Magnetism at the surface of transition-metal alloys*

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We study magnetic properties of transition-metal atoms at the surface of transition-metal alloys. Using two simple models for the local environment dependence of the magnetic moment of transition-metal atoms in transition-metal alloys, we determine the magnetic moments in the first few atomic layers parallel to the surface for various alloy compositions. Results are presented for Ni in Cu-Ni alloys. Results for different surface directions are given. Segregation and short-range order are taken into account. One finds that the magnetic properties at the surface of the alloys are strongly affected by surface segregation. Furthermore, in view of our results one expects changes in the magnetic behavior of transition-metal alloys due to chemisorption. We expect that surface studies are a reasonable tool to study the dependence of magnetic moments on local atomic environment.

I. INTRODUCTION

It is well established from studying various alloys that the magnetic behavior of transition-metal atoms is strongly determined by the local atomic environment.[1-7] Therefore, one expects that the magnetic behavior of transition-metal atoms at the surface of transition-metal alloys may differ considerably from the behavior in the bulk. This difference in magnetic behavior will depend on the alloy composition, surface roughness, etc. Assuming thet the magnetic moment of an atom depends on the number of nearest- and next-nearest-neighbor magnetic atoms then upon varying the alloy concentration it is possible, for example, to find atoms in the nonmagnetic state at the surface while in the bulk they possess a local magnetic moment. Note that the opposite situation may also be possible.

It is the purpose of this paper to study in detail the variation of the local magnetic moment in the vicinity of transition-metal alloy surfaces by applying the phenomenological models for the dependence of the magnetic moments on their local atomic environment. Numerical results for the magnetic moment of Ni atoms in the surface layer and second atomic surface layer of $Cu_{1-x}Ni_x$ alloys are presented. Surface segregation is taken into account. Calculations are performed for different surface planes. The results were obtained by using the local environment model of Robbins *et al.*[3] and Jaccarino and Walker.[1]

II. LOCAL MAGNETIC MOMENTS AT THE SURFACE OF TRANSITION-METAL ALLOYS

The crystal is subdivided into atomic layers parallel to the surface. Then

$$\bar{\mu}_i(\ldots,x_{i-1},x_i,x_{i+1},\ldots)$$

denotes the average local magnetic moment in the ith layer with concentration x_i. Short-range atomic order may be taken into account by determining the number of nearest-neighbor Ni atoms in the ith layer around a Ni atom in the $Cu_{1-x}Ni_x$ alloys from $\zeta_i=(1-x_i)\alpha_1^i+x_i$. Here α_1^i is the first-shell short-range order parameter referring to the ith layer. The layer-dependent concentration x_i include surface segregation. The average magnetic moment $\bar{\mu}_i$ of the ith atomic layer is given by

$$\bar{\mu}_i=\sum_{n,m}P_{nm}^i\mu_{nm}^i \quad , \tag{2.1}$$

where μ_{nm}^i denotes the magnetic moment of a Ni atom in the ith layer when surrounded by n nearest-neighbor and m next-nearest-neighbor Ni atoms. The probability to find such an atomic environment around the considered Ni atom in the ith layer is given by P_{nm}^i. We use now the following two model for μ_{nm}^i: First we assume

$$\mu_{nm}^i=\mu_{\mathrm{Ni}}\begin{cases}1, & n\geq n_{\min} \quad ,\\ 0, & n<n_{\min} \quad ,\end{cases} \tag{2.2}$$

where μ_{Ni} is the magnetic moment in pure Ni and $n_{\min}$ is the minimum number of nearest-neighbor Ni atoms required for a Ni atom to have a local magnetic moment. This is the model proposed by Jaccarino and Walker[1] and others to determine the bulk magnetic properties of Cu-Ni and other alloys which result from Ni clusters. Thus, we obtain from Eqs. (2.1) and (2.2) the expression

$$\bar{\mu}_i = \mu_{\mathrm{Ni}} x_i \left(\sum_{n_i+n_{i+1}+n_{i-1}=n,\ n>n_{\min}} C_{\nu_i}^{n_i} C_{\nu_{i+1}}^{n_{i+1}} C_{\nu_{i-1}}^{n_{i-1}} \zeta_i^{n_i} (1-\zeta_i)^{\nu_i - n_i} \zeta_{i+1}^{n_{i+1}} (1-\zeta_{i+1})^{\nu_{i+1}-n_{i+1}} \zeta_{i-1}^{n_{i-1}} (1-\zeta_{i-1})^{\nu_{i-1}-n_{i-1}} \right) . \tag{2.3}$$

Here ν_{i-1}, ν_i, and ν_{i+1} are the number of nearest-neighbor sites in the $(i-1)$th, and $(i+1)$th layer, and n_{i-1}, n_i, and n_{i+1} are the number of Ni atoms sitting in these sites. In Table I we give the values for ν_1, ν_2, and ν_3 for an atom sitting in the first surface layer in the (100), (111), and (110) directions. In Table II we give the corresponding values for an atom in the second layer. The coefficients C_β^α are defined by $C_\beta^\alpha = \beta!/\alpha!(\beta-\alpha)!$. Neglecting concentration fluctuations, then $\mu_i = \mu_{\mathrm{Ni}} x_i$ for $\nu_{i-1}x_{i-1} + \nu_i x_i + \nu_{i+1}x_{i+1} > n_{\min}$.

Secondly, we determine $\bar{\mu}_i$ by using $\mu_{nm}^i = \mu_{nm}$ and for μ_{nm} values ($0 \leq \mu_{nm} \leq 0.6$) proposed by Robbins, Claus, and Beck[3] for calculating the magnetic properties of Ni clusters in the bulk of Cu-Ni alloys. Then one obtains

$$\bar{\mu}_i = \sum_{n,m} P_n^i P_m^i \mu_{nm} , \tag{2.4}$$

where

$$P_n^i = \left(\sum_{n_i+n_{i+1}+n_{i-1}=n} C_{\nu_i}^{n_i} C_{\nu_{i+1}}^{n_{i+1}} C_{\nu_{i-1}}^{n_{i-1}} \zeta_i^{n_i} (1-\zeta_i)^{\nu_i-n_i} \zeta_{i+1}^{n_{i+1}} (1-\zeta_{i+1})^{\nu_{i+1}-n_{i+1}} \zeta_{i-1}^{n_{i-1}} (1-\zeta_{i-1})^{\nu_{i-1}-n_{i-1}} \right) \tag{2.5}$$

and

$$P_m^i = \left(\sum_{m_i+m_{i+1}+m_{i-1}=m} C_{\lambda_i}^{m_i} C_{\lambda_{i+1}}^{m_{i+1}} C_{\lambda_{i-1}}^{m_{i-1}} x_i^{m_i} (1-x_i)^{\lambda_i-m_i} x_{i+1}^{m_{i+1}} (1-x_{i+1})^{\lambda_{i+1}-m_{i+1}} x_{i-1}^{m_{i-1}} (1-x_{i-1})^{\lambda_{i-1}-m_{i-1}} \right) . \tag{2.6}$$

ν_{i-1}, ν_i, ν_{i+1}, n_{i-1}, n_i, and n_i have the same meaning as in Eq. (2.3) and λ_{i-1}, λ_i, λ_{i+1}, m_{i-1}, m_i, and m_{i+1} have similar meaning for second nearest neighbors. In Table I we give also the values for λ_1, λ_2, and λ_3 for the different surface directions, and in Table II we give the values for λ_1, λ_2, λ_3, and λ_4 for an atom in the second surface layer. Neglecting the concentration fluctuations described by P_{nm}^i then Eq. (2.4) simplifies to

$$\bar{\mu}_i = \mu_{\bar{n}_i,\bar{m}_i} x_i , \tag{2.7}$$

where $\bar{n}_i$ and $\bar{m}_i$ are the average number of nearest-neighbor and next-nearest-neighbor Ni atoms around a Ni atom in the ith layer. Due to the surface $\bar{n}_1 < \bar{n}_2$ and $\bar{m}_1 < \bar{m}_2$. For $\mu_{\bar{n}_i,\bar{m}_i}$, values are used as proposed by Robbins *et al.*

III. RESULTS AND DISCUSSION

In Figs. 1 and 2 results are shown for the concentration dependence of the average magnetic moment of a Ni atom in the first and second surface layer for $Cu_{1-x}Ni_x$ alloys, respectively, by using for μ_{nm}^i the two models proposed by Robbins, Claus, and Beck (RCB) and Jaccarino and Walker ($N_{\min}$). The results for different surface directions show the dependence of the average magnetic moment on the surface geometry. No segregation is taken into account.

In Figs. 3 and 4 we show how the results presented in Figs. 1 and 2 are modified when segregation is included. We used for the alloy composition in the first three layers the values published in a previous paper[8] and for the short-range order parameter the bulk value.[3,9] The average magnetic moment of a Ni atom in the first layer is reduced with respect to the value in bulk. Segregation has a strong effect on μ_i. As expected μ_i is affected strongest at the (110) surface plane, where five from the 12 nearest neighbors and two from the six nearest neighbors are missing. In the $N_{\min}$ model the average magnetic moment of a Ni atom in the (110) surface is zero for all concentrations since the highest number of nearest-neighbor Ni atoms is seven. For the (111) and (100) surface planes the average magnetic moment of a Ni atom in pure Ni ($x=0$) is the same in all layers, since $n > n_{\min}$. In the RCB model μ_i at the surface is smaller than in bulk for all concentrations. In the case that no segregation occurs, the Ni atoms in the second layer have a smaller μ_2 only at a (110) surface direction. For the (100) and (111) surface directions the average magnetic moment is already equal to the bulk value.

TABLE I. Number of nearest neighbors and next-nearest neighbors surrounding an atom in the surface plane lying in the same (ν_1, λ_1), second (ν_2, λ_2), and third layer (ν_3, λ_2) for different surface directions.

	ν_1	ν_2	ν_3	λ_1	λ_2	λ_3
100	4	4	0	4	0	1
111	6	3	0	0	3	0
110	2	4	1	2	0	2

TABLE II. Number of nearest neighbors and next-nearest neighbors surrounding an atom in the second surface layer lying in the first (ν_1, λ_1), second (ν_2, λ_2), third (ν_3, λ_3), and fourth (ν_4, λ_4) surface layer for different surface directions.

	ν_1	ν_2	ν_3	ν_4	λ_1	λ_2	λ_3	λ_4
100	4	4	4	0	0	4	0	1
111	3	6	3	0	3	0	3	0
110	4	2	4	1	0	2	0	2

If segregation is present, as is the case for Cu-Ni alloys, the average magnetic moment is reduced more strongly due to the enrichment of Cu in the surface layers. In this case, the average magnetic moment of atoms in the second layer are also different from the bulk ones for all surface directions as shown in Fig. 4. Note that our results show that upon alloying it happens that due to the surface the local magnetic moments of Ni atoms at the surface are quenched while in the bulk Ni atoms still possess a local magnetic moment. The results indicate that segregation might affect strongly the magnetic behavior of exchange enhanced transition-metal alloys. In this paper, we have assumed that the short-range order at the surface is the same as that in bulk. However, the short range order at the surface may be different from that in bulk and may vary from layer to layer[10,11] as in the case of long-range order.[12–14]

In view of our results one expects changes in the magnetic behavior of transition-metal alloys due to chemisorption, since the adsorbed atoms change the local atomic environment of the magnetically active atoms at the surface.

In this paper we have studied the effect of the surface on the local magnetic moment of Ni in Ni-Cu alloys. However, similar surface effects are expected for other transition-metal alloys. For example, in view of recent bulk studies[15,16] it would be also interesting to

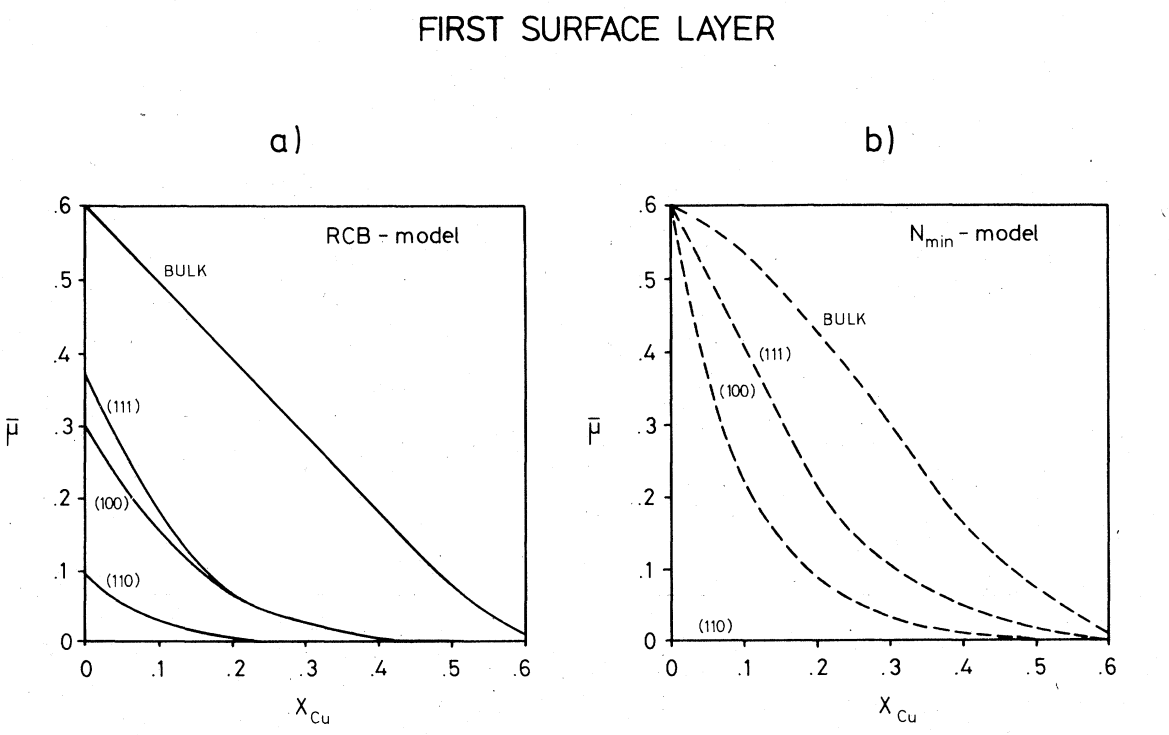

FIG. 1. Concentration dependence of the average magnetic moment $\bar{\mu}$ (in Bohr magnetons) of a Ni atom in the first surface layer for different surface layer for different surface directions. (a) Robbins- Claus-Beck model. (b) N_{min} model (Jaccarino-Walker). No segregation is assumed. The average magnetic moment of a Ni atom in bulk is also shown.

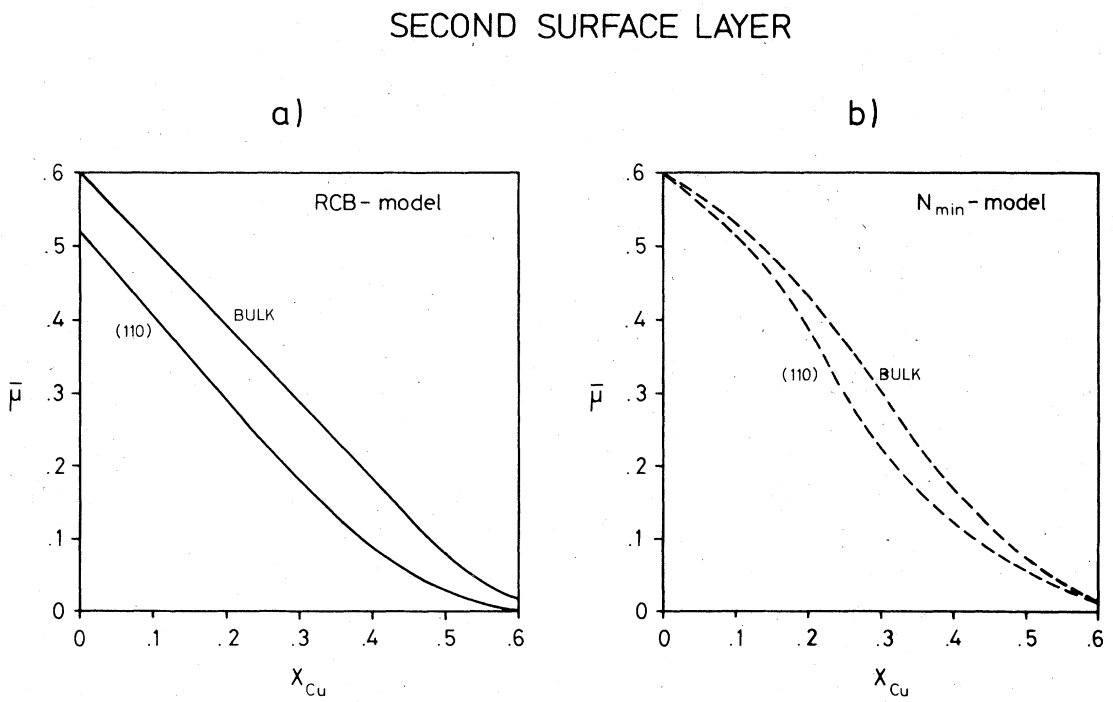

FIG. 2. Concentration dependence of the average magnetic moment $\bar{\mu}$ (in Bohr magnetons) of a Ni atom in the second surface layer for the (110) surface direction. (a) Robbins-Claus-Beck model. (b) N_{min} model (Jaccarino-Walker). No segregation is assumed. The average magnetic moment of a Ni atom in bulk is also shown.

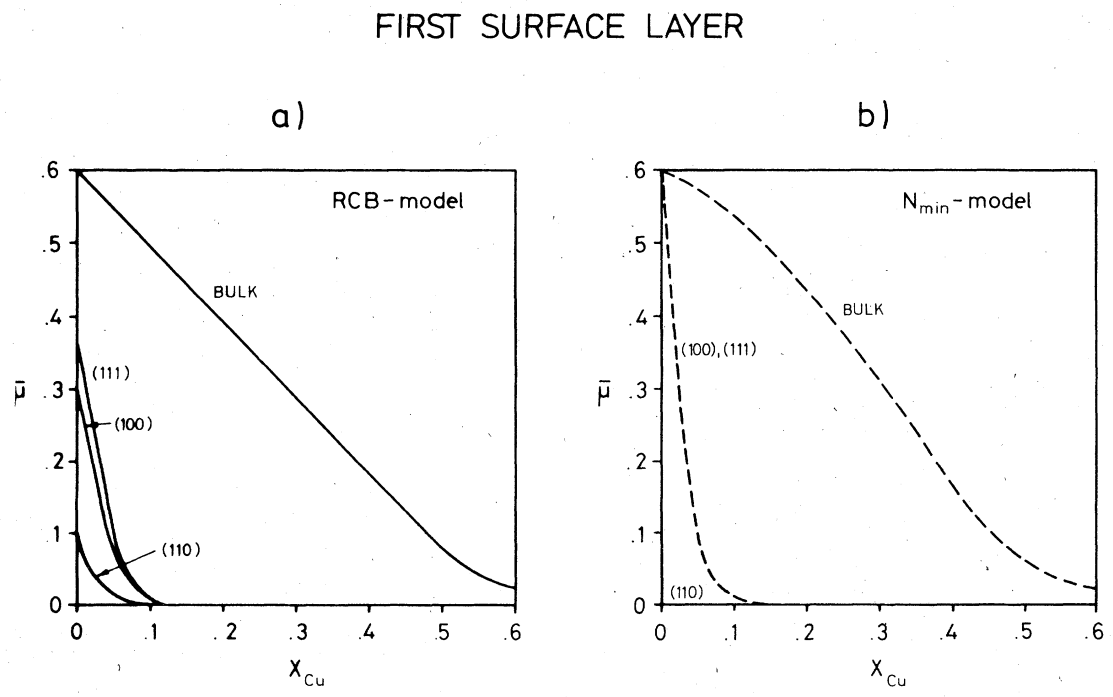

FIG. 3. Concentration dependence of the average magnetic moment $\bar{\mu}$ of a Ni atom in the first surface layer for different surface directions. (a) Robbins-Claus-Beck model. (b) N_{min} model. Segregation is taken into account.

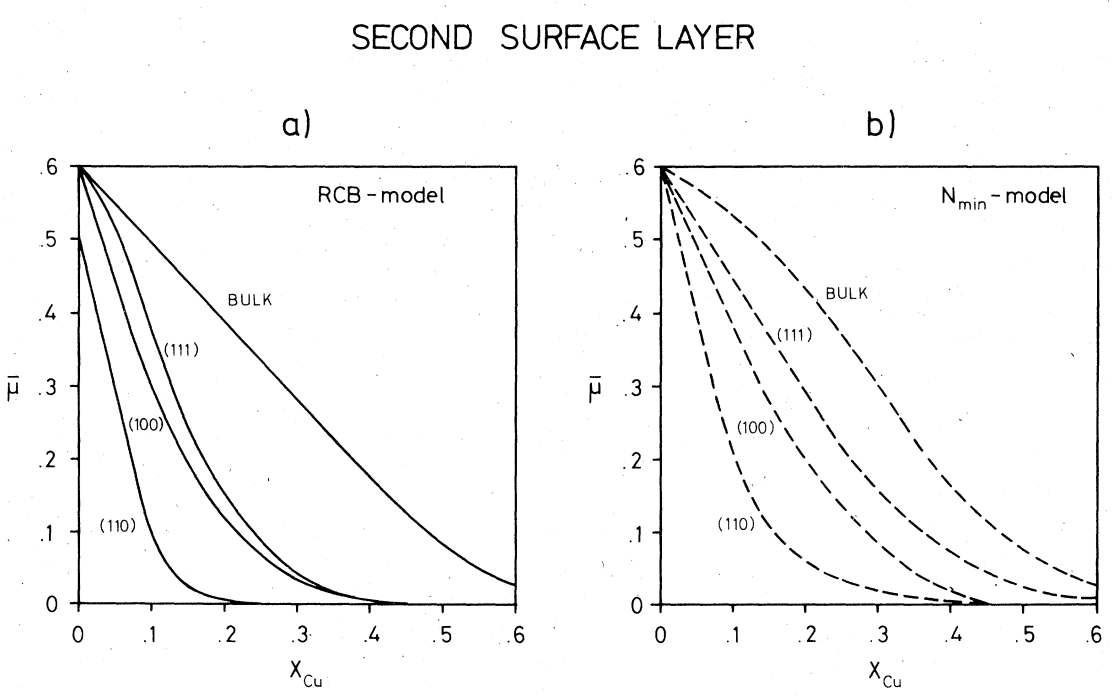

FIG. 4. Concentration dependence of the average magnetic moment $\bar{\mu}$ of a Ni atom in the second surface layer for different surface directions. (a) Robbins-Claus-Beck model. (b) N_{min} model. Segregation is taken into account.

study Ni-Rh alloys. Since one concludes from magnetic measurements of the bulk that the local magnetic moment of a Rh atom is $2\mu_B$ if surrounded by 12 Ni atoms and much smaller moments ($0.1\mu_B$) if surrounded by 11 Ni atoms, one expects for Ni rich Ni-Rh alloys that Rh atoms possess a local magnetic moment in the bulk, whereas Rh atoms at the surface have no magnetic moment.

Clearly, the surface will also affect the local spin susceptibility and hence the condition for the appearance of the local magnetic moment. The local spin susceptibility at an atom i is given by[17]

$$\chi_{ii} = \frac{\chi_{ii}^0 + \Sigma_{ii}}{1 - U_i(\chi_{ii}^0 + \Sigma_{ii})} \quad , \tag{3.1}$$

where χ_{ii}^0 is the spin-susceptibility if the intra-atomic Coulomb interaction U_i is zero, and where

$$\Sigma_{ii} = \sum_{j \neq i} \chi_{ij}^0 \frac{U_j}{1 - U_j \chi_{jj}^0} \chi_{ji}^0 + \sum_{j,l \neq i} \chi_{ij}^0 \frac{U_j}{1 - U_j \chi_{jj}^0} \chi_{jl}^0 \frac{U_l}{1 - U_l \chi_{ll}^0} \chi_{li}^0 + \cdots \tag{3.2}$$

results from the interatomic hopping of the electrons treated within the tight-binding approximation. The presence of a surface will affect Σ_{ii} and χ_{ii}^0 and possibly also U_i and thus χ_{ii}. Finally, we should like to mention that electron charge transfer resulting from the surface or from chemisorbed atoms will affect sensitively χ_{ii} and similarly μ_i.

In summary, we have shown that the local magnetic moments of Ni atoms in Ni-Cu alloys are strongly affected by the surface. The magnetic moments are strongly affected by surface segregation. While the two phenomenological models of Jaccarino and Walker and of Robbins *et al.* give similar results for μ_i in the bulk they give, however, different results for μ_i at the surface. It would be interesting to study these effects experimentally.

Finally, it should be pointed out that by using for $\mu_i = \mu_i(n_i, m_i)$ values deduced from bulk measurements we have treated the "missing" atoms at the surface as equivalent to Cu atoms in the bulk. This is certainly only approximately correct since the d-electron energies ϵ_d as well as the local electron density of states and thus μ_i on a Ni site will vary differently if a Ni neighbor to the Ni atom i is replaced by "no" atom or a Cu atom. Since it will be difficult to calculate accurately these corrections to the model presented above, it is interesting to test experimentally the applicability of $\mu_{bulk}(n_i, m_i)$ to the surface. Note that one can expect that replacing in a bulk a Ni atom by "no atom" will have a similar effect on the shape of the density of states as replacing it by a Cu atom. One may find in addition at the surface a shift in ϵ_d due to

a decrease of *s-d* Coulomb interaction and an increase in the ionic potential barrier. The importance of the "destructive effect" on the magnetic moment μ_i will depend on the sign of the shift with respect to ϵ_F.

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