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2007 J. Phys.: Condens. Matter 19 305021

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Ab initio electronic and magnetic properties of 1 ML Fe/Cu(001)

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Received 5 February 2007, in final form 28 February 2007

Published 13 July 2007

Online at stacks.iop.org/JPhysCM/19/305021

Abstract

The electronic structure and magnetic properties of 1 ML of iron on Cu(001) have been calculated using the embedding method within the density functional theory framework. The surface features will be described as concerns binding energies, dispersion and spin dependence. The changes in surface electronic states and magnetization, induced at the interface by the overlayer growth, will be evidenced, also analysing the electronic properties of the constituent elements of the system, clean substrate and unsupported iron monolayer. The different energy ranges of the two spin components in the Fe film reflect upon very different degrees of hybridization of these states with the substrate ones. This suggests that the overlayer states can be a spin fixed channel for conductivity, with interesting applications in devices in which the current should depend on the carriers' spin.

1. Introduction

The appearance of electronic and magnetic properties without counterparts in bulk crystal systems or at clean surfaces is one of the peculiarities of ultrathin magnetic films grown on metallic substrates [1–3]. The interest in such systems is related to the capability of controlling both the electrical conductivity and the magnetic character appropriately coupling different materials. Indeed multilayers have found application in magnetic recording systems and, more recently, in spintronic devices [4–7]. From a fundamental point of view the relationship between magnetism and structure is still an open question, which stimulated much theoretical research in the last decade [8–10]. Among the large number of possible couples of substrate/film materials with magnetic behaviour, only a few systems have been fully characterized up to now [1, 11–13], and Fe on Cu is certainly one of the most studied, mainly from a structural point of view [14–18]. Because of the very similar lattice parameters, the fcc phase of iron can be grown on the (001) surface of copper with nearly no mismatch.

Nevertheless, low energy electron diffraction (LEED) and STM experiments [16, 17, 19] evidenced a great variety of structural and magnetic phases, depending both on film thickness and growth conditions. Besides a gradual transition from the fcc tetragonally distorted phase, in the initial stage of growth, toward the bcc bulk structure, the iron film exhibits also superstructures, in plane shift, and vertical buckling of atomic rows, which also affect magnetic properties. It is well known that interface quality, dependent on the growth conditions and deposition technique used, strongly influences the magnetic behaviour. A pseudomorphic layer by layer growth can be obtained by pulsed laser deposition (PLD), with a low repetition frequency [20], as an alternative to the traditional thermal deposition, which favours the formation of three-dimensional islands (Volmer–Weber growth) or an inverted Cu/Fe configuration for the high or low deposition rate, respectively [21].

Despite the relevant number of studies on the Fe/Cu(001) system, to our knowledge none of them is centred on the investigation of spin-dependent adlayer-induced electronic features and their consequences on the magnetic properties of the film. In particular, the existing theoretical investigations mainly concentrate on the atomic structure and the relative stability of the different magnetic phases of the film [22, 23]. With this background, our purpose is to investigate the electronic structure of the Fe-covered Cu(001) surface by means of theoretical calculations, paying particular attention to its spin dependence.

In order to characterize the electronic structure of the Fe/Cu(001) system it is opportune to distinguish between bulk-related features and surface specific states; among the latter it is useful to separate the copper contributions from those strictly due to the overlayer. For this reason we also present in this paper the analysis of the semi-infinite clean Cu(001) surface and of an unsupported monolayer of iron. These results are finally used as a tool to investigate the interacting system constituted by the adlayer on the substrate.

The paper is organized as follows. In section 2 the theoretical framework will be presented together with the structural parameters of the system. In section 3 the electronic structure of the clean Cu(001) surface will also be discussed in comparison with results of recently performed experimental investigations. Section 4 will be devoted to the analysis of the electronic and magnetic properties of one monolayer (ML) of Fe/Cu(001), also by means of the information we have deduced from the model system represented by the unsupported iron monolayer. Section 5 is devoted to the conclusions.

2. Theoretical approach and structural parameters

In order to carry out a first principles study of the electronic properties of the Fe/Cu(001) metal surface, we used the embedding method of Inglesfield [24], with the implementation proposed by Ishida [25]. The distinctive feature of this method, based on the Green's function formalism, consists in its ability to treat a really semi-infinite system, including in the Hamiltonian an additional potential which accounts for the presence of the extended substrate. The improvement of this framework with respect to the commonly used supercell method is the capability of describing the true continuum of states and also the absence of spurious effects induced by the fictitious finite size of a substrate modelled with a slab.

In the embedding method the Schrödinger equation, or the Kohn–Sham one within the density functional scheme, is solved in the surface region only; such a restricted volume, in which the Green's function is calculated self-consistently, is called the 'embedded region' and is set up so as to include the perturbation due to the surface or the interface which breaks the periodicity along z . In metallic systems the efficient electronic screening allows one to consider as perturbed only a few surface layers. We have included in the embedded region only the two topmost copper layers for the clean surface calculation and a third one in addition when the Fe

overlayer is considered. Towards the vacuum, the surface perturbation is contained in a region of 5.3 Å width, also included in the embedded region.

The atomic positions of the Cu clean surface follow the geometry of the (001) face of the fcc lattice ($a_{\text{fcc}} = 3.61$ Å). As concerns Fe atoms in the 1 ML thick film, their location is chosen assuming an epitaxial growth. The primitive Cu(001) surface unit cell, in fact, can also be used as unit cell to describe the Fe covered surface since, as explained above, the adsorption geometry of the iron film can be modelled as pseudomorphic at this coverage, which corresponds to the epitaxial growth stage. The distance between the topmost Cu layer and the Fe one is 1.82 Å, while the geometry of the underlying Cu substrate corresponds to the unrelaxed fcc one.

The surface Brillouin zone (SBZ) has been sampled by a 14×14 mesh in reciprocal space corresponding to 36 independent k points. In the implementation adopted in this work the matrix elements of the Hamiltonian are evaluated using the full potential and a linearized augmented plane wave (LAPW) basis set, with 18.1 Ryd as cut-off and taking the spherical expansion inside the muffin tins up to $l_{\text{max}} = 8$. All the results are obtained within a generalized gradient approximation (GGA-PBE [26]) for the exchange and correlation potential.

3. Clean Cu(001) surface

The (001) surface of copper has been widely studied in the past both from a theoretical and experimental point of view [27–34]. Although the surface electronic structure of this system is already well known, its theoretical analysis is however a useful step, particularly in the investigation of more complex adsorption systems, in which the clean copper surface has the role of the substrate. Indeed, through the detailed analysis of the electronic features of Cu(001), it will be possible, in a second step dealing with the Fe film, to distinguish between substrate and iron contributions.

The electronic band structure of the clean Cu(001) surface has been recently mapped along $\overline{\Gamma X}$ and $\overline{\Gamma M}$ directions by means of high resolution ultraviolet photoelectron spectroscopy (HRUPS) [31], which detected some surface states never observed experimentally. The experimental findings were compared with theoretical electronic structure, calculated by a supercell method. As already underlined, the embedding method is able to give an improvement into the theoretical description of the continuum of states, allowing a better comparison with the real system.

Firstly in figure 1 we present the density of states (DOS) in the surface Brillouin zone for two different integration volumes: the surface and subsurface atoms. The energy range between -4.5 and -1.5 eV is occupied by d states while the sp contribution, more delocalized, extends on the whole considered energy range, also beyond the Fermi level. At a first glance the increase of the spectral weight in the higher energy part of the d band due to the reduction of coordination for the surface atom with respect to the subsurface one is evident.

In order to characterize the electronic spectrum, including bulk states and surface features, it is necessary to take into account the k_{\parallel} dependence of the DOS and hence to refer to the surface band structure. In fact, in general such k_{\parallel} resolved DOS shows either discrete peaks or broader features whose different localization in energy can correspond to different spatial localization of the electronic states. In figure 2 the surface density of states of Cu(001) at the SBZ high symmetry points $\overline{\Gamma}$, \overline{X} , and \overline{M} is reported. The labels used for the surface features are taken from [31]. It is immediate to distinguish between surface/resonant states (solid line) and the contributions from the bulk states (dashed line), which, in general, are spread over a large energy range. Of course, such assignment is confirmed by the analysis of the spectral weight also in the subsurface layer to ascertain the region where the features are spatially located. The

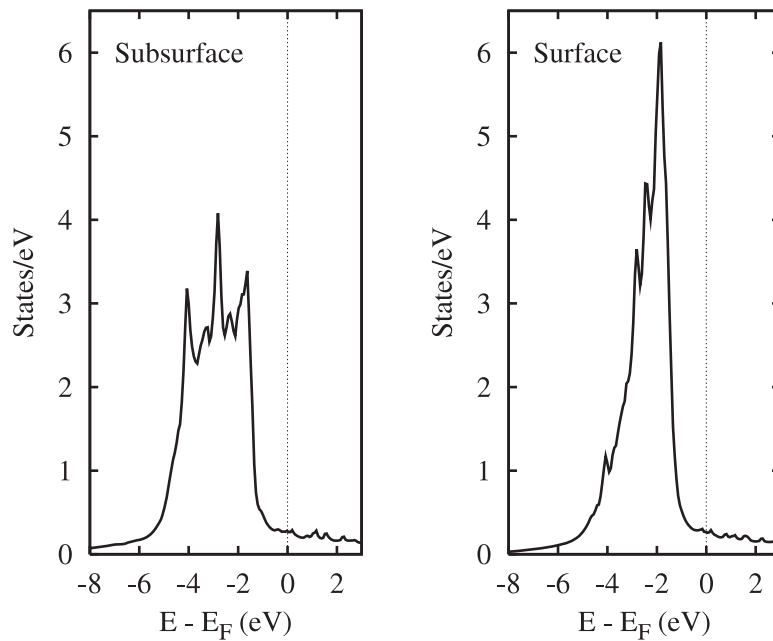


Figure 1. DOS evaluated on the subsurface and surface atom of the clean Cu(001). The reduction of atomic coordination is reflected in the displacement of spectral weight toward higher energies.

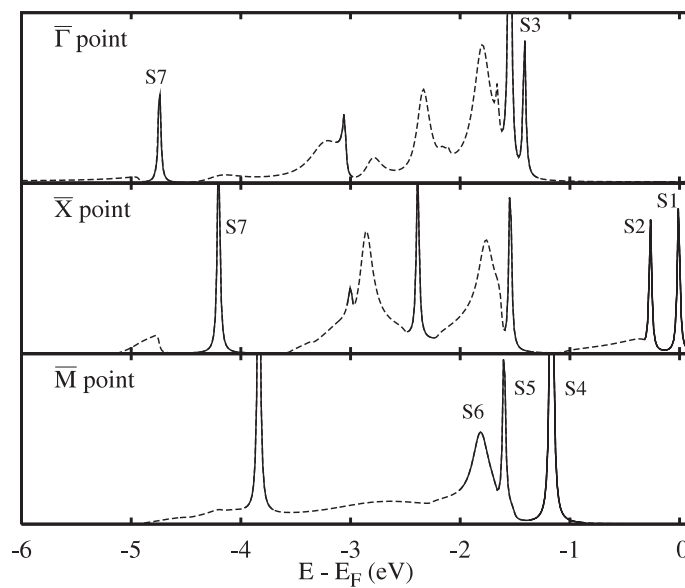


Figure 2. Surface density of states of clean Cu(001) at the high symmetry points: $\bar{\Gamma}$, \bar{X} , and \bar{M} . The surface features are reported with a solid line while the bulk contributions are drawn using dashed lines.

agreement with the previously reported theoretical calculation is very satisfactory, once one knows that in a supercell approach a threshold for the percentage of spectral weight required to be a ‘surface state’ must be fixed in a somewhat arbitrary way.

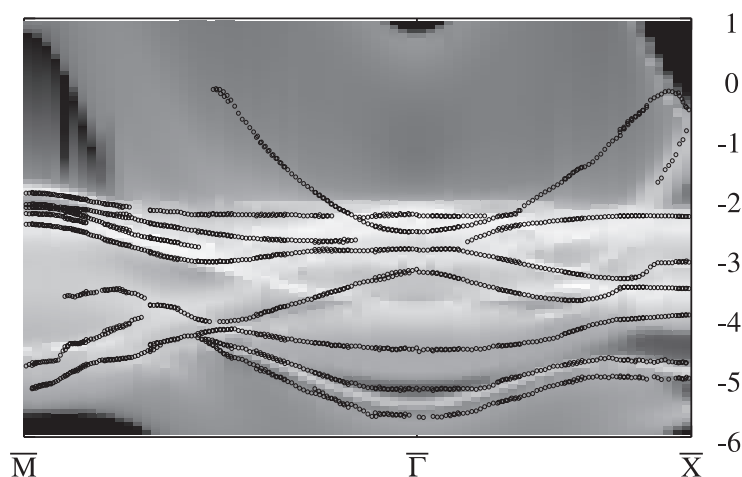


Figure 3. Clean Cu(001) surface: energy dispersion along $\overline{M\Gamma X}$ path in the surface Brillouin zone (with a rigid shift of 0.7 eV towards lower energies). Experimental dispersion has been superimposed (circles).

To display the electronic dispersion along a high symmetry path in the SBZ, a top view of the k_{\parallel} resolved DOS is a useful tool which allows one to evidence also the DOS intensity using a grey scale. In figure 3 the electronic dispersion obtained for the clean Cu(001) surface is shown. Different grey shades correspond to different intensities of the k_{\parallel} resolved DOS, namely dark areas describe in general small density of states until a threshold black colour, which represents energy gaps; bright areas describe instead large DOS values and report intense and in general discrete features, which may be surface states. The bulk continuum of states is of intermediate brightness. In order to compare our results with those reported in [31] (circles), we have shifted the former ones by 0.7 eV to lower energies. This error in the energy position of features which actually are quasi-particle properties has to be ascribed to the systematic error introduced by DFT methods and it has been exhaustively explained by Marini *et al* [35]. We find a good agreement with experimental results, both for binding energies and dispersion.

4. 1 ML Fe/Cu(001)

The electronic and magnetic properties of 1 ML Fe/Cu(001) are strictly related to the low dimensionality of the adlayer and to the different effect that the substrate–film interaction has on the two spin components. In order to investigate the former aspect we refer to figure 4, which presents the calculated Fe DOS as a function of reduction of the atomic coordination. The DOS of 1 ML Fe/Cu(001) (panel (b)) exhibits, differently from the Fe bulk case (panel (a)), a completely filled majority spin d band due to a band narrowing ascribable to the low coordination of overlayer Fe atoms. A similar spectral weight displacement also affects the minority spin d component, with a resulting change in occupancy. As a consequence of such different band filling, the magnetic moment per atom, equal to $2.84 \mu_B$, is enhanced with respect to the bulk value ($2.12 \mu_B$).

This trend is also confirmed by the DOS of the unsupported monolayer of iron (panel (c)), characterized by a more enhanced unbalancing of the spin components, which gives a magnetic moment of $3.02 \mu_B$. The minute discrepancy between the two latest results suggests that the presence of the substrate probably does not supply a considerable variation of film electronic properties.

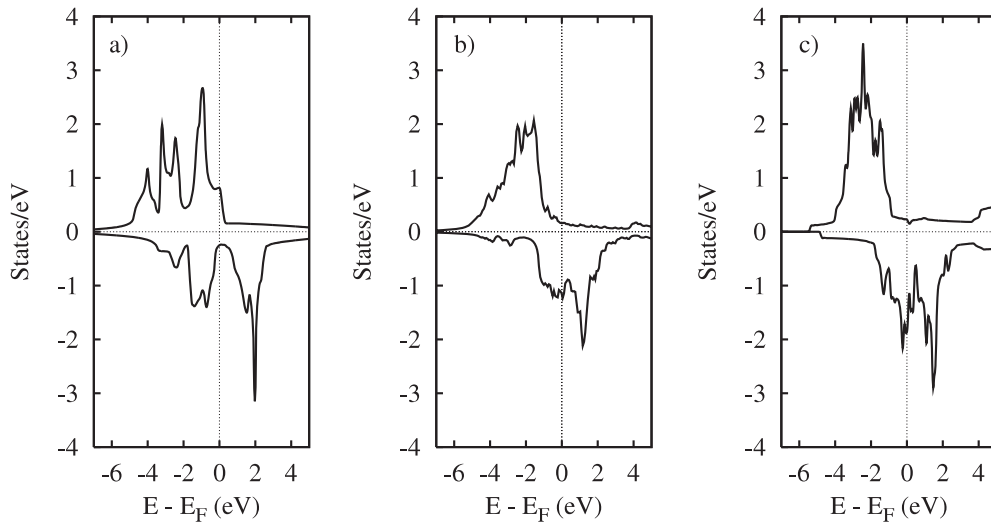


Figure 4. DOS for Fe in three different systems: bulk, adlayer on Cu, and unsupported monolayer.

In order to better clarify the role and extent of substrate–film interaction it is useful to refer to figure 5, which reports the dispersion relation along $\overline{M}\Gamma\overline{X}\overline{M}$ of 1 ML Fe/Cu(001). The differences with respect to the clean Cu(001) surface are mainly due to d-like Fe states that can be recognized as bright lines in the colorimetric map. The nearly complete correspondence between these states and the calculated band structure of a not supported iron monolayer (superimposed black lines), both in binding energy and dispersion, allows one to conclude that all these features are mainly due to the two-dimensional interaction between Fe atoms on the surface. The presence of copper has the effect of shifting some bands in energy, without significant modification of their dispersion. We verified that the more strongly modified bands correspond to those having a pre-eminent out of plane character. They can more easily interact with the substrate and also feel the symmetry change caused by the presence of the semi-infinite substrate on one side only. Although the substrate–film interaction is small, the charge transfer between the substrate and the film gives rise to a weak reduction of the work function. It becomes equal to 4.44 eV, while that for the clean surface is 4.61 eV, which is in agreement with the experimental work function of 4.63 eV [36].

Another peculiarity of electronic band structure concerns the hybridization between adlayer and substrate states, strictly dependent on their mutual energy position. The superposition of states with the same spin and symmetry gives rise to different broadening in the surface features for the two spin components which is reflected in different sharpness of bright lines in figure 5. In order to better evidence this aspect we refer to figure 6, which reports the DOS at $\overline{\Gamma}$ evaluated in the film. In particular, the Fe majority d states are in the same energy range of the substrate d band. This energetic correspondence reflects upon the hybridization of iron states with those of Cu, giving rise to surface resonances. In contrast, minority d states occupy an energy range in which substrate features are completely absent (gaps) or have different symmetries. The hybridization is then prevented by this energy-symmetry barrier, which confines iron states in the overlayer, making them discrete-like quantum well states. Also the states due to the Cu substrate cannot penetrate into the Fe adlayer, making this an efficient barrier but only for the minority component. Spin polarized quantum well states have been already observed in non-magnetic spacers between magnetic multilayers, where they are

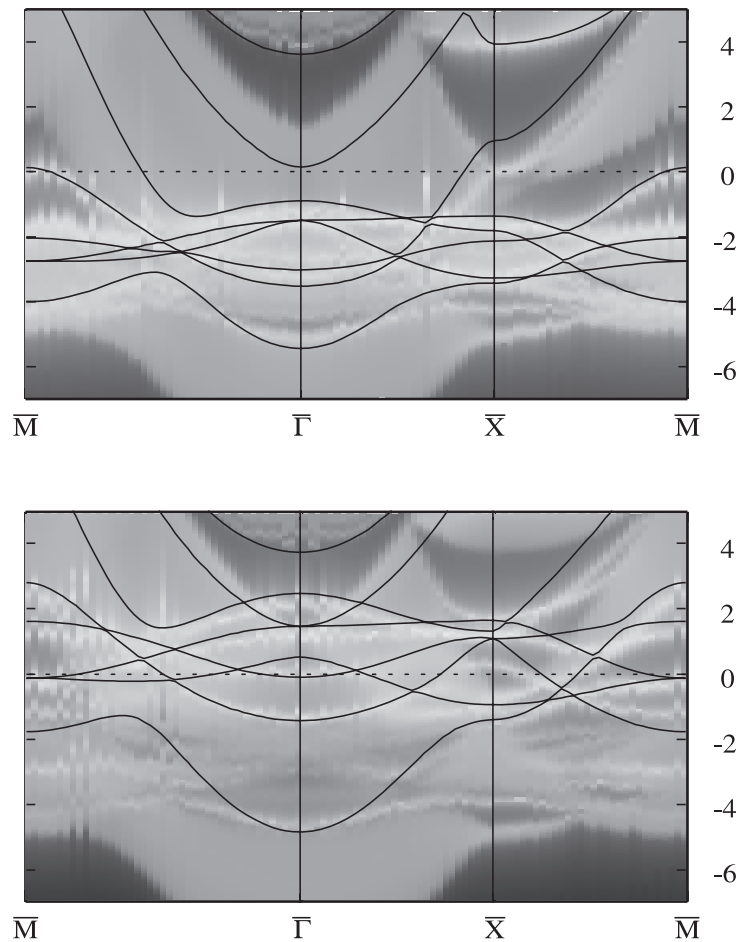


Figure 5. Energy dispersion of 1 ML Fe/Cu(001) along $\overline{M}\Gamma\overline{X}\overline{M}$ in comparison with the band structure calculated for a unsupported Fe monolayer, along the same path. Majority and minority spins are reported in the upper and lower panels, respectively.

considered mainly responsible for indirect magnetic coupling [12, 37]. The straight relation between their energy position and the ‘well width’, represented by the film extension, leads to the tunability of minority spin electronic properties simply by varying the film thickness.

5. Conclusions

In this work we have investigated the variation of electronic and magnetic properties of 1 ML Fe/Cu(001) as a consequence of dimensionality reduction and interaction with the substrate. By means of a comparative analysis of the band structure of single constituent elements (copper substrate and not supported monolayer) and that of the whole system we have deduced a very weak film–substrate interaction, almost completely restricted to symmetry aspects. In addition, the magnetic character of the overlayer led to different surface band structure for the two spin components and to the appearance of spin fixed quasi-discrete features which originate directly from the confinement of the wavefunction in the overlayer.

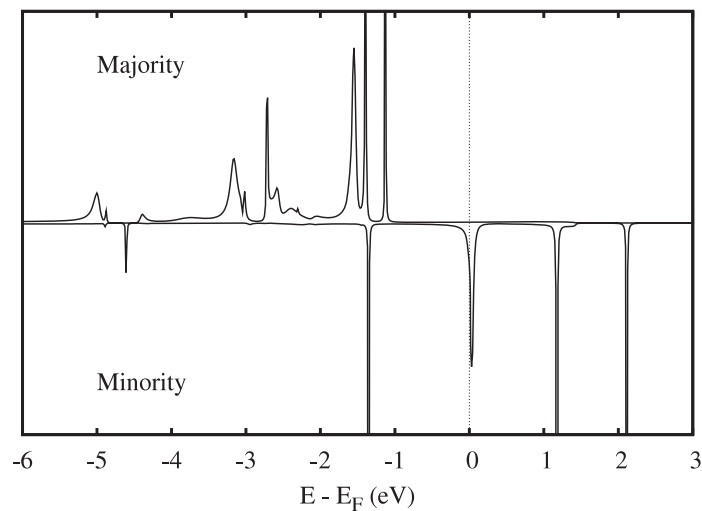


Figure 6. Surface density of states of 1 ML Fe/Cu(001) at the $\bar{\Gamma}$ point for both the majority (upper panel) and the minority (lower panel) components.

The capability to diversify and easily control the behaviour of majority and minority spin populations is the fundamental aspect on which experimental and theoretical research in spintronics focused. Consequently, the ultrathin Fe film on Cu(001) reveals surface electronic properties that could find application in production of spintronic devices.

Acknowledgment

This work was supported by the EU Network of Excellence NANOQUANTA (grant No NMP4-CT-2004-500198).

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