Pt steps decorated by 3d nanowires calculated via an order-N method

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We present the magnetization energy and magnetic moments of 3d monowires aligned along the step edges of Pt (533) and (322) vicinal substrates. We employ an electronic structure method which scales linearly with the size of the system. This allows us to treat with ease both ferromagnetic and antiferromagnetic solutions, and in principle the method should allow for the evaluation of more complex systems, such as wires deposited on rough step edges. We find that Co, Fe, and Mn are almost perfect Heisenberg systems, with almost no change in the moment between antiferromagnetic and ferromagnetic solutions. A large polarization of the Pt substrate is also observed. Our results are in close agreement with recent experimental results obtained for the case of a Co monowire. As expected the trend is for the late d series to be stabilized by ferromagnetic long range order and the middle of the d series by antiferromagnetic order. Since our method is only locally self consistent we discuss as some length the convergence of the results with respect to the size of the region which is treated self-consistently.

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I. INTRODUCTION

Physics on the nanoscale has developed enormously in the last decade and the construction of a wide variety of nanoscale systems has become possible. This usually proceeds through either an atom by atom manipulation using STM, or by growth on a substrate favorable to the formation of the desired nanostructure. Stand out amongst the latter category of experiments has been the production of parallel monoatomic chains aligned along the step edges of a Pt vicinal substrate. Vicinal substrates, created by the controlled miscut of the crystal off a high symmetry plane, present an ordered array of step edges and thus form an ideal template for the growth of monoatomic wires.

One of the fundamental issues which arises in the context of nanophysics is how very well known phenomena of nanoscale systems. The nature of the 3d metal Co deposited in one-dimensional chains on the Pt(997) surface showed a dramatically enhanced spin and orbital moment.

From the theoretical point of view one of the problems with the study of low dimensional systems is that the reduction in symmetry and the corresponding increase in system size mean that the calculations can become quite demanding. This is simply due to that fact that most of the theoretical approaches scale as $N^3$, with $N$ the number of inequivalent sites. Alternative ab initio techniques with more favorable scaling do exist however. In particular, Bellini et al have determined the magnetic structure of 4d monoatomic rows on Ag vicinal surfaces, using an ab initio method that scaled as order $N$ with the number of substrate layers. However the scaling with the number of inequivalent wire atoms remained $N^3$. This, as the authors noted, meant that calculations involving inequivalent wire atoms (needed for the calculation of antiferromagnetic wire configurations) became again very demanding. On the other hand, Eisenbach et al have recently deployed a genuine ab initio order $N$ method in the study of Fe monowires embedded in a Cu matrix. Using this approach they were able to determine the magnetic structure of the Fe wire. Ab initio order $N$ methods clearly hold a lot of promise for the investigation of systems on the nanoscale. With the ability to calculate systems of several hundred atoms one can consider, for example, magnetic clusters either embedded within the bulk of another material or deposited on a substrate. However, the favorable scaling of order $N$ methods comes at a certain price of accuracy. This is due, in the case of the method deployed by Eisenbach et al. and to the related method used by us in this work, to their being only locally self consistent. Hence, it is necessary to establish that the magnitudes of...
quantities one is interested in are within the scope of the method.

In this work we investigate the magnetic properties of 3d nanowires deposited on the step edges of a Pt vicinal surface. We consider both ferromagnetic (FM) as well as anti-ferromagnetic (AFM) magnetic configurations, and establish the accuracy of the method for the relevant magnetization energies. Although the calculations we perform here do not have spin-orbit (SO) coupling this will not be important for the determination of energy differences between FM and AFM magnetic configurations, which will be order the order of mRy and hence orders of magnitude bigger than the magnetic anisotropy from the SO interaction.

II. VICINAL GEOMETRY AND SUPERCELL

A vicinal surface is one created by miscutting away from a high symmetry plane. These surfaces necessarily display a periodic array of steps aligned along some specific direction, separated by terraces of the high symmetry plane the surface was miscut from. We will consider here a surface miscut off the high symmetry (111) plane. In this case there are two possible vicinal surfaces with steps that have either (100) or (111) microfacets. These two families of surfaces are described by the Miller indices \((p+1, p-1, p-1)\) and \((p-2, p, p)\) respectively with \(p\) being the number of atomic rows in the terraces separating steps.

The template that we use for depositing the 3d monowires on will in this study be the \((p+1, p-1, p-1)\) vicinals, and we consider surfaces with 2 atom wide and 4 atom wide terraces. As usual we replace the semi-infinite geometry with that of a supercell which is then periodically repeated in space. This leaves us with a slab with two surfaces, one of which we will decorate with a monowire. It is important that these slabs should not interact and also that the two surfaces should not interact across the slab. Here we accomplish this by separating the slabs which are 8 (111) layers in thickness by 7 (111) vacuum layers. This leads to supercells of 25 atoms and 55 atoms for the \((311)\) and \((533)\) vicinals respectively. In order to consider the possibility of anti-ferromagnetic solutions of the monowire we simply double the supercell in the wire direction, leading to supercells of 50 and 110 atoms.

III. THE ORDER-N LOCALLY SELF-CONSISTENT GREEN’S FUNCTION METHOD

The Locally Self-consistent Green’s Function method (LSGF) is based on an approach whereby a supercell of \(N\) sites is divided into \(N\) separate local interaction zones (LIZ) each of \(M\) sites. The motive for this construction is the observation that that the properties of the central site in each LIZ will approach those that would be found by a full solution of the supercell as \(M \to \infty\). This is very similar to the Locally Self-consistent Multiple Scattering (LSMS) method used by Eisenbach et. al in their work on Fe wires embedded in Cu. Essentially, the only difference between the two approaches is that in the LSMS method each LIZ is embedded within a free electron gas whilst in the LSGF method one embedded the LIZ into some judiciously chosen effective medium.

Formally this is achieved by writing a Dyson equation for the central site of each LIZ

\[
g_{RR} = \tilde{g}_{RR} + \sum_{R'=1}^{M} \tilde{g}_{RR}(\tilde{P}_{RR} - P_{RR})g_{RR} \tag{1}
\]

By solving this equation for every site in the supercell one finds the diagonal element of Green’s function matrix \(g_{RR}\) for all sites, and from this set one can construct the effective medium Green’s function \(\tilde{g}_{RR}\). This process is then iterated to self-consistency being first initiated by some suitable guess. One must note that although the full Green’s function matrix \(g_{RR}\) will not correspond to that of the supercell under consideration, provided \(M\) is large enough, the site diagonal element will. Since it is the only the site diagonal elements that are required to determine the local density of states for each site one may extract reliable information on charge density, one electron energy, and total energy of the supercell from this method.

The effective medium plays only the role of a boundary condition for the LIZ, but convergence with LIZ size will be strongly affected by this choice. In the case of a highly inhomogeneous structure one way to proceed is by making the effective medium more complicated (for example by allowing for inequivalent effective atoms), however in the case of a vicinal surface this is not practical. (Since the number of inequivalent vicinal layers is equal to the number of sites in the supercell.) We therefore proceed by the use of the simplest single site effective medium construction. The criteria that such an effective medium should satisfy in such a case is that the “effective atom” most resembles the maximum number of sites. With only one type of effective medium site this is clearly not possible in the case of separate vacuum and metal regions in the supercell. A way that suggests itself is to satisfy the two natural limits by having an effective vacuum atom and an effective metal atom. Near the interface region the size LIZ will need to be large to eliminate the error at the central site, but away from the interface region the effective medium will come to resemble more and more closely the real material and hence the error with the same size of the LIZ is smaller.

For simplicity we choose here a single site effective medium constructed from all metal sites via the average t-matrix approach. The rational behind this can be seen by considering the LIZ around an atom in the surface. The error committed for vacuum sites in the LIZ should be less important, as the density of states there
is anyway small, while the error for the metal sites will be less for not having a spurious vacuum term in the effective medium, and indeed should vanish in those sites which no longer feel the perturbation of the surface.

One must emphasize that there is no direct scattering between distant sites in this method. Beyond the LIZ boundary the effective medium is single site and contains only information related to the underlying lattice and no information whatever about the geometry of the vicinal surface. Hence quantum effects due entirely to such direct scattering processes will be lost. This may be of importance when considering, for example, step-step interactions.

IV. COMPUTATIONAL DETAILS

The method deployed here was a real space technique based on the Korringa-Kohn-Rostoker Green’s function scheme in the atomic sphere approximation. The basis consisted of $s$, $p$, and $d$ orbitals, and corrections to the spherical charge density were included up to $l_{\text{max}} = 4$. The calculations were performed in the Local Density Approximation (LDA) with the Perdew, Burke, and Ernzerhof parameterization of the results of Ceperly and Alder. The integration of the Green’s function was taken in the complex plane with 16 energy points on a semicircular contour. The lattice parameter for Pt was taken to be the theoretical LDA value.

V. CONVERGENCE OF TOTAL ENERGY AND MAGNETIC MOMENT WITH LIZ

The success of the LSGF method as a genuine order-$N$ method for arbitrary structures depends on course on how quickly is the convergence with respect to the LIZ size. By construction the rate of convergence of the supercell will depend solely on the convergence of the individual LIZ’s. This in turn depends on how well the effective medium corresponds to the system at hand. A consequence of this is that the convergence of the total energy should become worse linearly with increasing $N$. In Table I are shown the total energies for the supercell consisting of a Co monowire deposited on Pt (533). From this one may conclude that a LIZ of 55 atoms is enough to capture the energetics of this system. In Table I are shown the wire and substrate magnetic moments and magnetization energies. The convergence is better for the wire than for the substrate quantities. For the moments this can be understood as due to the fact the the 3d monowire will be a very good local moment system whereas the Pt substrate is of more itinerant character. The more localised the magnetic moment the better it is expected to converge in real space.

Finally we show in Fig. IV.1 the convergence of the quantity $E_{\text{FM}} - E_{\text{AFM}}$ for all the 3d monowires from V to Ni deposited on a Pt (311) substrate. Clearly, the convergence is with LIZ is sufficient that one can state clearly which solution is preferable for each wire.

VI. MAGNETIC MOMENTS AND MAGNETIZATION ENERGIES

We now turn to the trends of wire moment and energetics versus the d band filling. In Fig. IV.1 we show the wire, substrate, and vacuum moments for the elements V to Ni, Ti and Sc being found to display no magnetic solu-

![Figure 1: Magnetic moments of 3d monowires and total moment of substrate and vacuum sites for monowires on Pt (311) (full symbols) and Pt (533) (open symbols). Results shown are for LIZ = 5.](image-url)
FIG. 2: Average magnetic moment per principle layer for 3d monowires on Pt (311) (full symbols) and Pt (533) (open symbols). Results shown are for $LIZ = 5$.

FIG. 3: Convergence with $LIZ$ of the difference $E_{FM} - E_{AFM}$ for 3d monowires on Pt (311) substrate.

TABLE II: Wire and substrate moments for FM Co wire on Pt(533) substrate. Also shown is the site projected energy for the wire site, and the sum of site projected energies for the substrate sites.

| LIZ (sites) | $m_{wire}$ ($\mu_B$) | $m_{sub}$ ($\mu_B$) | $\Delta E_{wire}$ (Ry) | $\Delta E_{sub}$ (Ry) |
|-------------|----------------------|---------------------|-------------------------|------------------------|
| 13          | 2.248321             | 5.375824            | -0.011791               | -0.032602              |
| 19          | 2.244615             | 2.252704            | -0.010016               | -0.003562              |
| 43          | 2.232509             | 1.195110            | -0.008607               | +0.002313              |
| 55          | 2.223575             | 1.198589            | -0.007790               | -0.001625              |
| 79          | 2.223889             | 1.186796            | -0.007556               | -0.002480              |
| 87          | 2.22924              | 1.172650            | -0.007771               | -0.001743              |

One can note that the substrate moment associated with the FM monowire has a node between Cr and Mn, so that only for V and Cr does the substrate couple antiferromagnetically to the FM monowire. The large polarization of the substrate associated with the FM configuration is to be expected considering work on 3d impurities in Pd and Pt where a large polarization cloud of several $\mu_B$ was observed experimentally and theoretically. This being due to the fact that bulk Pt is near a magnetic instability. In Fig. 2 we show the total magnetic moment of each principle layer of the (533) and (311) vicinals, the decay of the moment is fairly slow and one can observe that nearly all layers of the Pt slab have become polarised. On the other hand, the absence of a significant polarization of the substrate for the AFM monowire configuration indicates that the magnetic coupling is strongly ferromagnetic for the Pt vicinal surface. The magnetic moment associated with the vacuum sites is seen to be largest earlier in the d series, which is expected due to the larger spatial extent of the d orbitals for the early 3d transition metals.

We note that the values found here for the Co wire spin moment and associated substrate moments are in close agreement with the very similar vicinal studied ex-
FIG. 4: Energy difference $E_{FM} - E_{AFM}$ for 3d monowires on Pt (311) (open symbols) and (533) (full symbols) vicinals. Results shown are for $LIZ = 5$.

The quantity $\Delta E = E_{FM} - E_{AFM}$ is expected to possess two nodes across the d series and in Fig. 4 it can be seen that the second of these nodes occurs between Mn and Fe, whereas the first would likely be seen between Ti and V if the Ti monowire was magnetic. Thus we find that the V, Cr, and Mn monowires prefer an AFM structure whereas Fe, Co, and Ni monowire prefer the FM structure. Turning now to the site projected energies one can see that the contribution to $\Delta E$ from the vacuum and substrate sites is rather large away from the middle of the d-series. The origin of the importance of this terms lies in the very different polarization of the surrounding depending of the magnetic configuration of the wire. This might be expected to cause complications for approaches based on extracting effective interactions for a Heisenberg model via the force theorem. In this case one does perturbation theory on a particular magnetic structure, and thus would be unable to take account of the change in energy coming from the change in polarization of the environment.

VII. CONCLUSIONS

We have studied monowire of 3d elements deposited on Pt (311) and (533) vicinal surfaces using a real space order-$N$ method, and have investigated the convergence of various quantities as a function of the $LIZ$ size. We demonstrate that the method is suitable for a quantitative determination of the magnetization energies of the monowires, although the calculation of step-step interactions would appear to be at the limit of what the method can achieve. Nevertheless, there are many interesting magnetic structures, such as magnetic vicinals, which could be calculated with this approach.

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