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Theoretical study of magnetic layers of nickel on copper; dead or alive?

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Abstract. We studied the persistence of magnetism in ultrathin nickel films on copper. Layer-dependent magnetic moments in Ni films on the (001), (110) and (111) surfaces of Cu have been calculated using the Korringa–Kohn–Rostoker Green's function method. The results show that, at temperature $T = 0$, a single nickel monolayer is ferromagnetic on Cu(001) and Cu(110) but magnetically 'dead' on the more closely packed Cu(111) surface. Films of two and more layers of Ni are always ferromagnetic, with the magnetic moment enhanced in the surface layer but strongly reduced in the interface layer. Due to the short screening length, both the effect of the interface and that of the surface are confined to only a few atomic layers.

1. Introduction

In the last few decades, developments in epitaxial growth methods have enabled controlled studies of magnetism in ultrathin films and multilayer systems to be made [1]. As a parallel development, recent advances in core-level spectroscopies with polarized synchrotron radiation have made it possible to extract the element-specific spin and orbital magnetic moments from the x-ray magnetic dichroism [2, 3] with a sensitivity of 0.1 monolayer (ML) [4].

A long-standing issue, attracting a great deal of interest in surface magnetism, is that of magnetically 'dead' layers, i.e. paramagnetic layers [5]. This has an especially chequered history for Ni on Cu, which is a well-studied system as far as the (001) surface is concerned and which has applications as a heterogeneous catalyst [6]. Since Cu and Ni have the same crystal structure and almost match in lattice constant, they grow epitaxially [7–9].

The experimental reports on the magnetic behaviour at room temperature (RT) for Ni layers on Cu(001) are rather coherent. Up to ∼5 ML there is no remanent magnetic moment [10–13]; between ∼5 and ∼10 ML the magnetization is in the surface plane [11, 12]; a spin reorientation transition leading to perpendicular magnetization occurs for layers thicker than 10 ML [11, 12, 14–17]; and a further in-plane reorientation may take place for even thicker layers [12, 16, 17]. Canted spin structures arise in thin Ni layers grown on stepped Cu(001) surfaces [18]. The other two surfaces have been less well characterized. Recently, Sacchi *et al* [19] reported for Ni on Cu(110) at RT the absence of a net magnetic moment in the surface plane for up to 6 ML. The magnetization in thin films, however, is strongly temperature dependent. Magneto-optic Kerr effect measurements [20, 21] showed that the Curie temperature, T_c, is below RT for thicknesses up to 4 ML for Ni/Cu(100) and 2 ML for Ni/Cu(111). The absence of magnetic ordering for lower nickel coverages can therefore be ascribed to the thickness dependence of T_c [13, 20, 21].

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From temperature- and thickness-dependent measurements, Tjeng *et al* [10] and Huang *et al* [21] concluded that 1 ML of Ni on Cu(001) is non-magnetic. However, these results were obtained by extrapolation of measurements performed on two and more ML of Ni. Direct measurements, in contrast, showed a ferromagnetic ordering for 1 ML [22]. Also for the Cu(111) surface, the extrapolated results suggest that 1 ML is non-magnetic [21], whereas direct measurements give opposite results [20, 23]. Measurements have the limitation that they always have to be done on imperfect monolayers and at finite temperature.

Also on the theoretical side there is no agreement. For 1 ML Ni/Cu(001), Tersoff and Falicov [24, 25] find using a tight-binding model a moment of 0.48 μ_B/atom; Wang, Freeman and Krakauer [26] find using LAPW calculations 0.37 μ_B; and Pourovskii *et al* [27] obtain using LMTO calculations 0.30 μ_B.

For 1 ML Ni/Cu(111), Tersoff and Falicov [24, 25] calculate a magnetic moment of $\leqslant 0.1$ μ_B, which would be destroyed at finite temperatures. Pourovskii *et al* [27] obtain using LMTO calculations a zero magnetic moment; and Fu and Freeman [28] obtain with self-consistent full-potential linearized augmented-plane-wave (FLAPW) calculations 0.34 μ_B.

For 1 ML Ni/Cu(110), Pourovskii *et al* [27] find using LMTO calculations a magnetic moment of 0.49 μ_B.

Since there is no appreciable overlap between the d bands of Cu and Ni, the magnetization is quite sensitive to the degree of hybridization between the Ni d band and the sp conduction band of the non-magnetic substrate [24, 25]. For sufficiently weak coupling (a free-standing film would be the extreme case [29–31]) the magnetization will be larger than that in bulk Ni, giving rise to an enhanced moment at the surface. On the other hand, if the coupling is strong, the magnetic moment will be reduced. This suggests that the specific electronic structure of the substrate can be an important factor. This has recently been confirmed by Korringa–Kohn–Rostoker (KKR) calculations where the Ni magnetic moments in Ni/4 ML Co/Cu(001) and Ni/Cu(001) were compared as a functions of the film thickness [32]. The suppression of the film magnetism by the non-magnetic substrate is quite analogous to the suppression of impurity magnetism by the non-magnetic matrix; or in alloys by the non-magnetic constituent [24, 25]. Consequently, when Ni migrates into the Cu substrate, which can occur at temperatures above RT, the Ni might become non-magnetic, as has recently been verified by LMTO calculations [27].

Ni metal is found to exhibit similar behaviour to Ni/Cu. Relative to that of the bulk, the magnetic moment is significantly enhanced at the Ni(100) surface but not at the Ni(111) surface [24, 25, 33]. Furthermore, self-consistent calculations using the muffin-tin orbital film method show an increase in the orbital magnetic moment of 0.02 (0.01) μ_B for the surface (subsurface) layer [34]. An enhancement in surface orbital magnetic moment has been observed in studies of the magnetic circular dichroism in Ni 3p core-level photoemission [35].

Since conclusions drawn from different experiments and theoretical models are rather contradictory, we have performed KKR band-structure calculations in order to obtain the layer-dependent magnetic moments. We found that 1 ML of Ni on Cu(111) is non-magnetic at $T = 0$ and can be considered as a magnetically ‘dead layer’. In this respect our study confirms the results of Tersoff and Falicov [24, 25] and Pourovskii *et al* [27].

2. Computational method

The calculations presented in this paper were performed using the screened KKR Green’s function method for layered systems [36, 37]. The screened structure constants were calculated by a two-dimensional Fourier transformation from the screened constants in real space. A screening potential with a barrier height of 4 Ryd was used and the structure constants included coupling to the three next-nearest neighbours. In this representation the KKR matrices which need to be inverted are banded, which permits calculations for large systems to be carried out [36]. In the present case we considered surfaces made up of two vacuum layers, and six Ni layers deposited on Cu(001), Cu(110) and Cu(111) with the same interlayer distance corresponding to that of the Cu bulk lattice (the lattice parameter is 6.76 au). These Cu surfaces were represented by seven layers in the interface region. Semi-infinite vacuum and semi-infinite Cu bulk were treated with the surface Green function method [38]. The constant vacuum potential and work function were calculated self-consistently by solving the Poisson equation for an inhomogeneous system including monopole and dipole terms [38]. The energy integration was performed by means of Gaussian quadrature with 33 points on a semicircle. For the k-integration we used about 2000 k-points in the two-dimensional irreducible Brillouin zones of each of the (100), (110) and (111) planes for energies close to the Fermi energy, and about 100 k-points were taken for all remaining energy points on the contour. In the present calculations we used a Perdew–Wang exchange–correlation potential [39].

3. Results

For the three different Cu surfaces, figure 1 summarizes the theoretical results obtained for Ni films with thicknesses between 1 and 6 ML. The Ni magnetic moments of the surface layer, the subsurface layer, other intralayers and the interface layer are indicated by closed triangles, open circles, closed circles and closed squares, respectively. For comparison, the bulk value of 0.57 μ_B is indicated by the dashed line. For 1 to 3 ML, numerical values are also given in table 1. These results show several striking features.

Table 1. Layer-resolved magnetic moments (μ_B) in 1 to 3 ML of Ni on Cu(001), Cu(110) and Cu(111) for surface (S) layers (bold) and interface (I) layers (italic).

ML	Layer	Cu(001)	Cu(110)	Cu(111)
1	S = I	**0.1325**	**0.0798**	**0.0000**
2	I	*0.3813*	*0.2877*	*0.4074*
	S	**0.5935**	*0.5176*	**0.5006**
3	I	*0.3691*	*0.2718*	*0.3406*
	S − 1	0.5531	0.4756	0.5943
	S	**0.6387**	**0.6161**	**0.5265**

On Cu(100) the Ni surface layer has an increased magnetic moment for thicknesses of 2 ML and more. At the interface the Ni magnetic moment is reduced nearly to half the bulk value. The moments for the intralayers in films with 5 and 6 ML are approaching the bulk value. Similar trends are also observed for Cu(110), i.e. an increased Ni moment at the surface and a reduced moment at the interface. For 1 ML the Ni magnetic moment is strongly reduced. In addition to the similarities, there are also important differences between the two Cu surfaces, especially at low coverage. The magnetic moment is much larger for 1 ML of Ni on Cu(100) than for 1 ML of Ni on Cu(110); the values are 0.13 and 0.08 μ_B, respectively. For 2 ML of Ni on Cu(100) the Ni surface magnetic moment exceeds the bulk value, while for 2 ML of Ni on Cu(110) it is lower than in the bulk.

The magnetic behaviour of Ni on Cu(111) is quite different from its behaviour on the other two surfaces. First of all, for 1 ML of Ni on Cu(111) the magnetic moment is zero, so the monolayer is actually magnetically dead. A magnetic moment is only observed for 2 ML and

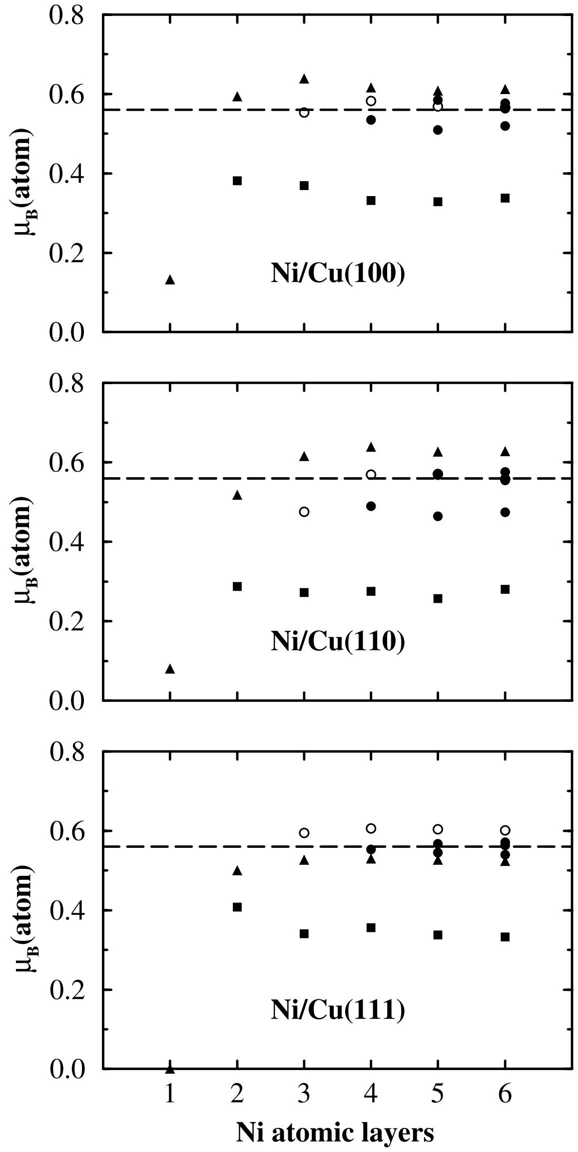

Figure 1. Layer-resolved magnetic moments (μ_B) in: Ni/Cu(001); Ni/Cu(110); and Ni/Cu(111) with 1 to 6 ML of Ni for the surface layer (closed triangles), the subsurface layer (open circles), other intralayers (closed circles) and the interface layer (closed squares). The dashed horizontal line indicates the bulk moment of 0.57 μ_B.

more. However, the surface magnetic moment remains smaller than that of the intralayers. The moment in these intralayers converges to the bulk value, while it is enhanced in the subsurface layer (S − 1).

Figure 2 shows the layer-resolved density of states (DOS) of 1 ML of Ni on the three different Cu surfaces. Displayed are the DOS of the Cu interface layer (full line) and that of the Ni surface layer, split into a majority-spin band (dotted line) and a minority-spin band (dashed line). For Ni on Cu(111) these two spin bands coincide.

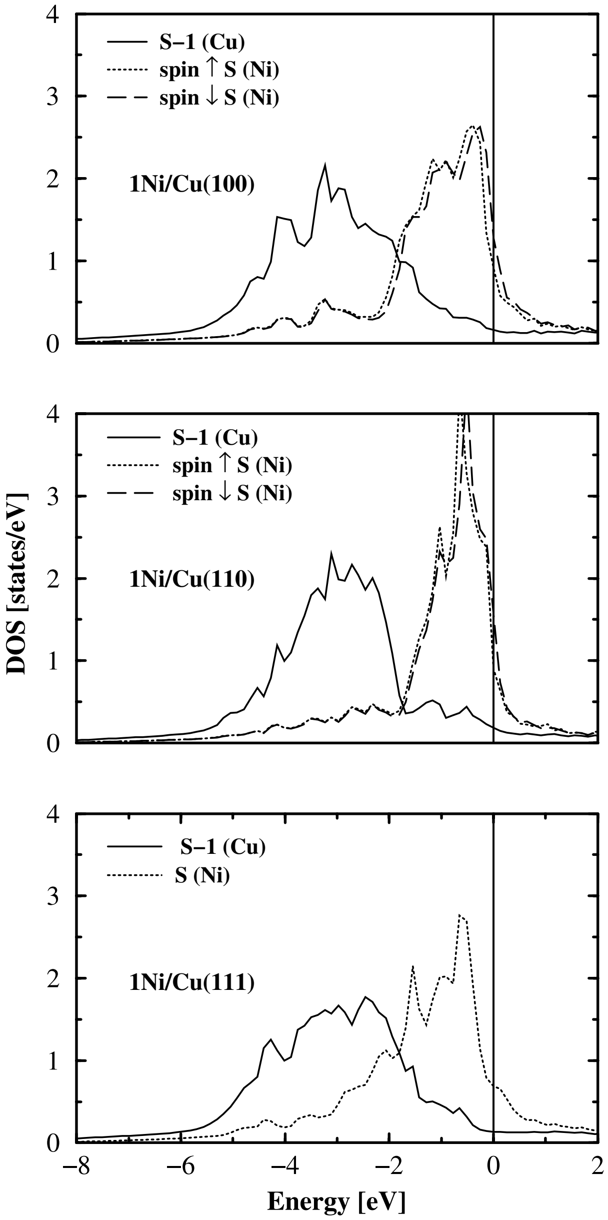

Figure 2. The layer-resolved density of states for 1 ML of Ni on Cu(001), Cu(110) and Cu(111): the Cu interface layer (full line), majority-spin states (dotted line) and minority-spin states (dashed line) of the Ni surface layer. 1 ML of Ni on Cu(111) is non-magnetic. The vertical line indicates the Fermi level.

The hybridization between the Ni and Cu at the interface is strong for the Cu(111) and weak for the Cu(110). This is clear from figure 2 which shows that the Ni DOS extends well into the Cu DOS. However, Ni on Cu(110) does not actually have the largest magnetic moment. In order to understand this, we note that the exchange splitting of Ni on Cu(100) is larger than that of Ni on Cu(110). This is because for the Ni monolayers the coordination of a Ni atom with other Ni atoms changes according to the surface orientation: the number of Ni nearest-neighbour atoms surrounding a Ni atom varies from only two for Ni on Cu(110) to four for Ni on Cu(100) and six for Ni on Cu(111). From the DOS we can therefore conclude that both the Ni–Ni and the Ni–Cu hybridization are determining factors for the magnetic properties of a single Ni layer on Cu.

4. Conclusions

The magnetic behaviour of Ni films in the few-monolayer coverage range deposited on Cu depends strongly on the crystallographic surface plane. Our Korringa–Kohn–Rostoker calculations showed that a single layer of Ni at $T = 0$ K is magnetically alive on the Cu(100) and Cu(110) surfaces but magnetically dead on the Cu(111) surface—the most closely packed of the three. Also, for more than 1 ML of Ni there are substantial differences between these three surfaces. Probably the most remarkable fact is that for Ni on Cu(111) the largest magnetic moment is carried by the Ni subsurface layer and not by the surface layer as is the case for the other two Cu surfaces. We also investigated the validity of the intuitive model put forward by Tersoff and Falicov [24, 25] stating that the Ni magnetic moment is reduced when the Ni–Cu hybridization is increased. The calculated Cu and Ni densities of states indicate that there must be at least one other determining factor, namely the Ni exchange splitting which scales with the Ni–Ni coordination. This is higher for Ni on Cu(100) than for Ni on Cu(110), so the magnetic moment of 1 ML of Ni on Cu(100) is larger, despite a strong Cu–Ni hybridization.

The conclusions presented in this paper are based on the study of idealized surfaces without considering atomic interchange at the interface. This might not be so unrealistic, as it was recently shown that this intermixing is essentially limited to the interface and has very little effect on the magnetic moments [40]. To perform further theoretical analysis of the experimental data it would therefore be more profitable to make finite-temperature studies and also investigate T_c as a function of Ni layer thickness and surface orientation.

References

[1] Himpsel F J, Ortega J E, Mankey G J and Willis R F 1998 *Adv. Phys.* **47** 511

[2] Thole B T, Carra P, Sette F and van der Laan G 1992 *Phys. Rev. Lett.* **68** 1943

[3] van der Laan G 1995 *Phys. Rev.* B **51** 240

[4] Dhesi S S, Dürr H A, van der Laan G, Dudzik E and Brookes N B 1999 *Phys. Rev.* B **60** 12 852

[5] Liebermann L N, Clinton J, Edwards D M and Mathon J 1970 *Phys. Rev. Lett.* **25** 232

[6] Sifelt J H, Cartel J L and Yates D J C 1972 *J. Catal.* **24** 283

[7] Wulfhekel W, Beckmann I, Lipkin N N, Rosenfeld G, Poelsema B and Comsa G 1996 *Appl. Phys. Lett.* **69** 3492

[8] Wulfhekel W, Beckmann I, Rosenfeld G, Poelsema B and Comsa G 1998 *Surf. Sci.* **395** 168

[9] Farle M 1998 *Rep. Prog. Phys.* **61** 755

[10] Tjeng L H, Idzerda Yu, Rudolf P, Sette F and Chen C T 1992 *J. Magn. Magn. Mater.* **109** 288

[11] O'Brien W L and Tonner B P 1994 *Phys. Rev.* B **49** 15 370

[12] O'Brien W L, Droubay T and Tonner B P 1996 *Phys. Rev.* B **54** 9297

[13] Srivastava P, Wilhelm F, Ney A, Farle M, Wende H, Haack N, Ceballos G and Baberschke K 1998 *Phys. Rev.* B **58** 5701

[14] Naik R, Kota C, Payson J S and Dunifer G L 1993 *Phys. Rev.* B **48** 1008

[15] Jungblut R, Johnson M T, aan de Stegge J, Reinders A and den Broeder F J A 1994 *J. Appl. Phys.* **75** 6424

[16] Bochi G, Ballentine C A, Inglefield H E, Thompson C V and O'Handley R C 1996 *Phys. Rev.* B **53** R1729

[17] Lee J, Lauhoff G, Tselepi M, Hope S, Rosenbusch P, Bland J A C, Dürr H A, van der Laan G, Schillé J P and Matthew J A D 1997 *Phys. Rev.* B **55** 15 103

[18] Dhesi S S, Dürr H A and van der Laan G 1999 *Phys. Rev.* B **59** 8408

[19] Sacchi M, Mirone A and Iacobucci S 1999 *Surf. Sci.* **422** 349

[20] Ballentine C A, Fink R L, Arayapochet J and Erskine J L 1990 *Phys. Rev.* B **41** 2631

[21] Huang F, Kief M T, Mankey G J and Willis R F 1994 *Phys. Rev.* B **49** 3962
[22] Kramer I and Bergmann G 1983 *Phys. Rev.* B **27** 7271
[23] Frank K H, Dudde R, Sagner H J and Eberhardt W 1989 *Phys. Rev.* B **39** 940
[24] Tersoff J and Falicov L M 1982 *Phys. Rev.* B **26** 459
[25] Tersoff J and Falicov L M 1982 *Phys. Rev.* B **26** 6186
[26] Wang C S, Freeman A J and Krakauer H 1981 *Phys. Rev.* B **24** 1126
[27] Pourovskii L V, Skorodumova N V, Vekilov Y K, Johansson B and Abrikosov I A 1999 *Surf. Sci.* **439** 111
[28] Fu C L and Freeman A J 1988 *J. Physique Coll.* **49** C8 1625
[29] Zhu X and Hermanson J 1983 *Phys. Rev.* **27** 2092
[30] Jepsen O, Madsen J and Andersen O K 1982 *Phys. Rev.* B **26** 2790
[31] Norffke J and Fritsche L 1981 *J. Phys. C: Solid State Phys.* **14** 89
[32] Ernst A, van der Laan G, Temmerman W M, Dhesi S S and Szotek Z 2000 *Phys. Rev.* B submitted
[33] Wang C S and Freeman A J 1981 *Phys. Rev.* B **24** 4364
[34] Ericksson O, Fernando G W, Albers R C and Boring A M 1991 *Solid State Commun.* **78** 801
[35] van der Laan G, Hoyland M A, Surman M, Flipse C F J and Thole B T 1992 *Phys. Rev. Lett.* **69** 3827
[36] Wildberger K, Zeller R and Dederichs P H 1997 *Phys. Rev.* B **55** 10 074
[37] Uiberacker C, Szunyogh L, Újfalussy B, Weinberger P, Ernst A and Dederichs P H 1998 *Phil. Mag.* B **78** 423
[38] Szunyogh L, Újfalussy B, Weinberger P and Kollár J 1994 *Phys. Rev.* B **49** 2721
[39] Perdew J P and Wang Y 1992 *Phys. Rev.* B **45** 13 244
[40] Lindner J, Poulopoulos P, Wilhelm F, Farle M and Baberschke K 2000 submitted