Surface States of Cobalt Nanoislands on Cu(111)

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The electronic structure of thin Co nanoislands on Cu(111) has been investigated below and above the Fermi level (E_F) by scanning tunneling spectroscopy at low temperature. Two surface related electronic states are found: a strong localized peak 0.31 eV below E_F and a mainly unoccupied dispersive state, giving rise to quantum interference patterns of standing electron waves on the Co surface. *Ab initio* calculations reveal that the electronic states are spin polarized, originating from $d_{3z^2-r^2}$-minority and sp-majority bands, respectively.

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The properties of ultrathin magnetic films and nanostructures on nonmagnetic metal surfaces have been a matter of intensive research for decades. This is due to their unique properties such as enhanced magnetic moments, modified magnetic anisotropy arising from the interface, coupling phenomena, etc. There is a fascinating and delicate interplay between the structure of ultrathin films, which is often influenced by the underlaying substrate, and the resulting electronic and magnetic properties. The understanding of how the magnetism is governed by the electronic structure may help to control the magnetic properties of nanostructures, which is important to advance magnetic storage technology and other magnetoelectronics applications [1,2]. Cobalt thin films on Cu(111) are model systems for magnetic studies, but only few investigations focusing on the electronic structure have been reported thus far [3–6].

There has been some controversy in the literature regarding a surface state on Co(0001). Early photoemission experiments by Himpsel and Eastman identified an sp-like surface state below the Fermi level (E_F) at -0.3 eV [7]. This was confirmed in a recent scanning tunneling spectroscopy (STS) experiment by Okuno *et al.* [8], although the peak was found at a slightly different energy (-0.43 eV) and ascribed to a d-like spin-polarized surface state [8]. In contrast to these findings, a theoretical study by Braun and Donath did not predict any surface state in this energy range [9]. STS measurements of Co islands on Cu(111) by Vázquez de Parga *et al.* [6] also did not observe any spectral feature below E_F.

In this Letter, we present a combined experimental and theoretical study of cobalt nanoislands and thin layers on the Cu(111) surface. Using STS, we observe two surface related electronic features on the Co nanoislands on Cu(111): A free-electron-like, mostly unoccupied state visible to the scanning tunneling microscope (STM) through Friedel oscillations in the local density of states (LDOS) over a wide energy range, and an energetically localized state below E_F giving rise to a very intense and sharp peak in the LDOS. In order to identify the origin of these states, we performed *ab initio* calculations based on density functional theory (DFT) and the Korringa-Kohn-Rostoker (KKR) Green's function method for low-dimensional systems [10]. The calculations are found to be in good agreement with the experiment and show that the former observed state is an sp-majority state and the latter originates from mostly a $d_{3z^2-r^2}$-minority state with a contribution from an sp-minority state.

The experiments were carried out using a homebuilt ultrahigh vacuum (UHV, $P < 1 \times 10^{-10}$ mbar) low temperature ($T = 6$ K) STM equipped with a W tip [11]. The single crystal Cu(111) sample was cleaned in UHV by sputter-anneal cycles. Cobalt was evaporated with a rate of $\sim$0.1 monolayers(ML)/min at 290 K using an e-beam evaporator. Immediately after evaporation, the sample was cooled quickly in order to prevent intermixing of Co and Cu and segregation of Cu to the surface of the Co islands [12]. STS was performed to obtain differential conductance (dI/dV) maps and spectra, which are proportional to the LDOS [13], using a lock-in technique with a 4.6 kHz bias voltage modulation of 5–50 mV. All bias voltages given are sample voltages with respect to the tip.

The growth of Co on Cu(111) has been extensively studied. At room temperature, Co grows at lower coverage as compact islands of triangular shape and bilayer height above the Cu surface [14]. Furthermore, one Co layer is believed to be buried in the Cu surface, thus leading to 3 ML thick islands [15]. At higher coverage additional single layers of Co grow on top of the islands leading to 3D growth [16]. This emphasizes the necessity of using a local probe such as the STM to study Co islands on Cu(111). At lower coverage, Co continues the fcc stacking of the Cu substrate, whereas at higher coverages ($\gtrsim 5$ ML) bulklike hcp stacking dominates [17,18].

A typical STM image of Co islands grown on Cu(111) at low coverage is presented in Fig. 1(a). It shows the

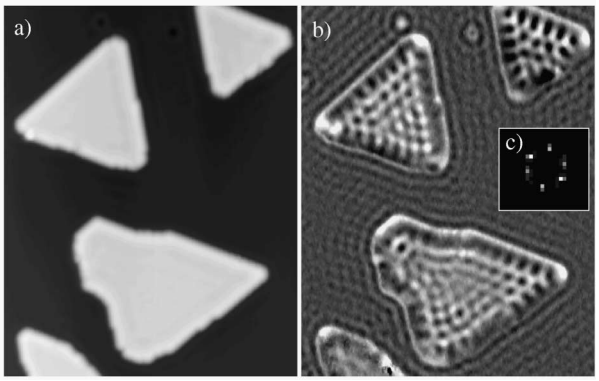

FIG. 1. (a) Constant-current image and (b) dI/dV map of 2 ML high Co nanoislands on Cu(111). The scan range is 32 nm $\times$ 41 nm and the tunneling parameters are $V = 0.5$ V, $I = 1.8$ nA. In the gray scale, brighter areas correspond to higher topography and larger LDOS, respectively. (c) Fourier spectrum of standing electron wave pattern on a Co island.

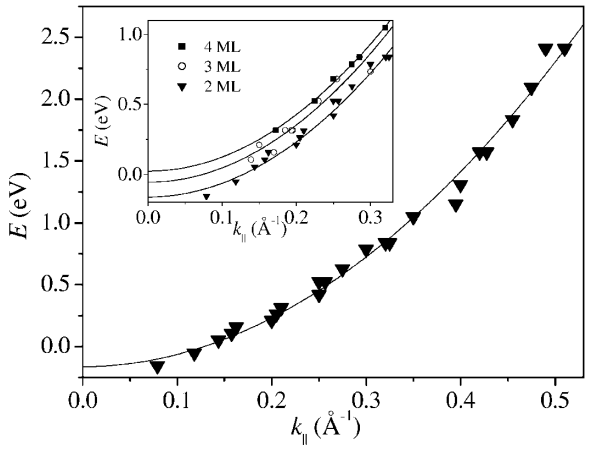

FIG. 2. Dispersion relation of the electronic state determined from standing electron waves on Co islands. The inset shows the coverage dependence of the dispersion. The solid lines represent parabolic fits. The fitting parameters E_0 and m^* are given in Table I.

well-known compact islands of triangular shape and bilayer height [14]. The two island orientations have been explained by initial nucleation on the two different threefold hollow sites of the Cu(111) surface, thus leading to a stacking fault at the interface for the one island orientation, whereas the other continues the exact fcc stacking of the substrate [6]. In Fig. 1(b), the simultaneously obtained dI/dV map is shown. On the Cu(111) surface, we observe the well-known standing wave patterns in the LDOS which are due to the quantum interference of surface-state electrons scattering off steps and defects [19,20]. We also observe a similar pattern of Friedel oscillations on the Co islands, evident of a free-electron-like surface state. dI/dV maps over a wide range of energies (-0.15 to 2.4 eV) showed a continuous variation of the wavelength of the standing wave pattern.

To analyze the dispersion of this state, the standing wave pattern was Fourier transformed and the corresponding parallel wave vector ($k_{\parallel}$) was determined [21]. Only the center part of an island was used, free of step edges. The Fourier spectrum [Fig. 1(c)] was isotropic (ring shaped) in the surface plane indicative of a free-electron-like state with isotropic effective mass [21,22], except for directions of increased intensity given by the shape of the island. The standing waves on a triangular shaped island thus gave a Fourier pattern of six distinct brighter spots lying on a ring. A radial average of the Fourier spectrum was used to determine $k_{\parallel}$. The uncertainty in the determination of $k_{\parallel}$, given by the full width at half maximum (FWHM) of the radial average, was about 10%. Care was taken to use islands large enough to contain at least five maxima in the standing wave pattern of the LDOS. The $E(k_{\parallel})$ dispersion is presented in Fig. 2. The data are perfectly fitted to a parabolic dispersion relation $E(k_{\parallel}) = E_0 + \hbar^2 k_{\parallel}^2/2m^*$, described by an onset just below the Fermi level at $E_0 = -0.16$ eV and an effective mass $m^* = 0.38 m_e$. All energies are relative to E_F. Islands of different shape, orientation, and size were investigated without finding any significant differences.

Evaporating larger amounts of Co on the Cu(111) surface results in 3D growth with single layers of Co on top of the bilayer high Co islands. It is thus possible with the STM to investigate a range of coverages in the same preparation. Figure 3 shows an STM image of Co layers at 2, 3, and 4 ML, where also patches of the free Cu(111) surface are still visible. The dI/dV signal in Fig. 3 has been combined with the topography. As on the bilayer high islands, the standing electron waves are also observed on the higher coverage Co islands. The dispersion relation of this electronic state has been determined for 3

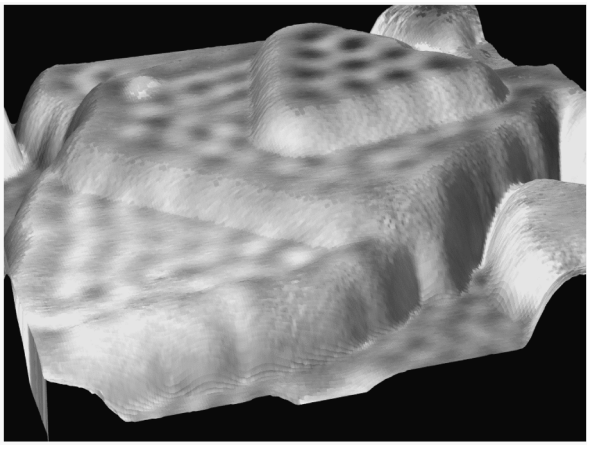

FIG. 3. Representation in 3D of the topography of a Co island on Cu(111), where the gray scale coding is given by the dI/dV signal at $V = 0.5$ V, $I = 1.1$ nA. The second, third, and fourth ML of Co as well as the Cu(111) surface are visible, with standing electron waves on all layers. The image size is 28 nm $\times$ 28 nm.

and 4 ML as described above, again using islands of sufficient size. We find again a parabolic dispersion (see inset of Fig. 2) with E_0 and m^* as listed in Table I, showing an unchanged effective mass and a small shift of the onset to higher energies with increasing coverage. Note that at 4 ML the state becomes completely unoccupied.

In order to interpret the experimental observations, we performed *ab initio* calculations of the electronic states for 2, 3, and 4 ML of Co on Cu(111). Our calculations are based on the local spin density approximation of DFT and the KKR Green's function method [10]. First, we treat the Cu surface as a two-dimensional (2D) perturbation of Cu bulk. Taking into account the 2D periodicity of the ideal surface, one can find the structural Green's function, using a Dyson equation. This is then used as the reference Green's function to calculate the Green's function of the perturbed system with the Co layer on the surface. The full charge density is taken into account. Self-consistent spin-polarized calculations are performed for the dispersion relation and the density of electronic states. Our study of the interlayer relaxations shows that the main results presented in this paper are not affected by relaxations.

Calculations for the Cu(111) surface give a surface-state band edge at $E_0 = -0.5$ eV and a surface-state Fermi wavelength $L = 30$ Å, in good agreement with the experiment [20]. For the Co monolayers on Cu(111), we find that the surface states are spin polarized. The quantum interference in the LDOS observed with the STM is due to scattering of sp majority electrons. Our calculations show that the majority sp states have a parabolic dispersion relation described by the theoretical parameters E_0 and m^* presented in Table I. The calculations are in agreement with the experimental results for all Co coverages. The trend of increasing E_0 with coverage is reproduced in the calculations. We expect the spin-polarized surface state to influence the surface magnetic properties of the Co islands. Furthermore, since the changing onset with coverage results in a varying density of the state below E_F, it allows us to control the contribution to the surface magnetism by varying the coverage.

The Co islands were further investigated by STS (Fig. 4). The dI/dV spectrum on the Co island consists of the (mostly unoccupied) electronic state described above, and a very pronounced and sharp peak in the LDOS at -0.31 ± 0.02 eV with FWHM $= 0.1 \pm 0.02$ eV. The errors given originate from averaging over a large number of spectra on many islands of varying size and orientation using different tips. We did observe a tendency that spectra of one island orientation have the peak centered ca. 0.03 eV lower than spectra taken on islands of the other orientation. Otherwise no significant dependence on island size or shape was observed. A state similar to the one reported here has previously been observed on Co(0001) [7,8]. Also, an additional feature at -1.1 eV is observed in our spectrum, believed to be due to the Co $3d$ bulk state [4]. To exclude any tip-induced effects, a reference spectrum on a clean part of the Cu(111) surface has been recorded with the same tip (see Fig. 4), reproducing the well-known onset of the surface state and being otherwise featureless [20]. Note that a similar clear onset of the free-electron-like surface state on the Co islands is difficult to detect since it is buried in the tail of the strong feature at -0.31 eV. The $dI/dV(V)$ spectra on the higher coverage islands have also been recorded. We find only small coverage effects where the peak energy remains constant and for both 3 and 4 ML we find an increased FWHM of ~40%, and a correspondingly decreased peak height keeping the overall integrated intensity unchanged relative to 2 ML.

Our calculations of the LDOS for the vacuum position above 2–4 ML Co on Cu(111) confirm the experimental results and show that the strong feature below the Fermi level is due to minority $d_{3z^2-r^2}$ states. As an example, we present in Fig. 5 the LDOS above 2 ML Co on Cu(111), which is in good agreement with the experiment. As shown in the inset of Fig. 5, the charge density distribution of the minority surface state at the $\bar{\Gamma}$ point has $d_{3z^2-r^2}$ character. Surface states of similar character have previously been observed with STS on, e.g., Fe(001), Cr(001) [23] and Co(0001) [8]. Here, however, the calculations

TABLE I. Experimental and theoretical data of m^* and E_0 for the dispersing surface state as a function of Co coverage [16] on Cu(111).

Co coverage /ML	E_0/eV (exp)	m^*/m_e (exp)	E_0/eV (theory)	m^*/m_e (theory)
2	-0.16 ± 0.03	0.38 ± 0.01	-0.17	0.42
3	-0.06 ± 0.05	0.37 ± 0.03	-0.15	0.40
4	0.04 ± 0.05	0.38 ± 0.02	-0.13	0.37

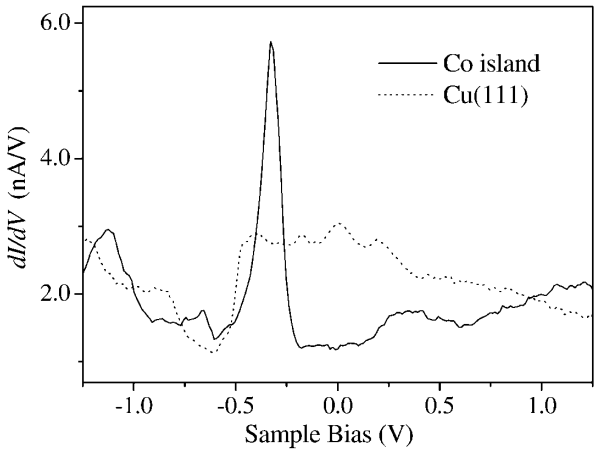

FIG. 4. STS spectra on 2 ML high Co nanoislands and on the bare Cu(111) surface taken with the same tip.

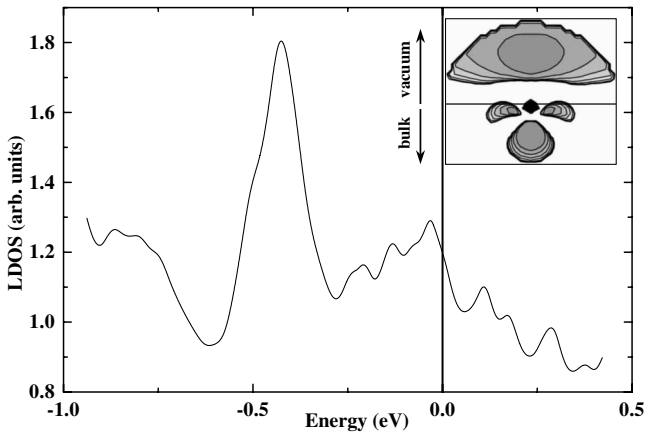

FIG. 5. Calculated LDOS 2.1 Å above a 2 ML Co film on Cu(111) [16]. The inset shows the charge density distribution of the minority $d_{3z^2-r^2}$ surface state at the $\bar{\Gamma}$ point in a (110) plane through the Co film.

show that a small minority sp contribution is present as well. Because of the spin-polarized nature of this state and the very strong intensity, we believe that the surface state observed in the present study may be of importance in tunneling magnetoresistance (TMR) devices [1]. The possible influence of hybridization of this state with the oxide spacer layer in a real TMR device has to be investigated in more detail, though.

Earlier (inverse) photoemission experiments on thin layers of Co on Cu(111) have concentrated on the bulk electronic structure [3,4] and the Fermi surface [5], and have not seen any of the surface related features reported here. They found only minor variations with coverage in the spectra around the Fermi level. For Co(0001), however, surface states of sp [7] and d [8] symmetry were observed. As our results show, both symmetries are present. On the other hand, a recent STM study by Vázquez de Parga *et al.* [6] observes no standing electron waves nor do they see a peak in the LDOS below E_F, but rather a smooth featureless spectrum. Contrary to our findings, they observe a significant difference between islands of different orientations, where the differential conductivity appears to be higher at positive energies for one island orientation. Whereas the sensitivity towards resolving the Friedel oscillations may be reduced since their experiment was performed at room temperature (RT), this seems an unlikely explanation for the absence of the peak. If the Co islands on Cu(111) in Ref. [6] have been prepared as previously by the same group [17], it is likely that intermixing as well as contamination of the surface from background adsorption with CO is the reason why none of the features presented here were observed, since surface states are known to be very sensitive to contaminations. We have measured spectra on islands grown at 345 K, where intermixing occurs, and on RT-grown islands followed by CO adsorption. In both cases we observed a strong suppression of the surface-state features.

In conclusion, we have investigated the electronic structure of Co nanoislands on Cu(111), where we identify two electronic features with STS. A mainly unoccupied state showed Friedel oscillations in the LDOS, which were used to determine its dispersion relation. Our *ab initio* calculations, which take into account the atomic arrangement at the interface and the interaction between Co layers and the Cu surface fully self-consistently, show that this state is an sp-majority state. The state shifts with coverage and is thus expected to have a coverage dependent influence on the surface magnetic properties. Furthermore, we observe an intense peak in the LDOS below E_F. This state is mostly due to a $d_{3z^2-r^2}$-minority band giving rise to a strong LDOS at the energy of its minimum.

[1] G. A. Prinz, Science **282**, 1660 (1998); J. Magn. Magn. Mater. **200**, 57 (1999).
[2] P. Gambardella *et al.*, Nature (London) **416**, 301 (2002).
[3] G. J. Mankey, R. F. Willis, and F. J. Himpsel, Phys. Rev. B **47**, 190 (1993).
[4] U. Alkemper *et al.*, Phys. Rev. B **50**, 17 496 (1994).
[5] J. Osterwalder *et al.*, Prog. Surf. Sci. **64**, 65 (2000).
[6] A. L. Vázquez de Parga, F. J. García-Vidal, and R. Miranda, Phys. Rev. Lett., **85**, 4365 (2000).
[7] F. J. Himpsel and D. E. Eastman, Phys. Rev. B **20**, 3217 (1979).
[8] S. N. Okuno, T. Kishi, and K. Tanaka, Phys. Rev. Lett. **88**, 066803 (2002).
[9] J. Braun and M. Donath, Europhys. Lett. **59**, 592 (2002).
[10] K. Wildberger *et al.*, Phys. Rev. Lett. **75**, 509 (1995).
[11] O. Jeandupeux *et al.*, Phys. Rev. B **59**, 15 926 (1999).
[12] A. Rabe *et al.*, Phys. Rev. Lett. **73**, 2728 (1994).
[13] J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985).
[14] J. de la Figuera *et al.*, Phys. Rev. B **47**, 13 043 (1993).
[15] M. Ø. Pedersen *et al.*, Surf. Sci. **387**, 86 (1997).
[16] The thickness of the Co islands will be given in ML above the Cu surface. The theory also includes a buried layer. Since the Co islands are modeled as films, this is equivalent to an additional layer and the theoretical results for a coverage n ML, as given in the text and table, is thus a calculation for $n + 1$ ML.
[17] J. de la Figuera *et al.*, Surf. Sci. **349**, L139 (1996).
[18] K. Heinz, S. Müller, and L. Hammer, J. Phys. Condens. Matter **11**, 9437 (1999).
[19] Y. Hasegawa and Ph. Avouris, Phys. Rev. Lett. **71**, 1071 (1993).
[20] M. F. Crommie, C. P. Lutz, and D. M. Eigler, Nature (London) **363**, 524 (1993).
[21] L. Petersen *et al.*, Phys. Rev. B **57**, R6858 (1998).
[22] Z. Song *et al.*, Appl. Phys. A **72**, S159 (2001).
[23] J. A. Stroscio *et al.*, Phys. Rev. Lett. **75**, 2960 (1995).