni_{d}/Cu, d = 1–11) and Ni-films on Cu-substrate (H/Ni_{d}/Cu_{7}/Ni_{d}/H, d = 1–6) with ordered p(1 × 1)H adsorbate overlayer as shown in Fig. 1.

![Figure 1: Surface layers of H/Ni_{d}/Cu(100) system.](image)

The in-plane experimental lattice constant of Cu a_{Cu} = 3.615 Å is used which 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...
Figure 2: Relaxation of interlayer distances for H/Niₙ/Cu(001) for n = 3−6 and for n = ∞. For clarity, the data sets are shifted by 0.1 a.u. Lines serve as guide to the eye.

codes [2]. 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 $E_{\text{cut}}$ 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 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/Niₙ/Cu₇/Niₙ/H, n = 3−6) are shown in Fig. 2 and compared with the relaxation of tetragonal p(1×1)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.

Table I: Interlayer distances in a.u.

|        | HNi₁₁H | HNi₆Cu₇Ni₆H |
|--------|--------|-------------|
| d_{23} | 0.63   | 0.60        |
| d_{34} | 3.30   | 3.28        |
| d_{45} | 3.18   | 3.16        |
| d_{46} | 3.20   | 3.19        |

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) influence strongly the interlayer distances in the overlayer slab. Note, that the calculated bond length $d_{H-Ni}$ 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 II: Magnetic moments in $\mu_B$

|        | HNi₁₁H | HNi₆Cu₇Ni₆H |
|--------|--------|-------------|
| Ni₁    | 0.238  | 0.239       |
| Ni₂    | 0.593  | 0.588       |
| Ni₃    | 0.640  | 0.636       |
| Ni₄    | 0.633  | 0.633       |

The layer-resolved spin magnetic moments $M_s$ for these systems are shown in Table 2. These values correspond to the magnetic moments in the Ni “muffin-tin” spheres ($R_{MT} = 2.2$ 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/Niₙ/Cu₇-films (n = 3−6) on Cu-substrate are shown in Fig. 3. We note that for very thin H/Niₙ/Cu₇-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 $M_s$ of 0.24 $\mu_B$ 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 $\approx 0.45 \mu_B$ for Ni/Cu interface layer (depending of the Ni-film thickness).

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

$$E/V = -K'_1 m_x^2 - K'_2 m_y^2 - K'_3 m_z^2 m_y^2 - \frac{2}{d}(K'_s m_x^2 + K'_s m_y^2 + K'_s m_z^2 m_y^2),$$

where, $K'_s$ terms are 2nd and 4th-order volume-type anisotropy constants, $K'_s$ 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 a thickness of magnetic film. We assume that the 4th-order terms in Eq. (1) are significantly smaller than 2nd-order uniaxial anisotropy constant $K_1$, and neglect them. The MAE then can be characterized with the difference in the total energy when magnetization is oriented along [100] (in-plane, $\parallel$) and [001] (out-of-plane, $\perp$) axes ($\text{MAE} = E[100] - E[001]$).

We use the relativistic version \textsuperscript{14} of the FP-LAPW method to solve self-consistently the Kohn-Sham-Dirac equations with spin-orbit coupling included to 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 \textsuperscript{15}: from the self-consistent ground state charge and spin density obtained for the [001] spin axis, a 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 the $d = 3$ we found small and negative MAE (-0.02 meV) keeping the Ni-film magnetization in [100] plane. It becomes positive for the $d = 5$ (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 $\text{MAE} = d \cdot K_V + 2 \cdot K_I$ 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 \textsuperscript{2} and extrapolated to $T=0$ K experimental value of 0.072 meV/atom of Ref. \textsuperscript{16}. The H/Ni “interface” $K_I$ is calculated to be substantially smaller than vacuum/Ni “surface” $K_S = -0.447$ meV/atom \textsuperscript{4} for free-standing Ni-films and extrapolated to $T=0$ K experimental value of -0.7 meV/atom \textsuperscript{5}. 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 $d_c$ critical thickness 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 $\text{SAE} = -2\pi M^2$ 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 \textsuperscript{5}). This additional negative SAE slightly shifts the MAE in Fig. 4 downwards yielding the $d_c = 4$.

Indeed, the H/Ni$_d$/H model is a way too simple to describe quantitatively the SRT in in Ni/Cu layers with H-adlayer. As it was already mentioned in Ref. \textsuperscript{2} 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 are originated from Ni magnetic film and not 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 the \( d = 3 \) 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.\(^2\) 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 originate from 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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