Selective d-state Conduction Blocking in Nickel Nanocontacts

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The lowest conductance step for a Ni nanocontact is anomalously small in comparison with the large expected number of conducting channels. We present electronic structure calculations for an extremely idealized Ni nanobridge consisting of just a monatomic nanowire. Our calculations show that no less than eight single spin bands cross the Fermi level in a nonmagnetic Ni monatomic wire, dropping marginally to seven in the more stable, fully ferromagnetic state. However, when we build in the wire a magnetization reversal, or domain wall, by forcing the net magnetization to be zero, we suddenly find that $d$ electrons selectively cease to propagate across the wall. $s$ electron propagation remains, and can account for the small observed conductance steps.

I. INTRODUCTION

Recent conductance data of nanocontacts and break junctions in a magnetic transition metals such as Ni have shown interesting and partly unexpected results. While early conductance histograms for Ni at room temperature in air appeared basically structureless [1], Oshima et al. [2], who worked in vacuum, at variable temperature, and with the possibility of a magnetic field, found conductance steps preferentially near 2 and 4 (in units of $g_0 = e^2/h$, the conductance quantum per spin) at RT and zero field, near 4 at 770 K and zero field, and near 3 (occasionally near 1) at RT with a field. Ono et al. [3], reported again 2 for Ni in zero field, and 1 for Ni in a field. Break junction data by Yanson [4] show a step at conductance about 3.2 in zero field. While the reasons for this diversity are not always clear, there seems to be a consensus, based also on other data for noble metals, that the ultimate contact must be monatomic. For a monatomic noble metal contact, for example, the availability of a single $s$ electron channel for both spins species immediately rationalizes a conductance step of 2, as is generally observed [1,3,4].

The general question which we broach – if not yet fully solve of course – is what to expect for the number of truly conducting electronic channels in a monatomic nanocontact of a magnetic transition metal, one possessing partly filled, bulk-polarized $d$ electron states besides the $s$. In order to pursue this first rationalization attempt we shall purposely adopt an oversimplified model, consisting of just a single monatomic, regular, tipless Ni chain. While that model is surely quite different from the true nanocontact, as it neglects the presence of the supporting tips and the general lack of regularity near the ultimate bridging atom, its simplicity is crucially useful. It allows a detailed microscopic study, that can bring to light new potential phenomena.

Because the model possesses no tips, the only measure of conductance we will discuss will be simply the number of one-dimensional bands for each given spin (“channels”) crossing the Fermi level, no allowance made at this stage for imperfect transmission, and for the ensuing noninteger values found in reality. Moreover, standard electronic structure calculations are mean-field in character, imply for a transition metal one-dimensional nanowire a magnetic long-range order which is in reality suppressed by fluctuations, or that can only be supported by tips under special spatial circumstances. Nonetheless, since our work is aimed at understanding many more basic questions, these problems are not really relevant at this stage. The mean field channel counting is moreover probably not bad anyway, as shown for example by the large U 1D Hubbard model, where $K_F = 1/2$ in that spin-singlet Luttinger liquid implies one effective conducting channel in place of two, exactly the same as if there were magnetic long-range order.

Our results indicate that the minimal channel number of the nonmagnetic monatomic Ni nanowire should be as large as 8, a large number when compared with experimental steps around 2 and 4 (large even after considering a limited transmission for a $d$ state). Ferromagnetic polarization, which in mean field is quite strong and lowers the energy considerably, only reduces the channel number to 7, and does not remove the disagreement. However, insertion of a single magnetization reversal (a sort of collinear "Bloch wall") inside the monatomic magnetic nanowire leads to a sharp drop from 7 to 2 channels, a value now much closer to the experiments. Inspection of calculated bands and wavefunctions clearly indicates that the magnetization reversal along the wire leads to a selective blocking of $d$-electron propagation, leaving only the $s$-electron fully conducting.
II. METHOD

Calculations were carried out in the framework of density-functional theory (DFT) in the local density approximation (LDA). The Perdew-Zunger parametrization \[ \] of exchange-correlation energy was used. The nuclei and the core electrons are described by ultrasoft pseudopotentials \[ \] with the parameters of Ref. [8]. The Ni single atom contact was simulated by a regular monatomic Ni wire, infinite along the z axis, and periodically repeated in a square lattice along x and y. The spacing used, 8.46 Å, was checked to be large enough to avoid measurable wire-wire interactions. The kinetic energy cut-offs of the plane wave basis set were 25 Ry and 300 Ry for the wave functions and the charge density, respectively. Integration of the 1D Brillouin zone was done on a uniform mesh of 80 k-points. These parameters proved sufficient to provide converged results. The integration up to the Fermi level was done by a standard broadening technique \[ \] with the smearing parameter of 0.002 Ry.

A single Ni atom per cell is required for both nonmagnetic and ferromagnetic states. To study the state with spin reversal (actually two spin reversals with periodic boundary conditions) we extended our cell up to 8 Ni atoms. While our calculations were restricted to collinear spins thus excluding for simplicity the possibility of spin moment rotation, the magnetization magnitude and sign were allowed to vary with total freedom as a function of position. In order to find the state of lowest energy with a given total magnetization we applied the fixed-spin-moment (FSM) method \[ \] introducing two Fermi energies \( E_F^\pm \) for different spin directions. The difference \( B = (E_F^+ - E_F^-)/2 \) is a magnetic field which is needed to stabilize the state at the chosen magnetization. The stable configurations correspond to zero magnetic field (when \( E_F^+ = E_F^- \)).

III. FERROMAGNETIC AND NONMAGNETIC MONATOMIC WIRES

The ground state of a monatomic Ni wire in a large interval of interatomic distances (including the limiting case of infinitely separated free Ni atoms) is calculated to be ferromagnetic (Fig. 1). The nonmagnetic state (magnetization everywhere identical to zero) has a higher total energy compared to the ferromagnetic one, by about 0.12 eV/atom at the equilibrium spacing (total energy minimum). The equilibrium interatomic distances both for nonmagnetic (\( a = 2.06 \) Å) and for ferromagnetic (\( a = 2.11 \) Å) Ni wires are found to be considerably smaller than the corresponding bulk value \( a_{\text{bulk}} = 2.42 \) Å. Not surprisingly, magnetism suddenly disappears, and the wire turns nonmagnetic below a critical spacing of about 1.9 Å. This situation is demonstrated in the inset of Fig. 1 where the magnetic moments of bulk Ni and of an isolated Ni atom are also indicated. As could be expected the equilibrium moment of the wire (\( M = 1.11 \mu_B \)) is intermediate between the atomic and the bulk values.

The ballistic conductance of a contact is given by Landauer’s formula which in the case of perfect transmission and independent channels has a simple form \( G = N g_0 \), where \( g_0 = e^2/h \) is the conductance half quantum and \( N \) is the number of conducting channels per spin. We thus estimated the total conductance by simply counting the number of channels, that is the number of bands of either spin crossing the Fermi level. In Fig. 2 we present the band structure of the nonmagnetic and ferromagnetic Ni wires at their equilibrium interatomic distances. The valence electrons in the atom are 3d and 4s, and each band is correspondingly labeled by its main atomic character. The s and d\(_{z^2}\) bands are strongly hybridized, while d\(_{x^2-y^2}\), d\(_{xy}\) are split from d\(_{xz}\), d\(_{yz}\) by the uniaxial wire crystal field. There are 8 channels in the nonmagnetic wire, reduced to 7 in the ferromagnetic wire. That is so much larger than the basic experimental conductance step of 2, to suggest the need to identify some mechanism blocking some of the channels – presumably the d channels and allowing only the remaining to conduct.

IV. NANOWIRE WITH A DOMAIN WALL: D ELECTRON BLOCKING

A ferromagnet generally contains Bloch walls, separating domains with different magnetization directions. Inside the wall, which is generally rather thick, the magnetization rotates gradually between one direction and the other. Given two tips connected by a nanocontact, it is possible that a wall might be trapped precisely there. Although in that case the spin reversal might be more abrupt, and thus more costly per unit section than in the bulk, the monatomic contact size could nonetheless minimize the total energy cost. We thus investigated the possibility that the two tips in the nanocontact under some circumstances might be magnetized in opposite directions forming thereby a spin reversal configuration. The spin reversal costs some energy so that this configuration should have an intermediate energy between the uniform ferromagnetic and the nonmagnetic states. To simulate this situation we considered large cell monatomic wire calculations where any local magnetization was allowed, but the total magnetization \( M \) was
required to vanish, $M = 0$. In a sufficiently long Ni wire, that must lead to a ground state consisting of periodically repeated up and down spin ferromagnetic segments, separated by walls. Moreover if the walls are sharp, which turns out to be the case, the cell length can be quite small, and we found a unit cell including 8 Ni atoms quite adequate. The resulting ground state has, roughly speaking, 4 atoms with positive and 4 atoms with negative magnetization (Fig. 3a). This state is more stable than the nonmagnetic state, because the cost of the two walls, estimated to be $\approx 2 \times 0.2$ eV, is smaller than the energy gained by magnetizing the two domains, roughly $8 \times 0.12$ eV. Moreover, symmetry at $M = 0$ requires that $B = E_F^+ - E_F^- = 0$, so that the auxiliary magnetic field of this state is zero, and the energy bands (Fig. 3b) are spin degenerate.

The new striking feature is that some of the $d$ bands, including the $d_{xy}, d_{x^2-y^2}$ bands, formerly crossing the Fermi level, have now turned into flat dispersionless levels. The wave functions of these bands (Fig. 4) are strongly localized and therefore cannot contribute to conductance. Vice versa the $s - d_z$ states which remain delocalized are still able to conduct. As a result the number of conducting channels has been reduced by the wall from 7 to 2.

This selective $d$ electron blocking is easily rationalized in terms of the up and down spin effective potentials, which inside each domain have a sizable offset, and which alternate as one moves from one domain to the next. The $d$ states, whose mass is large, form quantum well states in this alternating potential, and are localized. The $s$ states, much lighter by comparison, are simply scattered but do not localize.

V. CONCLUSIONS

We studied an idealized Ni monatomic wire, and discovered that a domain wall in that wire has a very important blocking effect, selectively suppressing the free motion of the $d$ electrons, but not of the $s$ electrons. At a nanocontact separating two tips with reversed magnetizations, the effective potential offset can act as a strong barrier yielding total reflection for the heavy $d$ electrons alone. It is believed that this effect may be at work in some of the data quoted, and it will be interesting to explore further consequences of this mechanism experimentally.

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The core radii (in a.u.) of our pseudopotentials are: $r_{cs}^c = (2.0, 2.5)$, $r_{cp}^c = (2.4, 2.6)$, $r_{cd}^c = (1.6, 2.5)$. Two values of the core radii indicate a channel which has been pseudized within the ultrasoft scheme. In such case the first value is the norm conserving core radius and the second is the ultrasoft one.

FIG. 1. Total energy of nonmagnetic and ferromagnetic Ni monatomic wires as a function of interatomic spacing. Inset: magnetic moment per atom of the ferromagnetic Ni wire. Bulk and atomic values are shown by dashed lines.

FIG. 2. Band structures of the nonmagnetic and ferromagnetic monatomic Ni wires at optimized interatomic spacing. The points where the bands cross the Fermi level are marked by circles and the corresponding conducting channels are numbered.

FIG. 3. Monatomic Ni wire with $M = 0$; a) planar profile of the magnetization along the wire. Note the formation of sharp domain walls; b) band structure with the band indices and the conducting channel indication. Note that some $d$ bands have turned to flat levels.

FIG. 4. Iso-electron density surfaces (4 levels from 0.0003 a.u.$^{-3}$ to 0.03 a.u.$^{-3}$) for a) the conducting $s$ – $d_{z^2}$ state and b) the localized $d_{xy}, d_{x^2-y^2}$ states. All the states are calculated at $K = 0.04$ (2$\pi/8a$). The lateral view (in the $yz$ plane) and the cross section (in the $xy$ plane) at the $z$ coordinate indicated by the dashed line are shown. The $d_{xy}, d_{x^2-y^2}$ electrons are clearly reflected by the domain wall, and here form a quantum well state between two consecutive walls.
Fig. 1  A. Smogunov, A. Dal Corso, and E. Tosatti
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Fig. 3  A. Smogunov, A. Dal Corso, and E. Tosatti
Fig. 4  A. Smogunov, A. Dal Corso, and E. Tosatti