Investigation of the magnetic and adsorption properties of a Fe$_x$Ni$_{1-x}$ monolayer film on nonmagnetic metal substrates

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Abstract. The adsorption energy of Fe$_x$Ni$_{1-x}$ monolayer film on the W, Ag and Au nonmagnetic substrates at low Miller index orientations of its surface face is calculated by the variational method of the spin-density functional (SDFT), depending on the concentration of the alloy components and the coating parameter. The temperature effects of the mixing of adsorbate and substrate atoms and the inhomogeneous distribution of magnetization are taken into account. Comparison of the values of the adsorption energy as a function of the concentration of the alloy components calculated at $\theta = 1$ T $= 0K$ within the framework of the variational and first-principle (VASP) approaches is presented.

1. Introduction
This article is devoted to a theoretical study the effects of mixing the adsorbate atoms and substrate under temperature influence on the adsorption properties of ultrathin films of transition metals [1-2] using the variational approach of the spin density functional method. There are important practical applications of films not only of pure metals [3], but also of their alloys, in particular permalloy (an alloy of Fe and Ni), which is widely used in radio-computer technology. Thin-film systems based on magnetically soft permalloy films are widely used in magnetic and biological sensors based on the effect of magnetic impedance [4]. The magnetic properties and resistivity of the alloy strongly depend on its composition. The easy magnetization of this alloy in weak fields is due to the practical absence of magnetic anisotropy and magnetostriction in it. There are two main groups of permalloys: low nickel (40-50% Ni; the typical representative is permenorm) and high nickel (70-83% Ni). The magnetic permeability of high-nickel permalloys is several times higher than that of low-nickel permeability and much better than the permeability of electrical steels. Classic permalloy is the alloy, the concentration of nickel in which is about 75%. Such classic permalloy possesses very high magnetic properties. The study of the properties of such alloys is devoted both to experimental [5] and calculated works [6,7]. The experimental studies [8,9] of the formation of submonolayer pure metal films and the distribution of metal atoms on the surface of the substrate revealed the effect of ejection of metal atoms by the substrate atoms on the surface. It was shown that formation of solid film or “islands” considerably depend on the properties of metal substrate and orientation of the substrate surface face.

In present work, SDFT calculations of Fe$_x$Ni$_{1-x}$ monolayer film on the W, Ag and Au nonmagnetic substrates at low Miller index orientations of its surface face are carried out. We study the dependence of adsorption characteristics on the coverage parameter $\theta$ and the iron content concentration $x$ in the ferromagnetic film for the above nanostructures.
2. Model, methods, and results

We applied a method [1-2], based on the use of the spin density functional theory with an allowance of temperature effects for calculating the energy characteristics of activated ferromagnetic films adsorption, for the two-component alloys with using a binary systems concept. The following characteristics of the ionic structure, such as the cutting radius \( r_c \) of the Ashcroft pseudopotential, valence \( Z \), and adsorbate interplanar spacing \( d^a \), have obtain the dependence on the concentration of components in the alloy film:

\[
\begin{align*}
\frac{xZ_{Fe}(r_c^{Fe})^3 + (1-x)Z_{Ni}(r_c^{Ni})^3}{xZ_{Fe} + (1-x)Z_{Ni}} &= Z = xZ_{Fe} + (1-x)Z_{Ni} \\
d^a &= xd_{Fe} + (1-x)d_{Ni}
\end{align*}
\]

We consider a model of semi-infinite substrate nonmagnetic metal, which is bounded by an infinite flat surface, and adsorbate film with a thickness \( h \). The surface of the substrate is reconstructed as a consequence of mixing adsorbed atoms with substrate atoms, which are typical for activated adsorption. Therefore, a surficial region of the substrate affected by reconstruction is marked out as a separat e layer with thickness \( l \):

\[
\begin{align*}
h &= pd^a + (1-p)d^s \\
l &= p'd^a + (1-p')d^s
\end{align*}
\]

where \( d^s \) is a substrate interplanar spacing and parameters \( p \) and \( p' \) which characterize the relative part of magnetic ions of adsorbate with respect to ions of the substrate in the region of film and in the surficial region of the substrate, accordingly.

We are taking into consideration the inhomogeneous spatial distribution of magnetization in the surface region as a consequence of mixing adsorbed atoms with substrate atoms [2] with parameter \( p \) which depend on the parameter \( \theta \), which determines the degree of coverage of the surface by adatoms. To describe the temperature dependence of the relative magnetization \( m(\theta, T) \), we use the results of renormalization-group finite-size description of the XY type systems.

\[
m(x, \theta, T) = \left[ \frac{T_c(x, \theta) - T}{T_c(x, \theta)} \right]^{0.23}
\]

The expression used for the Curie temperature is:

\[
T_c(x, \theta) = \theta[xT_c^{Fe}(\theta = 1) + (1-x)T_c^{Ni}(\theta = 1)],
\]

where the critical temperature of monolayer films are \( T_c^{Fe}(\theta = 1) = 521 \)K and \( T_c^{Ni}(\theta = 1) = 209 \)K.

We determine the adsorption energy as the work required to remove the adsorbed particle from the surface of the substrate per adsorbed atom:

\[
E_{ads}(T, \theta) = (\sigma_{exp} - \sigma_{min}(T, \theta)) / n_s,
\]

where \( \sigma_{exp} \) is experimental surface energy, \( n_s(p, \theta) \) is the surface atomic concentration in the film. In terms of the density functional theory, the interfacial energy \( \sigma \) is determined by minimizing the parameters \( p \) and \( p' \). The results of the calculation of parameter \( p \) and adsorption energy \( E_{ads} \) monolayer Fe\(_{0.75}\)Ni\(_{0.25}\) film for the close-packed surface of the W, Ag and Au nonmagnetic substrates are presented in Fig. 1-2. The results of calculations show that the adsorption energy decreases with increasing both the parameter \( \theta \) and \( T \). The change in the behavior of the curves, soft for \( E_{ads}(\theta) \) and sharp for \( p(\theta) \), is due to the transition from the paramagnetic to the ferromagnetic state.
Figure 1. Dependence of the adsorption energy $E_{\text{ads}}$ and structural parameter $p$ on the coverage $\theta$ at temperature $T=300K$ for the close-packed surface of different substrates.

The analysis of $p(\theta)$ in figure 1 shows that for substrates with lower surface energy than for the adsorbate material, as in the case Ag(111), the sandwich-like structure is realized with $p(\theta)\approx0$. Otherwise, for W(110) the mixing effects are feebly marked, and we see a clear tendency to the formation of monolayer film with $p(\theta)\approx1$ on the substrate surface. In the intermediate case, for Au(111) system the ferromagnetic ordering leads to a decrease of the mixing and to the formation of the monolayer film for $\theta\geq0.8$. The temperature dependence of $p$ doesn't appear until $T>T_c$, as presented in figure 2 for W and Au substrates.

Figure 2. Dependence of the adsorption energy $E_{\text{ads}}$ and structural parameter $p$ on the temperature at $x=0.75$ and $\theta=1$ for the close-packed surface of different substrates.

Next, we calculated the adsorption energy and parameter $p$, taking into account the orientation of the substrate surface face depending on the film alloy components concentration. Miller indices determine the lattice parameters and affect the electron-ion and ion-ion components of the interfacial interaction energy. The results of these calculations are presented in figures 3-4.

For W and Au, the most mixing is observed for the least close-packed face. The adsorption energy for a close-packed face is minimal for all presented systems.

The adsorption energy increases with increasing iron concentration more strongly for W(111) and for more close-packed faces of the Ag and Au substrates. The adsorption energy of the alloy atoms on the substrate W is greater than that on the Ag and Au substrate for the corresponding faces.
Figure 3. Dependences of the adsorption energy $E_{\text{ads}}$ and structural parameter $p$ on the film alloy components concentration at temperature $T=300K$ and coverage $\theta=1$ for different Ag and Au substrate surface plane orientations.

It is important that due to the fact that Fe has bcc, but Ni and Ag have the same fcc bulk structures, the dependence $p(x)$ for the Ag substrate (figure 3) shows that the difference in the crystal structure leads to an increase in mixing and the formation of a sandwich similar structure at $x \geq 0.5$. While for W and Au (figure 4), the effect of the difference in surface energies with nickel is stronger than the effect of the difference in crystal structures.

Figure 4. Dependences of the adsorption energy $E_{\text{ads}}$ and structural parameter $p$ on the film alloy components concentration at temperature $T=300K$ and coverage $\theta=1$ for different W and Au substrate surface plane orientations.

To compare the calculation results by variational and first-principle approaches of the DFT we made calculations with the use of VASP (Vienna Ab-InitioSimulation Package) software package [10] by means of the Projector Augmented Wave (PAW) method with PBE [11] version of generalized gradient approximation (GGA) to describe the exchange-correlation interactions. The monolayers of Fe$_x$Ni$_{1-x}$ alloy are placed pseudomorphically on each side of the Ag and Au slab to retain the inversion symmetry. The magnetic moment of atoms is directed collinearly along the axis perpendicular to the surface. The substrate is modeled by the five-layer slab. As an example, supercell for Fe$_{0.5}$Ni$_{0.5}$/Ag(111)/Fe$_{0.5}$Ni$_{0.5}$ system is given at figure 5. We used values of the plane waves cut-off energy $E_{\text{max}} = 350$ eV, Monkhorst Pack grid size 12x12x1 and 5Å thickness vacuum gap.
To determine the adsorption energy, it is necessary to calculate the difference between the total energy of the system $E$ and the energy of its components:

$$E_{\text{ads}} = 0.5[E - E_{\text{slub}} - 8xE_{\text{Fe Bulk}} - 8(1-x)E_{\text{Ni Bulk}}],$$

where $E_{\text{slub}}$ is the total energy of 5-ML substrate slab; $E_{\text{Fe Bulk}} = -8,2423\text{eV}$- iron 1 atom energy in bcc bulk structure; $E_{\text{Ni Bulk}} = -5,4728\text{eV}$- nickel 1 atom energy in fcc bulk structure.

Comparison of the values of the adsorption energy as a function of the concentration of the alloy components calculated at $\theta = 1$ $T = 0K$ within the framework of the variational and first-principle (VASP) approaches are presented in figure 6.

A good qualitative agreement of the results is observed. The averaging of the ion charge density over planes parallel to the surface, carried out by us in the variational method, can explain the monotonic behavior of the $E_{\text{ads}}$ dependency, in contrast to the VASP’s curves. One of the reasons of the quantitative difference is the small thickness of the substrate in VASP calculations, unlike the semi-infinite substrate in the variational approach.
3. Conclusions
In this work, we calculated the adsorption energies and values of the structural parameter $p$ for the Fe$_x$Ni$_{1-x}$ monolayer film on the surface with low Miller index of nonmagnetic substrates Ag, Au and W for different alloy components concentration and parameters coverage of the surface by adatoms at temperature from $T=0K$ to $T_c(\theta,x)$. The results of calculations show that the adsorption energy decreases with increasing parameter $\theta$ and temperature. A monolayer film without mixing is formed on Au and W substrate mainly for large values of the coating parameter and the concentration of iron. The adsorption energy for a close-packed face is minimal for all presented systems and increases with increasing iron concentration more strongly for W(111) and for more close-packed faces of the Ag and Au substrates. The adsorption energy of the alloy atoms on the substrate W is greater than that on the Ag and Au substrate for the corresponding faces.

This work was supported by RFBR according to the research projects 17-02-00279, 18-42-550003 and grant MD-6868.2018.2 of the President of Russia. Shared Facility Center Data Center of FEB RAS (Khabarovsk) is acknowledged for computational resources.

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