Unusual Kondo Physics in a Co Impurity Atom Embedded in Noble-Metal Chains

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We analyze the conduction bands of the one dimensional noble-metal chains that contain a Co magnetic impurity by means of *ab initio* calculations. We compare the results obtained for Cu and Ag pure chains, as well as O doped Cu, Ag and Au chains with those previously found for Au pure chains. We find similar results in the case of Cu and Au hosts, whereas for Ag chains a different behavior is obtained. Differences and similarities among the different systems are analyzed by comparing the electronic structure of the three noble-metal hosts. The *d* orbitals of Cu chains at the Fermi level have the same symmetry as in the case of Au chains. These orbitals hybridize with the corresponding ones of the Co impurity, giving rise to the possibility of exhibiting a two-channel Kondo physics.

Index Terms—Magnetic properties, nanostructures, nanowires.

I. INTRODUCTION

ONE of the most exciting areas of research in the last few years is the realization of pure one-dimensional (1-D) systems, as they open the possibility of studying not only theoretically but, also experimentally, the characteristic features triggered by low dimension that involve electronic transport, correlation and magnetic properties. Atomic-size contacts and nanowires can now be obtained by scanning tunneling microscope or in mechanically controllable break junctions experiments (MCBJ) [1]. It is with this last technique that it has been possible to create monoatomic chains of Ir [2], Pt [1] and Au [3]–[5]. Recently, it has been also demonstrated that impurity-assisted chain growth leads to a strongly enhanced tendency towards chain formation, when compared to pure noble-metal (NM) chains. In particular, *p*-like impurities, like N or O, lead to high chain elongation probabilities due to the strong directional bondings [6]–[11]. Given these experimental outstanding achievements, a new generation of nanodevices can in principle be conceived and designed to be used as tools for detecting nanomagnetism by conductance measurements through atomic metal contacts. One can indirectly sense the presence of magnetism by detecting zero-bias anomalies, while doing conductance measurements through an atomic contact. The origin of these zero-bias anomalies is usually due to Kondo screening of the spin, if a magnetic impurity is bridging the contact.

One of the prototype magnetic impurities in idealized models and computational simulations is Co atoms, as they develop a wide range of spin moments depending on the metal host and the dimensionality with usually high enough Kondo temperatures. Co impurities in Au, Ag and Cu surfaces have been extensively studied for several years and they are still the focus of research. Recently, Prüser and coworkers analyzed the Kondo resonance at Co atoms buried below a Cu(100) surface by map-

ping the local density of states of the surface itinerant electrons [12] and Surer *et al.* developed a multiorbital Kondo model to investigate the physics of Co atoms in Cu hosts [13]. On the other hand, Co impurities in noble-metal chains are interesting in order to study how the reduced dimensionality could lead to different and novel transport and magnetic properties and in this way eventually form part of a nanomagnetism detecting nanodevice.

In a previous work, we found that non-Fermi liquid behavior qualitatively similar to that of the two-channel Kondo (2CK) model is expected in a system of a Co impurity embedded in a Au chain which is in contact with Au leads, which break strongly enough the symmetry of the chain, reducing it to a four-fold one [14]. The proposed setup might be realized in break junction experiments if the symmetry of the contacts can be controlled or in STM experiments on (100) noble-metal surfaces.

In this contribution, we want to analyze if the same physical trends, that is, the presence of the 2CK physics and the non-Fermi liquid behavior, could be obtained when instead of Au chains we introduce a Co impurity in Cu and Ag chains. As mentioned previously, these last noble-metal chains could be stabilized by introducing light environmental nonmagnetic impurities in the experimental atmosphere [11]. With this purpose, we obtain and analyze the electronic structure of these metallic systems. In the case of Cu chains we check if the presence of stabilizing O atoms could destroy or not the eventual presence of a 2CK effect.

The paper is organized as follows. In Section II, we briefly recall the ground state properties of a Co impurity in a Au host, related to the Kondo effect. In Section III, we provide the details of our DFT first-principles calculations and analyze the band structure of the different noble-metal hosts and the consequences of these structures on the systems with an embedded Co impurity. Finally, a summary and conclusions are given in Section IV.

II. CO IMPURITY WITHIN AU CHAIN: KONDO EFFECT

A magnetic impurity of Co embedded in a Au chain, under a four-fold symmetry breaking field B, exhibits different trans-

port properties depending on the specific geometry of the leads [14]. The Co atom embedded in an Au chain has a total spin $S = 3/2$ in a $3d^7$ configuration. One d hole is shared by the half filled $3d_{xy}$ and $3d_{x^2-y^2}$ (Δ_4-symmetry), while the other two are in the empty and degenerate $3d_{xz}$ and $3d_{yz}$ (Δ_3-symmetry). On the other hand, the $5d_{xz}$ and $5d_{yz}$ of the pure Au chains are also degenerate and close to the Fermi level and will be pushed up by the presence of O impurities. Therefore, these represent two identical conduction bands that can screen the $S = 1/2$ spin of the $3d_{xz}$ and $3d_{yz}$ holes of Co. On the contrary, there is no density of states of Au with Δ_4 symmetry at the Fermi level that could be hybridized with states of the same symmetry at the Co site, leading to a frozen charge in the $3d_{x^2-y^2}$ and $3d_{xy}$ levels.

In the presence of B and in the absence of spin-orbit coupling, the microscopic model that describes the system consists of a spin 3/2 hybridized with two triplets of the d_8 configuration through two conduction channels (the $5d_{xz}$ and $5d_{yz}$ of Au) [14]. The corresponding physics is similar to that of the under-screened Kondo or Anderson models [15], [16]. However, the spin-orbit coupling induces a splitting D between the states with projection $M = \pm3/2$ and $M = \pm1/2$. This splitting has been calculated solving exactly the $3d^7$ configuration of Co including all correlations of the d shell [17]. For a negative D, larger than the characteristic Kondo temperature, the doublet $M = \pm3/2$ is lower in energy than the $M = \pm1/2$ one and, therefore, the two conduction bands cannot change the local $M = -3/2$ into the $M = +3/2$. Thus, the spin flip process of the Kondo effect is inhibited.

On the contrary, for positive D, which is the case for large enough B [14], the $M = \pm1/2$ doublet is lower in energy than the $M = \pm3/2$ one, being overcompensated by the two Δ_3 conduction leads. This overcompensation is usually the appropriate scenario to obtain experimentally the well-known 2CK physics [18]–[21], and similar physics is in fact confirmed by detailed calculations using the numerical renormalization group in the model [14]. In particular, the low-temperature entropy is $\ln(2)/2$ and the conductance through the device displays a $T^{1/2}$ behavior. However, the model presents some differences with the 2CK one. For example, the conductance at zero temperature is less than expected due to some degree of intermediate valence [14].

While the properties of the ground state, underscreened or overscreened Kondo physics, are determined by the symmetry properties of the leads and the strength of the four-fold crystal field B, the crucial point for observing the Kondo effect is the presence of $5d_{xz}$ and $5d_{yz}$ density of states of Au at the Fermi level. It is not obvious that the same trends can be obtained when chains of other materials are used.

III. RESULTS

We perform *ab initio* calculations based on spin polarized density functional theory (SP-DFT) using the full potential linearized augmented plane waves method, as implemented in the WIEN2K code [22]. The generalized gradient approximation for the exchange and correlation potential in the parametrization of PBE and the augmented plane waves local orbital basis are used. The cutoff parameter which gives the number of plane waves in the interstitial region is taken as $\mathrm{Rmt} * \mathrm{Kmax} = 7$,
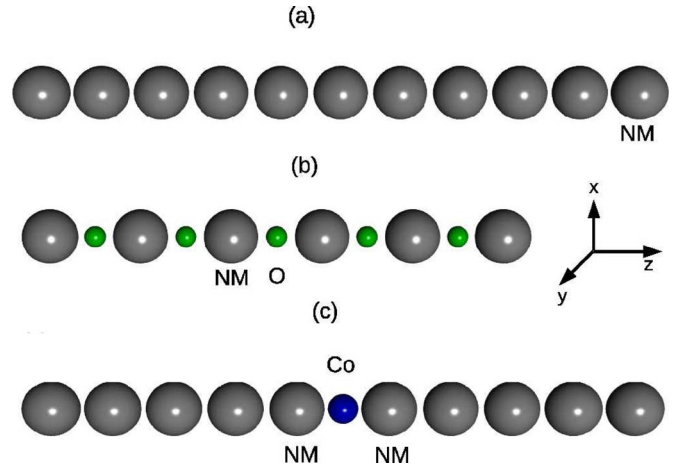

Fig. 1. Schematic representation of the systems studied. Noble-metal (NM) atoms are represented by large grey spheres, the smaller green spheres represent the O atoms, while the blue sphere stands for the Co magnetic impurity (color online).

where Kmax is the value of the largest reciprocal lattice vector used in the plane waves expansion and Rmt is the smallest muffin tin radius used. The number of $\mathbf{k}$ points in the Brillouin zone is enough in each case to obtain the desired energy and charge precisions, namely 10^{-4} Ry and 10^{-4}e, respectively. The muffin-tin radii were set to 2.09 bohr for Co, Cu, Ag and Au atoms and 1.52 bohr for the O impurities.

We set the coordinate system such that the chain axis is aligned along the z axis, as schematically shown in Fig. 1. For the noble-metal chains we consider one-atom unit cells [Fig. 1(a)] in a hexagonal lattice with $a = b = 10$ bohr and $c = d_{NM-NM}^{\mathrm{eq}}$, where d_{NM-NM}^{eq} is the chain's equilibrium lattice constant in each case ($d_{NM-NM}^{\mathrm{eq}} = 4.40, 5.09$ and 4.93 bohr for Cu, Ag and Au, respectively). In O doped NM chains, we consider, for simplicity, that the presence of O atoms results in ...NM-O-NM-O... linear chain structures, to make clear the doping effect on the noble-metal d-bands. The distances between the noble-metal to O atoms were relaxed in the z-direction, in all cases [Fig. 1(b)]. Finally, for the NM chains plus the Co embedded impurity, we consider an 11 atom unit cell [Fig. 1(c)], with the noble-metal to noble-metal distances d_{NM-NM} set equal to the equilibrium chain's lattice constant ($d_{NM-NM} = d_{NM-NM}^{\mathrm{eq}}$), while the noble-metal to Co impurity distance d_{NM-Co} is set equal to ($d_{NM-NM}^{\mathrm{eq}} + d_{Co-Co}^{\mathrm{eq}})/2$, where d_{Co-Co} is the optimal Co-Co distance in a Co chain.

To check if Ag and Cu chains could give rise to similar physics as Au chains in the presence of the Co impurities, we compare the band structure of Cu and Ag linear chains with that obtained for the Au one. The PDOS as well as the band structure of the different NM chains are presented in Fig. 2, where it is seen that the d bands of the Ag chain are well below the Fermi level (second panel of Fig. 2), while the Cu case is similar to the Au one, showing $d_{xz,yz}$ (Δ_3-symmetry) states at the Fermi level. For the three chains, the Δ_4 orbitals are more localized than the Δ_3 ones, and the more extended orbitals are those of d_z^2 (Δ_1)-symmetry.

From the spin polarized calculation of the electronic structure of a Co atom embedded in the Cu and Ag chains, it is ob-
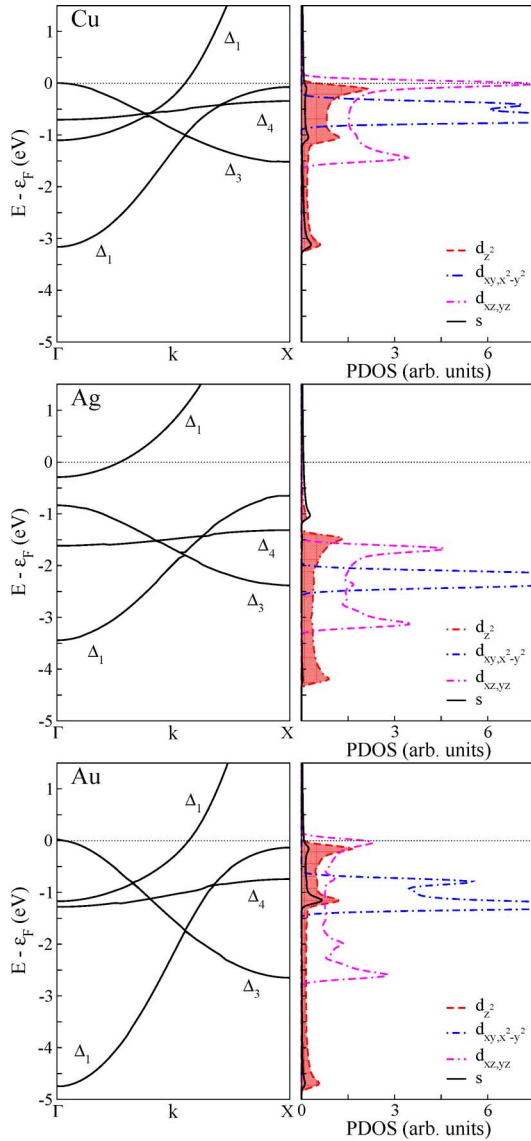
Fig. 2. Band structure and densities of states of (top) Cu, (middle) Ag, and (bottom) Au chains. Densities of states are additionally decomposed into the contributions coming from s and d states of different symmetries (color online).
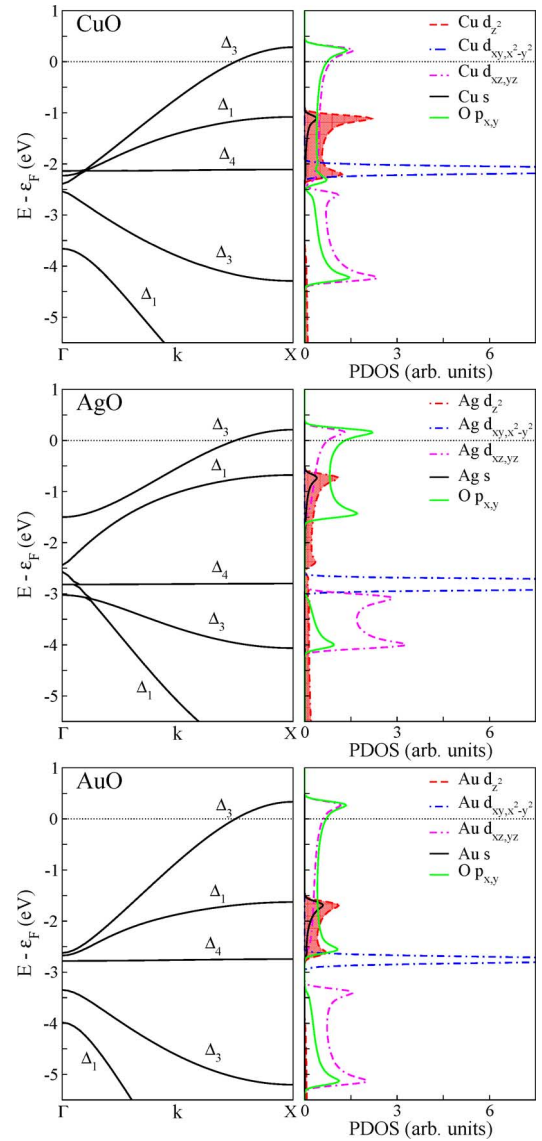
Fig. 3. Band structure and densities of states of NM chains doped with the O atoms. Densities of states are additionally decomposed into the contributions coming from s and d states of different symmetries (color online).

tained that similarly to what happens with a Co impurity in the Au chain, the Co atom presents a total spin $S = 3/2$. The Co atom exhibits three spin down holes, two with Δ_3 symmetry and the last one coming from the half-filled degenerate Δ_4 orbitals. Due to the fact that the Co impurity has the same structure when embedded in the three studied hosts, we can return now to the differences and similarities in the band structure of the different NM chains already discussed. As a direct result of the electronic structure of Cu chains, we can say that they would present the same Kondo behavior as the one expected for the corresponding Au system. The characteristic Kondo scale will, of course, depend on the specific parameters of each system. On the contrary, the Ag host does not provide the appropriate environment for the screening of the angular momentum characteristic in the Kondo effect.

As mentioned in the introduction, impurity-assisted chain growth helps to enhance the tendency towards noble-metal

chain formation. The question arises then, what is the effect of O doping on the Kondo trends of the NM chains with the embedded Co impurity? After calculating the electronic structure of NM chains doped with stabilizing oxygen atoms, we find that Co is again in a $S = 3/2$ spin state, showing the same holes' symmetry as before. In the NM chains doped with oxygen, we find that the Δ_3 orbitals are pushed up towards the Fermi level due to hybridization of these states with the $p_{x,y}$ degenerate orbitals of the O atoms. This is in agreement with the results presented in [11], where the *ab initio* calculations were performed using a different code. In Fig. 3, we show the densities of states for the three studied NM chains when doped with one O atom per NM atom. It is noteworthy to say that this is considered a strong doping limit case just to strengthen the role of the O atoms in the behavior of the NM d-bands. Due to the metallic character of the chains as a consequence of the presence of partially filled s bands (which screen the on-site

Coulomb repulsion), we expect that the role of correlations is less important than, for example, in CuO linear chains in $CuGeO_3$, $SrCuO_2$ [23] or in superconducting cuprates [24] and have a small impact on the relative position of the different bands. In the high doping limit we observe that all the systems present the Δ_3 band crossing the Fermi level, giving rise to the possibility of hybridization of these states with the $3d_{xz,yz}$ Co orbitals. In particular, it is clear from the second panel of Fig. 3 that the Ag doped chain could now provide the proper environment for the development of the Kondo physics. Although this seems to be the main result of this contribution, we also notice that the strength of the chain when doping with O impurities is even larger than the corresponding one for the Au pure chains (see [11, Fig. 7]). Therefore, the presence of O impurities plays an important role in the case of Ag; it pushes up the Δ_3 orbitals towards the Fermi level increasing the tendency towards Kondo physics, and it strengthens the bonds within the Ag chain enhancing its feasibility. The same conclusion holds for the Au and Cu doped chains.

For the sake of the comparison with the previous study in Au chains, in the case of the Cu pure chain we also added a four-fold breaking symmetry FCC lead. We obtain that the splitting between the $3d_{x^2-y^2}$ and the $3d_{xy}$ orbitals is large enough to produce a positive value of D, in agreement with the one obtained for the Au pure chains reported in [14]. Thus we expect that, in this particular case, the ground state will present the physics of the overscreened Kondo model.

IV. CONCLUSION

In this contribution we analyze the necessary conditions to obtain the Kondo physics in noble-metal chains with a Co embedded impurity. We find that Cu and Au leads behave electronically in a similar way in the presence of a Co impurity. The characteristic Kondo scale will depend on the specific parameters of each system. On the contrary, Ag chains lack the necessary Δ_3 symmetry at the Fermi level which should provide the screening of the angular momentum, characteristic of the Kondo effect. In an atmosphere of O atoms, the probability of developing the Kondo physics is enhanced in the Ag chains, while the Cu and Au chains increase their mechanical stability and also improve the 2CK existence conditions. The physics of the overscreened Kondo model and non-Fermi liquid properties are also foreseen in the case of Cu pure chains when adding a four-fold breaking symmetry field in the leads.

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