Magnetism and structure of atomic-size nanocontacts

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(Received 27 August 2004; published 16 November 2004)

State of art *ab initio* calculations in a fully relaxed geometry reveal the interplay between structure and magnetism in atomic-sized nanocontacts. Our studies for Co, Pd, and Rh nanocontacts sandwiched between Cu electrodes demonstrate that atomic relaxations strongly affect magnetic states and lead to an inhomogeneous distribution of magnetic moments on atoms of nanocontacts. Stable ferromagnetic solutions with large magnetic moments are found for Co and Rh nanocontacts before breaking of the contact. We predict that Pd nanocontacts are nonmagnetic before the breaking, however, the energy difference between ferromagnetic and nonmagnetic states is only 6 meV. Our results suggest that variations in the structure, temperature or applied field could lead to transitions between magnetic and nonmagnetic states in Pd nanocontacts.

DOI: 10.1103/PhysRevB.70.195420 PACS number(s): 75.75.+a, 73.63.Rt

Progress in atomic engineering makes it now possible to produce nanocontacts suspended between electrodes.[1] In fact, it is possible to shrink the nanocontact to just a few atoms, or even to a single atom.[2] Such new nanostructures have enormous potentialities for developing a variety of physical properties which may be important for future nanodevices.

One of the most challenging aim of the current research in this field is to explore magnetic properties of nanocontacts. According to the theorem of Lieb and Mattis[3] the ground state of 1D systems is nonmagnetic. However, nanocontacts suspended between electrodes are not strictly one-dimensional structures. To our knowledge, there is no theorem that prevents the existence of ferromagnetism in a quasi-1D systems. Also, one should note that the magnetic anisotropy energy (MAE) barriers to reach the ground state can make the observation of 1D magnetism in experimental setups possible.[4] Due to the prediction of Dorantes-Davila and Pastor[5] 1D structures have the MAE an order of magnitude larger than in two-dimensional thin films. Transport experiments of Rodrigues *et al.*[6] on Co, Pd, and Pt nanocontacts have suggested a magnetic behavior in these systems at room temperatures. The half-integer peaks in conductance are usually considered as evidence for spin polarization in nanocontacts. However, very recent experiments of Untiedt *et al.*[7] have demonstrated that features in the conductance similar to fractional quantization can appear due to the presence of gas molecules. An important result of this work is that the magnetic states of a nanocontact are not related in a simple manner to its conductance. Despite considerable progress in understanding the physics of nanocontacts,[2] their magnetic properties are still under debate.[8]

On the theoretical side, very few studies have been presented for magnetic 1D nanocontacts mainly using three-dimensional codes for infinitely long straight wires with equidistant atoms.[9–12] While such calculations have provided some important insight into magnetism in atomic contacts, they are less effective for a quantitative description of magnetic phenomena, because electrodes and nanocontacts may exhibit a strongly inhomogeneous strain relaxations.[13] The first calculations of magnetic properties in Al nanowires sandwiched between Al electrodes in the optimized atomic geometry have been recently performed by Ono *et al.*[15] using first-principles molecular-dynamics simulations. A rich variety of magnetic states depending on the wire length has been discovered. Similar studies for large systems having *d* electrons are still beyond the capabilities of modern *ab initio* methods.

There has been some controversy in the literature regarding magnetism in Pd nanowires. In a very recent paper by Delin *et al.*,[9] large magnetic moments of $0.7\mu_B$ per atom for long Pd nanowires and about $0.3\mu_B$ for short ones have been reported. The magnetic solutions were found to be the ground states with a significant energy gain with respect to the nonmagnetic one. These results strongly differ from those of Bahn and Jacobsen [11] who found no magnetism in Pd nanowires. In both studies an idealized geometrical structure has been used in calculations of the magnetic moments. Because almost nothing is known about the real structure of Pd nanocontacts suspended between electrodes, their magnetism seems to be still an open question.

In this paper we present state-of-the-art *ab initio* calculations for metal nanocontacts having *d* electrons in a fully relaxed geometry. We concentrate on Co, Rh, and Pd atomic contacts suspended between semi-infinite Cu(001) electrodes.[16] Our results show that structural relaxations strongly affect the magnetic states in nanocontacts and lead to an inhomogeneous distribution of magnetic moments on the atoms of the contacts. We predict a ferromagnetic coupling between atoms in Rh contacts before the breaking with a giant magnetic moment at the central atom. Total energy calculations reveal that Pd nanocontacts are nonmagnetic in the ground state. However, the energy difference between nonmagnetic and magnetic states before the breaking is only 6 meV. This result suggests that small variations of external parameters such as temperature or applied field could lead to transition between magnetic and nonmagnetic states in Pd nanocontacts.

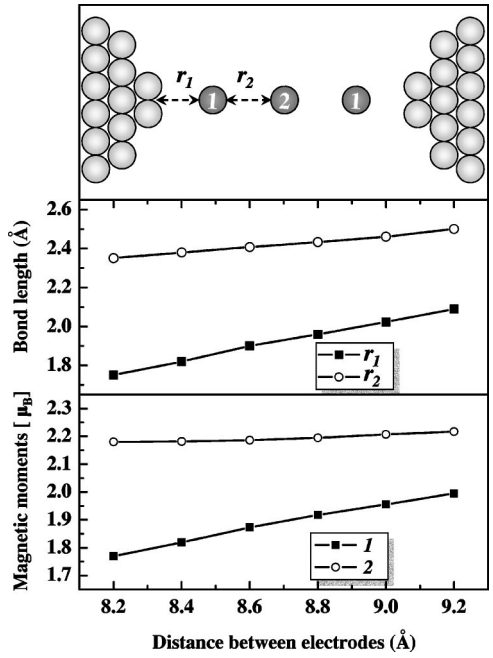

FIG. 1. Bond lengths and magnetic moments in Co3 nanocontacts for different separations between Cu electrodes.

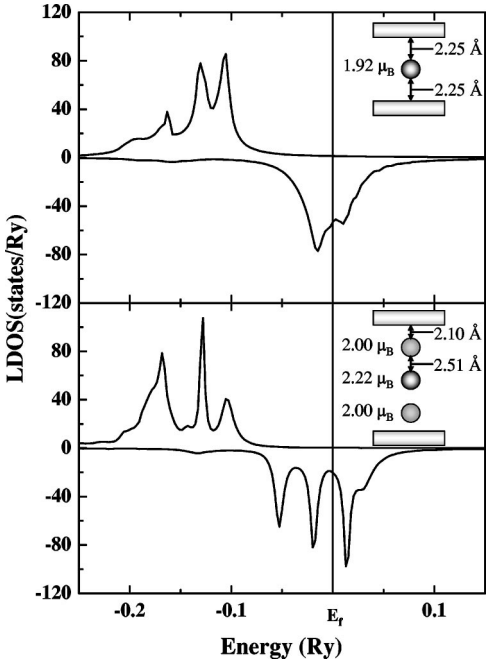

FIG. 2. The LDOS at the single-atom Co1 contact and at the central atom in Co3 before the breaking; only *d* components of the LDOS are presented.

We performed self-consistent calculations in the relaxed geometry for contacts and electrodes by means of the full-potential Korringa-Kohn-Rostoker (KKR) Green's function method.[13,17,18] Details of our method and its first application for Cu nanocontacts have recently been presented.[13] Here we only shortly describe our approach. The atomic contact suspended between two semi-infinite electrodes is considered as the perturbation of electrodes. The Green's function of the contact is calculated by solving the Dyson's equation in the real space representation. The multiple-scattering of electrons by atoms of the electrodes and the contact is treated fully self-consistently performing spin-polarized calculations for relaxed atomic structures. The equilibrium structure of contacts and electrodes is determined using *ab initio* fitted many-body potentials formulated in the second moment tight-binding approximation.[13] Such an approach should be justified, therefore we also perform *ab initio* self-consistent KKR Green's function calculations of the Hellman-Feynman forces acting on atoms in the nanocontact in the relaxed geometry to check whether these forces are small.[14] Computational details and parameters of potentials will be presented elsewhere.

First, we discuss the magnetic properties of Co nanocontacts. As an example, our results for the Co chains of three atoms (Co3) for different distances between Cu electrodes are presented in Fig. 1. The bond lengths and magnetic moments per atom during the nanocontact stretching have been calculated in the relaxed geometry. The largest electrode-electrode separation shown in Fig. 1 corresponds to the breaking point.[19] It is seen that the magnetic moments on atoms near the electrodes are strongly reduced compared to the moment on the central atom. This is basically a consequence of the effect of the higher coordination of these atoms. The interaction between the *d* states of the Co atom and the *sp* states of the nearest four Cu atoms of the electrode suppresses the magnetic moment. Due to the increased hybridization with the electrodes these atoms react more sensitive to environmental changes. For example, the magnetic moments on atoms in the proximity of electrodes increase strongly during stretching of the nanocontact, while the moment on the central atom changes only slightly (see Fig. 1). The same trend is seen for the bond lengths: the bond lengths of the central atoms are almost saturated. In other words, bonds in the area of electrodes are "softer" than for the central atom. We have found similar trends for longer atomic chains suspended between electrodes.[20]

In order to get insight into the formation of magnetic states in 1D contacts we calculate the local density of states (LDOS) of Co chains consisting of 1 to 5 atoms (Co1–Co5). For every chain before breaking the LDOS are determined for both spin directions at each atom. The changes in the LDOS are particularly large as the number of atoms in the chain increases from 1 to 3. Figure 2 shows, as an example, *d* components of the LDOS for the Co1 (single atom contact) and the LDOS at the central Co atom in the Co3 chain. In both systems Co atoms have the majority-spin *d* states completely filled. At the same time, the Fermi level is located within the minority-spin states, which exhibit strong environmental effects. A splitting of the minority spin levels in the Co3 chain caused by reduced interaction with electrodes and the nearest Co atoms is well seen. The LDOS at the Fermi level and the number of spin-down electrons are significantly reduced on the central atom in Co3 chain compared to Co1. As the result of this effect, the magnetic moment in Co3 is strongly enhanced. Our calculations for longer chains have shown that the structural relaxations mainly affect the minority-spin *d* states near the Fermi level. However, the

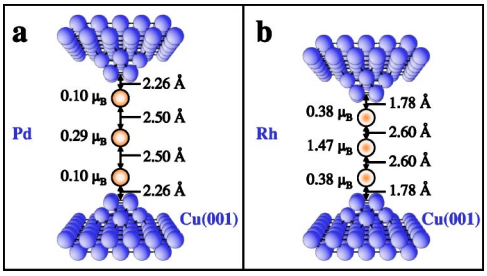

FIG. 3. (Color online). Bond lengths and magnetic moments in Pd3(a) and Rh3(b) nanocontacts before the breaking.

behavior as a function of the size of the chain is irregular leading to a small variation of the magnetic moment (between $2.2\mu_B$ and $2.1\mu_B$) on the central atom.

Now we turn to our results for 4*d* metal contacts suspended between Cu electrodes. Several theoretical studies have shown that magnetism in 4*d* systems is strongly influenced by a number of factors, such as symmetry, coordination and interatomic distances.[17,21] One can expect that due to the large extension of the 4*d* wave functions the influence of atomic relaxations on magnetic moments of 4*d* systems should be stronger than for the 3*d* ones. We have performed spin-polarized and paramagnetic calculations for Pd and Rh chains of different sizes before the breaking in the relaxed geometry. As an example, we present in Fig. 3 the structure and magnetic moments for Pd3 and Rh3 nanocontacts. We have found the existence of ferromagnetic solutions for both systems. In the case of Pd3, the moments at the center and at the edge atoms are very small $0.3\mu_B$ and $0.1\mu_B$, respectively.[22] The moments at the edge atoms are strongly suppressed due to the interaction with electrodes. Our analysis of the charge distribution in the Pd3 reveals that the rather surprising existence of the magnetic moments originates from *sd* hybridization that depletes the *d* contribution around the Pd atoms and leads to an open-shell-like behavior similar to that obtained in calculations for free Pd clusters.[23] In contrast to the results of Delin *et al.*,[9] our total energy calculations for fully relaxed Pd3 nanocontacts show that the energetic balance between ferromagnetic and nonmagnetic states is very delicate: the nonmagnetic state is lower than the ferromagnetic one by only 6 meV. Taking into account the fact that the atomic chain configuration is a metastable structure,[2] even small variations in the structure, temperature, or applied field could lead to a transition between magnetic and nonmagnetic states in Pd nanocontacts. We expect that in a similar manner to free and supported clusters,[24] magnetic nanocontacts can exhibit a metamagnetic behavior which might lead to magnetic fluctuations between different magnetic states. Studies of this effect are currently in progress.

Our calculations reveal that the central atom in Rh3 nanocontacts has a very large magnetic moment of $1.47\mu_B$ before the breaking, in sharp contrast to studies of Rh nanowires in the idealized geometry,[25] where a very small mean-field magnetic moment of about $0.3\mu_B$ was found. The magnetic moment on atoms in the proximity of electrodes drastically reduces to $0.38\mu_B$, a reduction of about a factor of 4 compared to the moment on the central atom. Atomic relaxations and interactions with electrodes turn out to be decisive in Rh nanocontacts and lead to a strongly inhomogeneous distribution of magnetic moments on atoms. Our calculations show that the ferromagnetic state in Rh nanocontacts has an energy 0.2 eV lower than the nonmagnetic one. None of the above results for Pd and Rh nanocontacts could be predicted from former studies on idealized infinite nanocontacts which can give only mean-field magnetic moments.[9,10,25]

Finally, we would like to note that our studies on Rh clusters[26] demonstrated that the magnetic moment of Rh atoms can be strongly affected by chemisorption of hydrogen. We believe that this ability may be used to alter the magnetic properties of Rh nanocontacts.

In summary, *ab initio* calculations have demonstrated the subtle interplay between structure and magnetism in transition metal nanocontacts. We have found that atomic relaxations in nanocontacts suspended between electrodes strongly affect magnetic states and lead to an inhomogeneous distribution of magnetic moments on atoms. We predict that Rh nanocontacts are magnetic, and have giant magnetic moments on the central atom before the breaking. Calculations of magnetic states in Pd nanocontacts have revealed that the energy difference between the nonmagnetic and the magnetic states before the breaking is only 6 meV. The nonmagnetic state has been found to be the ground state. Our results suggest that transitions between magnetic and nonmagnetic states in Pd nanocontacts can be caused by small variations of external parameters like temperature or applied field and can exist in experimental setups.

This work was supported by the Deutsche Forschungsgemeinschaft (DFG).

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