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LETTER TO THE EDITOR

Strain-induced tetragonal distortions in epitaxial Ni-films grown on Cu(001)

D Spišák and J Hafner

Institut für Materialphysik and Center for Computational Materials Science, Universität Wien, Sensengasse 8/12, A-1090 Wien, Austria

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Abstract. The structural and magnetic properties of thin Ni films epitaxially grown on Cu(001) substrates have been investigated using *ab-initio* local-spin-density calculations in the generalized gradient approximation. We show that the lattice mismatch at the Ni–Cu interface induces a tetragonal distortion of the Ni-films of about 6%, superposed at the free surface by an inward relaxation of the Ni top-layer which is slightly larger than in bulk fcc Ni(001). The magnetic moments of the Ni atoms are enhanced at the free surface, but reduced at the Ni–Cu interface relative to the value in bulk Ni. The effect of the surfactant Cu layer is examined and it is shown that this effect can account for the existing discrepancies between calculated and measured structural features of thin Ni films.

In recent years spin-reorientation transitions in ultrathin magnetic layers have been widely investigated. Thin Fe and Co films epitaxially grown on Cu(001) substrates show a strongly enhanced magnetic anisotropy compared to the bulk metals. Below a critical thickness of the film this surface-induced anisotropy is large enough to overcome the demagnetizing field and to orient the magnetic moment normal to the film plane [1, 2]. The spin-reorientation transition (SRT) from perpendicular to in-plane magnetization is found at an increasing thickness of the film. The critical number of layers for the SRT depends strongly on the morphology of the films [2]: room-temperature grown (and hence relatively smooth) Fe/Cu(001) show perpendicular anisotropy for a thickness of up to 10 to 12 monolayers (ML), whereas the rougher low-temperature grown films switch to in-plane magnetization already between 5 and 6 ML. The magnetic properties of thin Fe and Co films, including the thickness dependent SRT are rather well understood on the basis of local-spin-density theory of itinerant magnetism [3–7]. In ultrathin Ni-films grown on Cu(001) or Cu(111) substrates a completely different behaviour has been observed by ferromagnetic resonance, circular dichroism, and magneto-optic Kerr-effect measurements [8–11]. Below a thickness of 7 ML the magnetization is spontaneously oriented in the film-plane, switching to perpendicular orientation in thicker films. The perpendicular magnetic anisotropy is maintained over an exceptionally broad Ni thickness range of up to about 60 Å ($\sim$ 35 ML) [9]. The reversed sign of the magnetoanisotropy energy (MAE) of Ni/Cu(001) as opposed to Fe or Co films on Cu(001) in the few ML limit has been attributed to the different sign of the thickness-dependent surface anisotropy favouring in-plane magnetization for Ni and out-of-plane magnetization for Fe and Co. The SRT which occurs at about 7 ML Ni is believed to be driven by positive, thickness-independent volume anisotropy. Above the critical thickness the volume anisotropy, together with the demagnetizing energy, overcompensates the negative surface anisotropy. For a cubic system like Ni, a large volume-anisotropy can only be obtained if the Ni/Cu(001) films are tetragonally distorted. Indeed low energy electron diffraction (LEED)

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experiments [12–14] have demonstrated the existence of considerable tetragonal distortions persisting at least to a thickness of 11 ML. The return to in-plane magnetization in thicker Ni/Cu(001) films, however, implies that the tetragonal distortion induced by the pseudomorphic growth on the Cu substrate disappears in sufficiently thick films [9]. It must also be emphasized that the scatter among different sets of LEED data is quite large, in particular close to the free surface and near the Ni–Cu interface. These discrepancies were tentatively attributed to the contamination of the surface by adsorbed molecules such as CO [14] or to the formation of a surfactant layer of Cu floating on top of several monolayers of Ni [13].

A number of theoretical studies of the Ni/Cu(001) system have been published [13,15–20]. These investigations agree on a reduction of the Ni-moment at the Ni–Cu interface resulting from a strong Ni–Cu hybridization and an enhancement of the Ni moment at the free surface. A similar enhancement of the magnetic moment has also been predicted for the surfaces of bulk Ni [18,21]. It has also been demonstrated that a tetragonal distortion of fcc Ni leads to a dramatic increase of the uniaxial magnetic anisotropy of Ni [19]. Uiberacker *et al* [20] have demonstrated that if a sufficiently large homogeneous tetragonal distortion of the Ni film is assumed, this can indeed explain the occurrence of a SRT in a thickness range comparable to that found in the experiment. The relaxation of Ni monolayers grown on Cu(001) has been calculated by Kim *et al* [13], predicting a 10% inward relaxation which is substantially larger than the inward relaxation of the top layer on a Ni(001) surface [21]. However, so far the relaxation of thicker Ni/Cu(001) films has not been studied theoretically.

This is precisely the aim of the present study. We use *ab-initio* local-spin-density (LSD) theory to calculate the geometric and magnetic structure of Ni/Cu(001) films with up to 7 ML of Ni. Even with present day computational tools, the calculation of a multilayer relaxation remains a formidable task. In the present work the multilayer relaxation of Ni/Cu(001) has been calculated using the spin-polarized version of the Vienna *ab-initio* simulation package VASP. VASP works on a plane-wave basis and uses ultrasoft pseudopotentials for describing the electron-ion interaction [22,23]. We have used the Ceperley-Alder spin-density-functional [24] together with the generalized gradient corrections (GGC) proposed by Perdew and Wang [25].

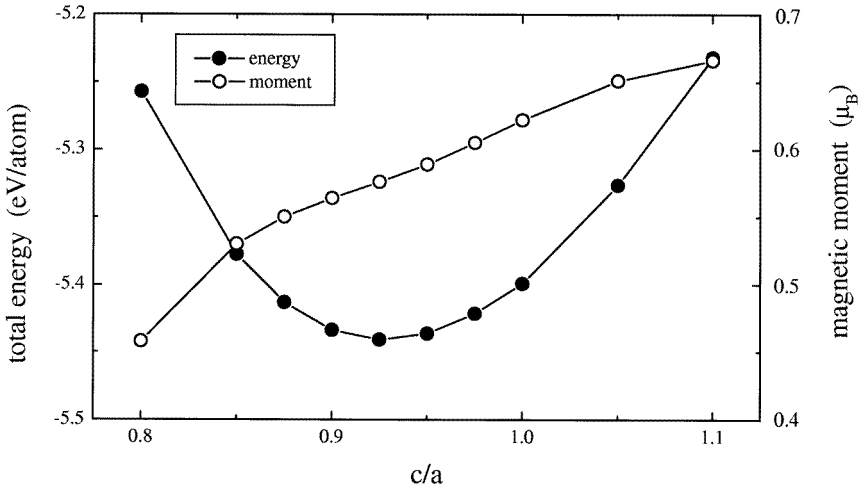

Figure 1. Variation of the total energy (left hand scale) and the magnetic moment (right hand scale) of fct Ni as a function of the c/a ratio. The in-plane lattice constant has been fixed at the calculated value $a_{\mathrm{Cu}} = 3.637$ Å of the Cu substrate.

In the LSD–GGC approximation the equilibrium lattice constants of Cu and Ni are $a_{\mathrm{Cu}} = 3.637$ Å and $a_{\mathrm{Ni}} = 3.526$ Å (exp: $a_{\mathrm{Cu}} = 3.61$ Å, $a_{\mathrm{Ni}} = 3.52$ Å). For the (001) surfaces of both metals we calculate an inward relaxation of -3.6% (Cu) and -3.6% (Ni), in reasonable agreement with experiment. The lattice mismatch of about 3% should lead to a substantial tetragonal distortion of Ni films epitaxially grown on a Cu(001) surface, because of the smaller lattice constant of Ni we expect the interlayer distance in the Ni film to be about 6% smaller than in the Cu substrate—this is very close to the distortion assumed by Uiberacker *et al* [20]. Figure 1 shows the total energy and the magnetic moment of a face-centered-tetragonal (fct) Ni with in-plane lattice constant constrained to the calculated lattice constant of fcc Cu. The total energy is indeed minimized at an axial ratio of $c/a \sim 0.94$, the tetragonal distortion also induces a slight decrease of the magnetic moment to $m = 0.58\ \mu_B$ compared to $m = 0.61\ \mu_B$ in fcc Ni. For this fct phase of Ni we used the real-space tight-binding LMTO technique [6, 26, 27] to estimate the influence of the distortion on the magnetic anisotropy (MAE). The effect of the tetragonal distortion on the MAE is large because in the tetragonal phase the leading contribution to the MAE is of second order in the spin-orbit coupling, but only of fourth order in the cubic phase. For fcc Ni the measured anisotropy energy $E(001) - E(111) \simeq 2.7\ \mu$eV/atom is of the same level as the degree of convergence that can be achieved in both real- and k-space calculations [28, 29]. Due to the tetragonal distortion, the MAE increases by more than one order of magnitude. At $c/a = 0.94$ we find $\Delta E = E_{100} - E_{001} = 52 \pm 2\ \mu$eV/atom, in reasonable agreement with recent k-space calculations [$\Delta E = 60\ \mu$eV/atom (reference [19]), $\Delta E = 65\ \mu$eV/atom (reference [30])]. We also note that the MAE changes sign with the tetragonal strain. At $c/a = 1.06$ we find $\Delta E = -74\ \mu$eV/atom. Hence the existence of a large strain-induced MAE in fct Ni is confirmed.

Table 1 summarizes the multilayer-relaxations in Ni/Cu(001) films with up to 7 ML. The calculations were performed for slabs with 4 ML Cu and 1 to 7 ML Ni and p(1×1) geometry in the film plane with the in-plane lattice constant fixed at the Cu-bulk value. The thickness of the vacuum separating the periodically repeated slabs is about 11 Å. In addition we have calculated the surface relaxation of a fct Ni crystal with $c/a = 0.94$, using a thick slab with the deeper layers frozen in the fct geometry. Brillouin-zone integrations were performed using $(5 \times 5 \times 2)$ up to $(9 \times 9 \times 2)$ grids of special points depending on the model size. A modest Methfessel–Paxton smearing [31] was used. For a single ML of Ni on Cu(001), the predicted inward relaxation of -6.2% lies between the experimental values of Kim *et al* [13] (-7.0%) and Platow *et al* [14] (-4.7%). In a two ML film, the inward relaxation of the surface layer increases to about -12%, while the distance between the Ni and Cu layers at the interface is reduced only by -1.9%. In a three ML film we find again a very strong inward relaxation at the surface, a modest relaxation at the Ni–Cu interface and between the inner Ni layers a reduction of the interlayer distance which is already quite close to that calculated for the bulk fct phase strained to the lateral lattice constant of Cu. For thicker films, the calculations converge to a tetragonal distortion of $\simeq -6\%$ in the interior of the film, which is superposed at the free surface by an additional inward relaxation comparable with that present at the surface of bulk fcc Ni ($d_{12} = -3.6\%$, reference [21]) so that the relaxation of the top-layer is about -11%. A similar result was also obtained at the surface of fct Ni. At the Ni–Cu interface a much smaller reduction of the interlayer distance of only $\sim -1\%$ is predicted. While the calculated tetragonal distortion in the deeper layers is in quantitative agreement with the LEED data of Müller *et al* [12] and with the very recent LEED work of Platow *et al* [14], the predicted large inward relaxation at the surface contrasts with the weak outward relaxation deduced from LEED experiments [12] or with the homogeneous fct structure of the Ni films found in the more recent work [14]. Possible sources of the disagreement are discussed below.

Table 1. Interlayer relaxations in Ni/Cu(001) films with up to 7 Ni monolayers, calculated relative to the interlayer distance $d_{Cu} = 1.819$ Å in the Cu substrate. For comparison data from LEED experiments are given (in this case the reference value is $d_{Cu} = 1.805$ Å as derived from exp. lattice constant of bulk Cu). The last column shows the relaxations calculated for the (001) surface of the face-centered-tetragonal Ni with $c/a = 0.94$. The horizontal lines separate Ni–Ni, Ni–Cu and Cu–Cu interlayer distances. For a 5 ML film we have considered both ferro- and paramagnetic solutions.

ML	1				2			3				5				7		fct Ni
												FM	PM					
d_{12}(%)	−6.2	−1.8[a]	−7.0[b]	−4.7	−11.9	−2.4	−5.0	−11.4	−3.5	−1.1	−4.4	−11.3	−11.3	1.6	−7.2	−11.0	−5.3	−11.1
d_{23}(%)	0.2	−1.9	−1.0	−1.9	− 1.9	−1.0	−4.7	− 7.4	−7.5	−3.9	−5.3	− 6.0	− 7.9	−6.1	−5.3	− 5.8	−6.1	− 6.2
d_{34}(%)				−1.1	0.5	−0.5	−1.7	− 3.2	0.4	−2.8	−5.0	− 7.0	− 8.1	−5.0	−5.8	− 5.9	−6.1	− 6.9
d_{45}(%)							−0.8	0.0	6.6	−1.1	−2.5	− 8.1	− 7.7	−5.6	−5.0	− 5.3	−5.8	− 7.0
d_{56}(%)											−0.8	− 3.1	− 3.5		−4.2	− 6.0	−5.3	
d_{67}(%)												0.1	− 0.6			− 6.2		
d_{78}(%)																− 0.7		
d_{89}(%)																2.0		
Reference		[13]	[13]	[14]		[13]	[14]		[13]	[12]	[14]			[12]	[14]		[14]	

[a] LEED estimate for buried Cu/Ni/Cu(001) monolayer.
[b] LEED estimate for Ni/Cu(001) overlayer.

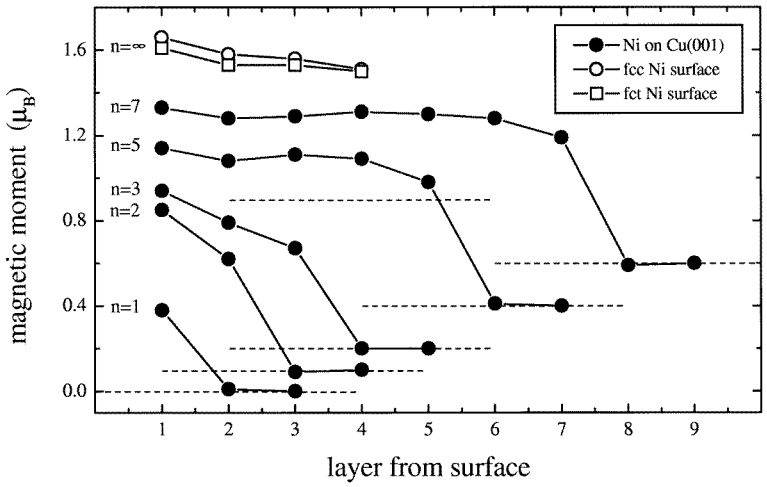

Figure 2. Magnetic moment profiles for fct Ni films on Cu(001), showing in addition the profiles at the surfaces of fcc and fct Ni. Moment values are shifted by $0.1(n-1)\ \mu_B$ with increasing number of Ni monolayers. The moments obtained for a Ni(001) surface are shifted by $0.9\ \mu_B$.

Figure 2 summarizes the results for the magnetic moments in the Ni layers and for the small moments induced in the top layers of the Cu substrate. Except for the Ni/Cu(001) monolayer where the magnetism is reduced by the strong hybridization of the Ni- and Cu-d bands the average magnetic moments are bulk-like and the magnetic profiles of the films follow a common pattern. (a) At the free surface, we find substantially enhanced moments of $m \sim 0.73 - 0.77\ \mu_B$. The enhancement is due to the Ni-band narrowing at the surface and is similar to that found on the (001) surface of Ni [21]. (b) At the Ni–Cu interface the strong Ni-d–Cu-d hybridization leads to a reduction of the Ni-moments to $m \sim 0.44 - 0.50\ \mu_B$. (c) A reduced magnetic moment is also found in the subsurface Ni-layers, varying between 0.53 and 0.55 μ_B. Again this weakly oscillatory momentum profile is very similar to that found on the (001) surface of Ni.

The disagreement we find between the calculated top layer relaxation and the reported LEED result is disconcerting. Physically, the theoretical result is plausible, because the predicted relaxation of the film is approximately equal to the sum of the strain-induced tetragonal distortion and the surface relaxation of bulk fct or fcc Ni. Similar disagreements between room-temperature LEED experiments and zero-temperature *ab-initio* calculations are quite frequent in surface science. Cho and Scheffler [32] have argued that the observed difference is due to an anisotropic thermal expansion reducing the inward relaxation of the surface layer with increasing temperature. To test this possibility, we have performed *ab-initio* molecular dynamics simulations for 3 ML Ni/Cu(001) at $T = 270$ K, for 7-layer models with 14 and 28 atoms respectively. The results show no significant variations in the interlayer relaxations driven by temperature effects.

In addition, we have investigated the possibility that a paramagnetic calculation could yield a different result. The results for a 5 ML films are included in table 1. As expected on the basis of the weak magnetovolume effect of Ni, no sizeable magnetic effect on the interlayer distances could be detected. This agrees with the LEED measurements reporting no dramatic structural changes at the Curie temperature [14].

The discrepancies between the three sets of LEED data are very problematic. The very

recent work of Platow *et al* [14] concluding that the Ni film shows essentially a homogeneous tetragonal distortion of about 6% contradicts earlier studies of the same group [12] reporting an expansion of the top spacing. As a possible explanation of the discrepancy Platow *et al* suggest a contamination of the samples on which the experiments of Müller *et al* [12] had been performed by CO adsorbed on the surface. Kim *et al* [13] claim that both the analysis of the LEED characteristics and first-principle density functional calculations lead to the conclusion that subsurface growth of Ni monolayers covered by a surfactant Cu overlayer is favoured compared to overlayer growth. However, the calculations were performed only for Ni monolayers. Moreover, there are significant discrepancies between their theoretical and experimental results and their analysis was contested by Platow *et al* [14] who pointed out that the scattering properties of Ni and Cu are too similar to produce significant chemical contrast in the LEED data.

Table 2. Interlayer relaxations, magnetic moments and total energies calculated for a Ni overlayer, a CuNi surface alloy and a Ni subsurface layer on Cu(001) substrate.

	Ni/Cu(001)	CuNi/Cu(001)	Cu/Ni/Cu(001)
d_{12} (%)	−6.2	−3.6/−10.6[a]	−7.2
d_{23} (%)	0.2	−0.2/−0.8	−3.9
$m_{\mathrm{Ni}}(1)$[b] (μ_B)	0.407	−0.006	—
$m_{\mathrm{Ni}}(2)$ (μ_B)	—	−0.002	0.048
$m_{\mathrm{Cu}}(1)$ (μ_B)	—	−0.001	0.003
$m_{\mathrm{Cu}}(2)$ (μ_B)	0.003	0.000	—
$m_{\mathrm{Cu}}(3)$ (μ_B)	−0.004	0.000	0.001
E_{tot} (eV/at.)	−3.7464	−3.7737	−3.8057
ΔE (eV/at.)	0.0593	0.0320	0.0000

[a] Interlayer relaxations are given in % of the interlayer distance in bulk Cu, for the surface alloy a significant buckling is predicted.
[b] Magnetic moments for atoms in layer i from the surface.

Here we reexamine the possibility of subsurface growth. For a monolayer equivalent of Ni on Cu(001) we compare (i) a Ni overlayer, (ii) a two ML thick (2×2) CuNi surface alloy, and (iii) a compact Ni ML below a surfactant Cu ML, see table 2. The results are obtained for 6-layer slabs and a fine grid of 65 k-points in (1×1) cells and 16 k-points in the (2×2) cell of the surface alloy. Surface alloying is found to be strongly preferred over the formation of a compact Ni overlayer. In the surface alloy the magnetic moments of the Ni atoms are essentially nonmagnetic and we also predict a significant buckling (the Ni atoms showing the larger inward relaxation). However, the formation of a buried Ni layer below a surfactant Cu overlayer is energetically even more favourable. The buried Ni layer is nonmagnetic, the total relaxation is even slightly larger than for the compact Ni overlayer, in agreement with Kim *et al* [13] who claim to have observed a surfactant overlayer.

More important is the analysis of thicker Ni films. Table 3 presents the results for a 5 ML Ni film with and without surfactant Cu overlayer. Even in this case the formation of a surfactant Cu overlayer is energetically preferred and leads to considerable change in the interlayer relaxations. With a surfactant Cu layer, the tetragonal distortion of the Ni film is homogeneous within the accuracy of the calculations and of the LEED experiments. Due to the Cu overlayer the surface-induced enhancement of the Ni moments disappears, at both Ni–Cu interfaces the d–d hybridization leads to reduced magnetic moments. The overall magnetic polarization of the Ni films changes only by about 10%, though. Hence we can conclude that

Table 3. Interlayer relaxations (compared to bulk Cu), magnetic moments and total energies calculated for a Ni_5/Cu(001) $CuNi_5$/Cu(001) films.

	Ni_5/Cu(001)	$CuNi_5$/Cu(001)
d_{12} (%)	−11.3	−5.8
d_{23} (%)	−6.0	−7.1
d_{34} (%)	−7.0	−6.7
d_{45} (%)	−8.1	−6.5
d_{56} (%)	−3.1	−7.7
d_{67} (%)	0.1	−2.5
d_{78} (%)	0.3	0.3
$m(1)(\mu_B)$	0.698	−0.017
$m(2)(\mu_B)$	0.617	0.368
$m(3)(\mu_B)$	0.650	0.577
$m(4)(\mu_B)$	0.588	0.647
$m(5)(\mu_B)$	0.397	0.620
$m(6)(\mu_B)$	−0.013	0.484
$m(7)(\mu_B)$	−0.010	0.004
$\bar{m}_{\mathrm{Ni}}$ (μ_B)	0.590	0.539
E_{tot} (eV/at.)	−4.4401	−4.4628
ΔE (eV/at.)	0.0227	0.0000

the density-functional calculations show that there is a surfactant effect during the formation of Ni films on Cu(001) and that the surfactant effect eliminates the discrepancy between theory and LEED experiments. Whether a surfactant Cu overlayer will actually be formed, is of course dependent on the deposition conditions.

The effect of capping overlayers on the magnetic properties of ultrathin Ni/Cu(001) films have been investigated by O'Brien *et al* [33]. They found that in the presence of a capping Cu overlayer the critical thickness for the SRT was reduced, reflecting the fact that the Cu–Ni surface anisotropy is weaker than the Ni surface anisotropy. This is consistent with our prediction of a reduced magnetization due to the surfactant layer.

In this context it is interesting to compare the structures of Ni/Cu(001) and Fe/Cu(001) films. In ultrathin fcc Fe films the situation is complicated by the simultaneous presence of a ferromagnetic coupling at the surfaces (due to the strongly enhanced surface magnetism) and an antiferromagnetic coupling in the deeper layers. In combination with the large difference in the magnetovolume effect in ferro- and antiferromagnetic fcc Fe [23], this leads to an expansion of interlayer distances between ferromagnetically coupled planes and to a contraction of the distances between antiferromagnetically coupled layers [34,35], superposed by complex lateral reconstruction [12]. LSD-GGA calculations [34,35] describe the complex film structure rather well, however, again excepting the distance between surface and subsurface layers. Also for Co/Cu(001) films our preliminary results for the optimized film structure indicate that at the free surface the overall tetragonal distortion is superposed with an additional inward relaxation, resulting in a situation very similar to that discussed here for Ni/Cu(001).

In conclusion, we have used *ab-initio* local-spin-density calculations to investigate the structure of ultrathin Ni films on Cu(001) substrates. We have shown that the lattice mismatch at the Ni–Cu interface induces a tetragonal distortion of the Ni film of about 6%, superposed at the free surface by an inward relaxation of the top Ni layer which is slightly larger than on a Ni(001) surface. The tetragonal distortion predicted for the deeper layers is in reasonable agreement with LEED experiments, but the inward relaxation of the top layer disagrees with

the most recent experiments showing a homogeneous tetragonal structure of the films. We have demonstrated that the formation of a surfactant overlayer of Cu on top of the Ni films is energetically favoured and leads to a structure in almost perfect agreement with the LEED data.

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