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Cobalt impurities on noble-metal surfaces

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First-principles calculations, based on the local-spin-density approximation, are performed for cobalt atoms deposited on noble-metal surfaces. The local density of states at the cobalt site shows a narrow peak at the Fermi energy, which is of minority spin and *d* character. The *d* orbital of $m=0$ symmetry, which must be mostly responsible for tunneling conductance from this surface site, makes a substantial contribution at E_f. Due to hybridization the same peak also appears, but reduced, at neighbor atoms. This result can be used for the interpretation of recent cryogenic scanning tunneling microscopy experiments. [S0163-1829(99)02113-X]

The local electronic structure of an isolated magnetic atom in a nonmagnetic host has been a subject of interest for over 30 years. It is usually referred to as the Kondo problem, and the theoretical interpretation of the data is that the local spin of the magnetic impurity is screened by the host metal electrons giving rise to a many-body ground state.[1] However, only very recently have there been indirect measurements of this local electronic structure, on a surface, using a scanning tunneling microscope (STM).[2] The system studied has isolated cobalt atoms deposited onto the (111) face of a clean gold crystal at 4 K. These experiments show that the tunneling conductance has a very narrow feature (10 meV) that appears only when the tip is over the Co atom and decreases to zero within a radius of less than 10 Å from it. It is therefore interesting to perform an electronic structure calculation specially designed to reproduce as closely as possible the experimental situation.

We show in this paper that the local densities of states obtained from *ab initio* calculations using the local-spin-density approximation (LSDA) also have a very strong feature at the Fermi energy. A large peak appears in the local density of states of the adsorbed Co atom, of *d* character and minority spin, that is due to the reduced number of neighbors of the adsorbed atom and by hybridization it also shows up in the local densities of states of neighboring Au atoms. The width of the Co minority *d* band is about 400 meV but the peak at E_f is an order of magnitude narrower, of the order of the precision of *ab initio* calculations, and could be related to the feature seen by the STM experiments.

To attempt a band-structure study of a system with impurities one has two possibilities: to start from a disordered alloy, treated with an approximate method such as the coherent potential approximation, and eventually let the impurity concentration go to zero, as in Ref. 3, or to use periodic systems with increasingly large unit cells as for example in Ref. 4. We have chosen this last procedure, for simplicity and also to avoid further approximations. The surfaces are represented by using repeated slabs, thus forming a system which is periodic in three dimensions, the succesive slabs being separated by enough empty space so that they do not interact with each other. The larger the unit cell in the lateral direction the more dilute the alloy can be, and therefore the closer the calculation to the experimental set up, where Co atoms are separated by 6 Å or more.

We have performed calculations for systems with up to four atoms per layer and up to seven layers in the unit cell, separated by the same width of empty space. We use the WIEN97 code,[5] which is an implementation of the linearized augmented plane-wave method, based on density-functional theory. The local-spin-density approximation (LSDA) for exchange and correlation as given by Perdew and Wang[6] is used and scalar-relativistic effects are included in the calculations.

Several systems have been studied, all of them containing Co atoms, either adsorbed or embedded in Au and Ag slabs. We show here the results for one calculation of that type, that attempts to represent as closely as possible the experimental setup of Ref. 2. The unit cell has five layers of Au atoms, with three atoms in each layer. One Co atom is located on each side of the slab at one of the hollow sites of the Au(111) slab structure forming a $\sqrt{3}\times\sqrt{3}$ adsorbed layer. The Co position is relaxed in the direction perpendicular to the surface, giving a nearest-neighbor Co-Au distance of 2.42 Å. The distance between Co and Au (Ag) atoms, optimized for different crystal structures containing these atoms, is always very close to the average between Co-Co and Au-Au (Ag-Ag) distances in their corresponding equilibrium structures. However, when relaxing the position of an adsorbed atom in a system with a large unit cell, so that it is almost isolated, it ends up being about 10% closer to the substrate. The distance between adsorbed Co atoms is 4.98 Å, quite close to the experimental 6 Å. For this calculation we used a muffin-tin radius of 2.2 a.u. for both metals and 600 **k** points in the Brillouin zone. We have proved for systems with smaller

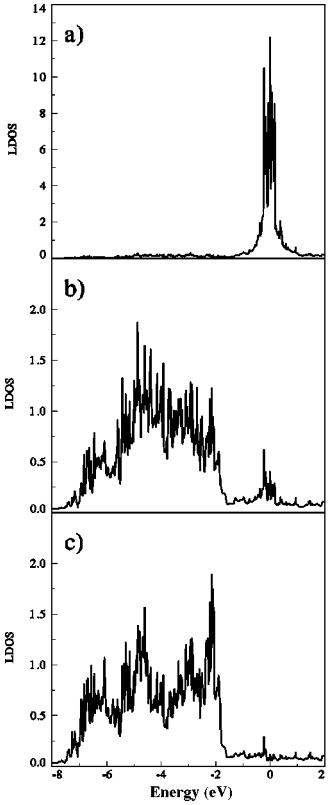

FIG. 1. Local minority-spin densities of states for Co adsorbed on the (111) Au surface. Energies are in eV and referred to the Fermi energy. (a) at the Co atom, (b) at the Au atom, nearest neighbor to the Co atom, (c) at the Au atom, second-nearest neighbor of Co.

unit cells that the relevant features of the densities of states, such as width and position of the peaks with respect to the Fermi energy, do not significantly change with increasing number of plane waves. We therefore use in this calculation $RK_{\mathrm{max}}=7$, which gives matrices of size 1900 to be diagonalized.

Figure 1 shows the local densities of states of minority spin at the Co site and at the Au atoms in the surface and in the first underlayer. These are computed by means of the modified tetrahedron method[7] with an energy mesh of 0.001 Ry. Plots similar to these were obtained for slabs grown in the (001) direction and for Ag atoms instead of Au atoms. Complete adsorbed layers and superlattices of repeated layers of Co and Au (or Ag) have also been studied. In all the cases Co atoms have the majority-band completely filled and when they are on the surface the local magnetic moment is higher than in the bulk, between 1.7 and $2.0\mu_B$, while it decreases to about $1.4\mu_B$ when they are impurities embedded in the nonmagnetic bulk. These results agree with previous calculations.[8–10] Due to the large magnetic moment, and in order to preserve the number of d electrons, the minority d band must contain the Fermi energy and due to the small hybridization with Ag or Au it should be narrow. For adsorbed atoms there are two further narrowing effects, one is the smaller number of neighbors at the surfaces, the other is of symmetry character, as the crystal field changes in this case with respect to the bulk, leaving the $m=0$ orbitals really on top of E_f. Our main point is that only when there are nearly isolated adsorbed atoms of Co in the surface is there a narrow and very strong peak in the energy range covered by the recent experimental results,[2] 0.1 eV on either side of E_f. The symmetry of this peak is of mixed d character, containing contributions of the different d orbitals. However, the orbital with $m=0$, which is assumed to contribute most to the STM image,[11] is included there and its partial density of states is peaked at the Fermi energy, as can be seen in Fig. 2.

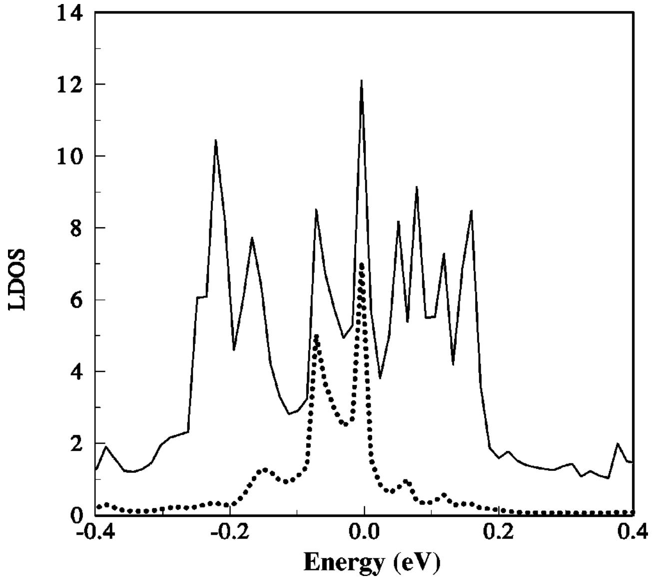

FIG. 2. Same as Fig. 1(a) but enlarged around E_f. The dotted curve is the d partial density of states with $m=0$ symmetry.

For Co-Cu superlattices similar results have been shown in previous calculations,[12] but in that case the peaks are not so narrow as the hybridization is larger, due to the proximity of Co and Cu $3d$ bands and also to the similar nearest-neighbor distances in bulk Cu and Co. For these reasons one would not expect a similar experimental result for Co impurities on a Cu surface.

For the interpretation of STM experiments it is usually assumed that the conductance dI/dV is directly proportional to the local densities of states . However, it has been recently suggested that the tunneling conductance may be itself calculated,[13,14] for instance using the Kubo formula, in the same way as the CPP (conductance perpendicular to the plane) for multilayers. These authors noted that in cases where localized states (impurities, surface states, interface states, quantum-well states, etc.) appear at E_f, the dependence with the density of states is more complicated.

In the system under study, as the d bandwidth of the adsorbed atoms is of competing magnitude with the value of the screened Coulomb interaction for $3d$ metals, we are in the limit for an LSDA calculation. In it, the electronic correlation is considered only in a mean-field approximation, and a better consideration of this effect would produce a further narrowing of the band at E_f. However, we believe that the partial densities of states of adsorbed Co atoms on the Au (111) surface, in the LSDA approximation, which show a narrow peak at E_f of minority spin and d character, give the basic information for the interpretation of the STM feature experimentally observed.

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