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2004 J. Phys.: Condens. Matter 16 S5833

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***Ab initio* study of canted magnetism of finite atomic chains at surfaces**

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Received 8 April 2004

Published 19 November 2004

Online at stacks.iop.org/JPhysCM/16/S5833

doi:10.1088/0953-8984/16/48/058

Abstract

By using *ab initio* methods on different levels we study the magnetic ground state of (finite) atomic wires deposited on metallic surfaces. A phenomenological model based on symmetry arguments suggests that the magnetization of a ferromagnetic wire is aligned either normal to the wire and, generally, tilted with respect to the surface normal or parallel to the wire. From a first-principles point of view, this simple model can be best related to the so-called magnetic force theorem calculations being often used to explore magnetic anisotropy energies of bulk and surface systems. The second theoretical approach that we use to search for the canted magnetic ground state is the first-principles adiabatic spin dynamics technique extended to the case of fully relativistic electron scattering. First, for the case of two adjacent Fe atoms on a Cu(111) surface we demonstrate that the reduction of the surface symmetry can indeed lead to canted magnetism. The anisotropy constants and consequently the ground state magnetization direction are very sensitive to the position of the dimer with respect to the surface. We also performed calculations for a seven-atom Co chain placed along a step edge of a Pt(111) surface. As far as the ground state spin orientation is concerned, we obtain excellent agreement with experiment. Moreover, the magnetic ground state turns out to be slightly non-collinear.

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1. Introduction

Magnetic devices on the atomic scale recently became a subject of intensive experimental and theoretical research (see, e.g., the ‘Viewpoint’ of Kübler [1]). Understanding and design of the relevant physical properties—magnetic moments, magnetic anisotropy energies, thermal stability, switching—of atomic scaled magnets demand a detailed knowledge of their electronic and magnetic structure. For this reason a considerable amount of theoretical work has been published investigating the—mostly non-collinear—magnetic ground state of free and supported metallic clusters [2–8].

Quite recently, Gambardella *et al* [9] reported well characterized experiments on linear chains of about 80 Co atoms located at a step edge of a Pt(111) surface terrace. At 45 K the formation of ferromagnetic spin blocks of about 15 atoms was found with an easy magnetization axis normal to the chain, tilted by 43° with respect to the surface normal towards the step edge. Stimulated mainly by this experiment, in the present work we present a study of the magnetic ground state of linear atomic chains deposited on an fcc(111) host surface. We first focus on the origin of the unusual canted magnetism. In the case of two adjacent Fe atoms placed into a Cu(111) surface we investigate how the orientation of the magnetization depends on the position of the dimer with respect to the surface. Then we calculate and analyse in some detail the ground state spin configuration of a finite Co chain at a Pt(111) step edge.

2. Theoretical methods

Let us write the magnetic moment of a ferromagnetic system in terms of spherical coordinates, $\mathbf{M} = M(\sin \theta \cos \phi, \cos \theta \sin \phi, \cos \theta)$, where $0 \leq \theta \leq \pi$ and $0 \leq \phi \leq 2\pi$ are the azimuthal and polar angles in a usual rectangular frame of reference, and assume that the magnitude of the magnetic moment, M , is independent on the orientation. In the case of a linear chain of atoms deposited along the x axis of an fcc(111) lattice (see, e.g., figure 1) the system has at best one symmetry operation, namely, a mirror symmetry with respect to the (y, z) plane; therefore, invariance of the energy implies up to second order in the magnetization that

$$E(\theta, \phi) = E_0 + K_{2,1} \cos 2\theta + K_{2,2}(1 - \cos 2\theta) \cos 2\phi + K_{2,3} \sin 2\theta \sin \phi, \quad (1)$$

where $K_{2,i}$ ($i = 1, 2, 3$) are so-called anisotropy constants. Solving the corresponding Euler–Lagrange equations gives the result that, depending on the actual values of the anisotropy constants, the easy magnetization axis corresponds either to $\phi = \pi/2$ and $\theta \in \{\theta_0, \theta_0 + \pi/2, \theta_0 + \pi\}$, where

$$\theta_0 = \frac{1}{2} \arctan\left(\frac{K_{2,3}}{K_{2,1} + K_{2,2}}\right) \quad \left(-\frac{\pi}{4} < \theta_0 < \frac{\pi}{4}\right), \quad (2)$$

or to $\theta = \pi/2$ and $\phi = 0$. Clearly, only in the special case of $K_{2,3} = 0$ can the ground state magnetization point along the z axis (perpendicular to the planes).

The so-called magnetic force theorem (MFT) represents a straightforward and relatively simple way to calculate anisotropy constants, based on the local spin density approximation (LSDA). Here, a self-consistent calculation is carried out for only one selected orientation of the magnetization. Then, by keeping these potentials and effective fields fixed, the orientation of the spin magnetization (in the LSDA parallel to the effective field) is varied, whereby—neglecting further self-consistency—only the single-site (band) energy is considered; see [10] for several applications of this method in ordered and disordered layered systems. Note that, in principle, the magnetic dipole–dipole interaction energy also has to be added to the band energy. For the case of small nanostructures the estimated magnitude of this energy is, however, less by at least one order than that of the band energy.

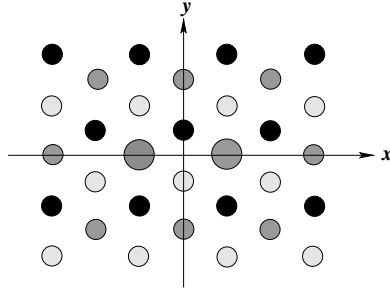


Figure 1. A schematic top view of two impurities (big shaded circles) placed into fcc(111) layers as nearest neighbours. The host atoms in the same layer are displayed as small shaded circles and those in the layer above as full circles, while those in the layer below appear as empty circles.

A numerically efficient technique for searching for an equilibrium spin arrangement is tracing the time evolution of the spin moments until a stationary state is achieved. According to the so-called first-principles adiabatic spin dynamics (SD) founded by Antropov *et al* [11], for a system with well defined local (atomic) moments the evolution of the time dependent orientational configuration, $\{\mathbf{e}_i(t)\}$, is described by a microscopic, quasi-classical equation of motion:

$$\frac{d\mathbf{e}_i}{dt} = \gamma \mathbf{e}_i \times \mathbf{B}_i^{\text{eff}} + \lambda [\mathbf{e}_i \times (\mathbf{e}_i \times \mathbf{B}_i^{\text{eff}})], \quad (3)$$

where $\mathbf{B}_i^{\text{eff}}$ is an effective magnetic field averaged over cell i , γ is the gyromagnetic ratio and λ is a damping (Gilbert) parameter. Following the arguments of Stocks *et al* [12, 13], in this equation at any moment of time the orientational state has to be evaluated within a constrained density functional theory (DFT). Here a local constraining field, $\mathbf{B}_i^{\text{con}}$, ensures the stability of a non-equilibrium orientational state. This implies that the internal effective field that rotates the spins in the absence of a constraint and, therefore, has to be used in equation (3) is just the opposite of the constraining field [12]. In combination with the locally self-consistent multiple-scattering (LSMS) method, the SD technique has been applied so far to bulk metals and alloys [12–14] and, very recently, to interfaces [15].

In order to deal with exchange splitting and relativistic scattering on an equal theoretical footing we combined the first-principles SD scheme based on constrained DFT by solving the Kohn–Sham–Dirac equation,

$$[c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + V(\mathbf{r}) + \mu_B \beta \boldsymbol{\sigma} \cdot (\mathbf{B}^{\text{xc}}(\mathbf{r}) + \mathbf{B}^{\text{con}}(\mathbf{r})) - E] \psi(\mathbf{r}) = 0, \quad (4)$$

where $\boldsymbol{\alpha}$ and β are the usual Dirac matrices, $\boldsymbol{\sigma}$ are the Pauli matrices, $V(\mathbf{r})$ stands for the Hartree and the exchange–correlation potential, while within the local spin density approximation (LSDA) $\mathbf{B}^{\text{xc}}(\mathbf{r})$ is an exchange field interacting only with the spin of the electron. Equations (3) and (4) form the very basis of a relativistic *spin-only* dynamics, inasmuch as no attempt is made to explicitly trace the time evolution of the orbital moments.

We applied, in conjunction with both the MFT and the SD technique, the multiple-scattering Green function embedded cluster method developed by Lazarovits *et al* [16]. Here, first a self-consistent calculation is carried out for the surface system in terms of the relativistic screened Korringa–Kohn–Rostoker (SKKR) method [17], and then the nanostructure is embedded into this host according to the equation

$$\boldsymbol{\tau}^c(\epsilon) = \boldsymbol{\tau}^r(\epsilon) [\mathbf{I} - (\mathbf{t}^r(\epsilon)^{-1} - \mathbf{t}^c(\epsilon)^{-1}) \boldsymbol{\tau}^r(\epsilon)]^{-1}, \quad (5)$$

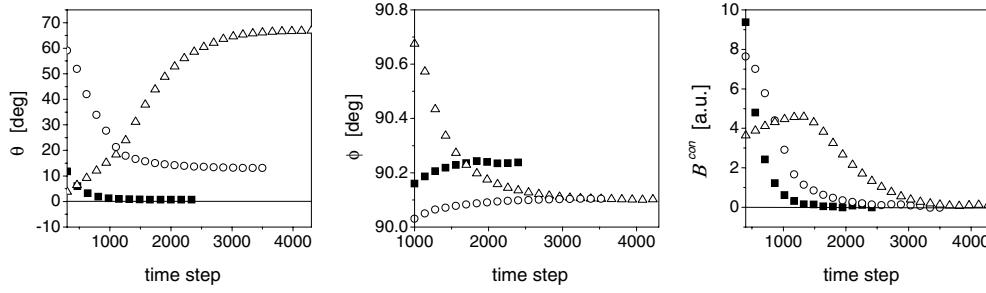


Figure 2. The evolution of the direction of magnetization and the magnitude of the constraining field according to a spin dynamics calculation for two Fe impurities placed into different layers of a Cu(111) surface: \blacksquare , $S + 1$; \triangle , S ; \circ , $S - 1$. For better clarity, the corresponding results for the first 300–1000 iterations are not shown. Only the data for one of the Fe atoms are displayed (see the text).

where $\tau^r(\mathbf{t}^r)$ and $\tau^c(\mathbf{t}^c)$ are site and angular momentum matrices of the scattering path operators (single-site t operators) of the host surface system and the cluster, respectively, and ϵ is the energy. By solving also the corresponding Poisson equation with appropriate boundary conditions, a self-consistent calculation for the selected cluster can be performed that takes full account of the environment [16]. It is important to underline that this description does not rely on periodic boundary conditions applied to the (embedded) cluster. In all calculations, we used the atomic sphere approximation (ASA) and an angular momentum expansion up to $\ell_{\max} = 2$.

3. Two Fe impurities at Cu(111) surfaces

The simplest system that reduces the symmetry of the fcc(111) layers to just one mirror plane is a pair of nearest neighbour defects, as illustrated in figure 1. We embedded two such Fe impurities on top, i.e., into the first vacuum layer (labelled $S + 1$), into the surface (S) layer and into the subsurface ($S - 1$) layer of a Cu(111) surface. First a self-consistent SKKR calculation was performed by relaxing the potentials of six Cu layers and three empty sphere layers in order to describe the surface region from the bulk to the vacuum. Then, by employing equation (5), for the three cases above the Fe dimers were calculated self-consistently. Since these calculations are intended to provide us only with qualitative predictions, for simplicity, we neglected relaxations of the potentials of the host atoms.

As mentioned before, the present implementation of our SD scheme serves (only) for finding the magnetic ground state of the system; therefore, it is sufficient to consider only the second (damping) term on the right-hand side of equation (3). The evolution of the spin orientation is then measured on a timescale with a unit (time step) of $1/\lambda$. In figure 2 the evolution of the θ and ϕ angles and the magnitude of the constraining field are plotted on this artificial timescale for one of the Fe atoms. Note that during the SD procedure, the magnetic configuration of the two Fe atoms was confined to being symmetric with respect to the (y, z) plane. (We checked, however, that the final result is independent of the starting configuration.)

Actually, in a few time steps, for all three layer positions, the magnetic state of the two Fe atoms became nearly ferromagnetic and perpendicular to the line connecting the two impurities ($\phi \simeq 90^\circ$). A satisfactory convergence was, however, achieved only thousands of time steps later, when—as can be seen from figure 2—the constraining fields converged to zero. The final magnetic states can be summarized as follows: $\theta = 0.73^\circ$, 66.8° and 13.1° , as well as

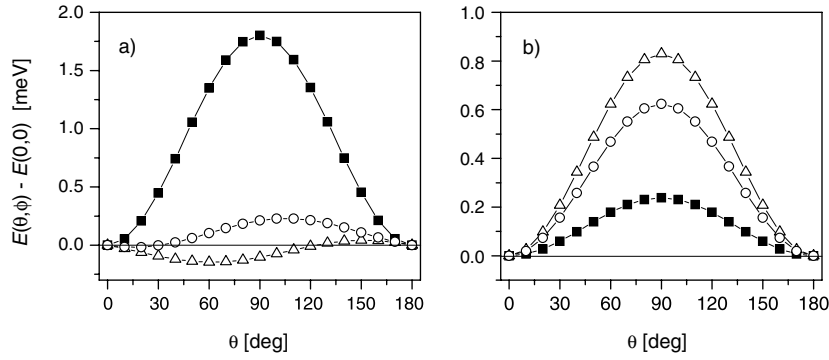


Figure 3. Band energy differences from MFT calculations for two Fe impurities at a Cu(111) surface: \blacksquare , $S+1$; \triangle , S ; \circ , $S-1$; (a) $\phi = 90^\circ$, (b) $\phi = 0^\circ$. Solid lines show curves fitted to equation (1) with the parameters contained in table 1.

Table 1. Anisotropy parameters (in units of meV)—see equation (1)—fitted to energies calculated within the MFT for two Fe impurities placed in different layers of a Cu(111) surface. The azimuthal angle corresponding to the global minimum of the energy is also displayed.

Layer positions	$K_{2,1}$	$K_{2,2}$	$K_{2,3}$	θ_0 (deg)
$S+1$	-0.51	-0.39	-0.0026	0.083
S	-0.18	0.23	-0.079	62.0
$S-1$	-0.21	0.10	-0.065	15.7

$\phi = 90.2^\circ$, 90.1° and 90.1° , for one of the Fe atoms in layer $S+1$, S and $S-1$, respectively, and a symmetric orientation for the other Fe atom. Clearly, these magnetic ground states are in qualitative agreement with the predictions of the simple phenomenological theory; see equations (1) and (2).

We carried out MFT calculations by using the output of the SD calculations. Figure 3 shows (band) energy curves obtained while scanning the (uniform) direction of the magnetization through the paths $0 < \theta < 180^\circ$ for $\phi = 90^\circ$, i.e., in the (y, z) plane, and for $\phi = 0^\circ$, i.e., in the (x, z) plane. All the calculated data fit almost precisely the function in equation (1) with the parameters listed in table 1. For all three cases the minimum of the energy is found in the (y, z) (symmetry) plane at an azimuthal angle, θ , also shown in table 1. These angles coincide remarkably well with those obtained from the SD calculations. It should be noticed, however, that by using the output of self-consistent calculations with a magnetization fixed along the z axis, in particular for an Fe dimer placed in layer S , we obtained an apparently different ground state orientation ($\theta = 46.5^\circ$). This clearly demonstrates that the applicability of MFT is quite limited.

It is obvious that a pair of Fe atoms in layer $S+1$ represents the case of strong perpendicular anisotropy with a corresponding anisotropy energy of about 0.9 meV/Fe atom. This clearly explains the relatively fast convergence of the SD scheme, while in the other two cases due to the smaller spin-orbit coupling the convergence was much slower (see figure 2). For Fe dimers immersed into layers S and $S-1$ a change of the orientation from the z to the x direction costs much more energy than a corresponding variation within the symmetry plane, because the otherwise remarkably reduced anisotropy constants, $K_{2,1}$ and $K_{2,2}$, differ in sign. Concomitantly, the relative increase of the magnitude of $K_{2,3}$ gives rise to a canted ground state; see equation (2). It should be noted that, like the case discussed in [18], the change of

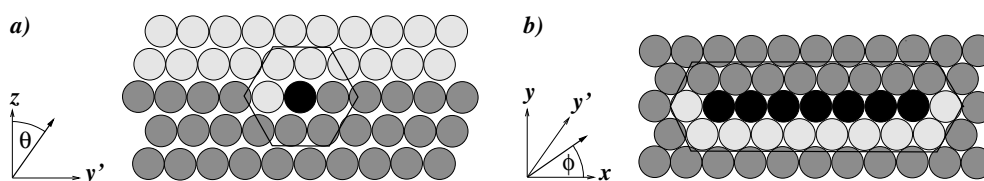


Figure 4. A schematic view of the geometry of a seven-atom Co chain along a Pt(111) step edge. Full circles: Co atoms; shaded circles: Pt atoms; open circles: empty spheres. a): side view; b): top view of the surface Pt layer with the Co chain. The cluster embedded is indicated by solid lines. The coordinate system is referred to the azimuthal and polar angles, θ and ϕ , that characterize the orientation of the magnetization. (Note that in [9] a different coordinate system and the opposite notation for the angles is used.)

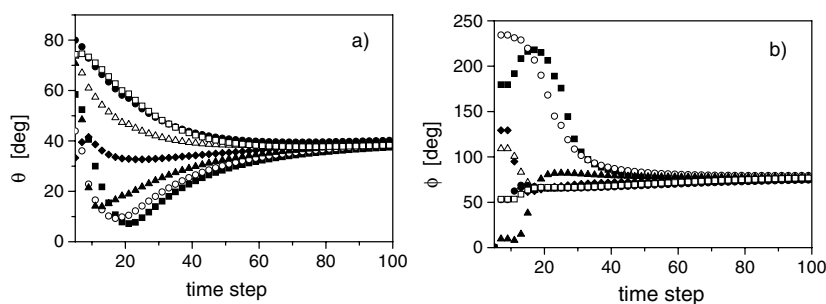


Figure 5. Evolution of the angles θ , part (a), and ϕ , part (b), defining the orientation of the spin moments for the seven Co atoms in the finite chain depicted in figure 4. The symbols refer to the following Co atoms numbered from left to right in part (b) of figure 4: ■, 1; ○, 2; ▲, 3; ◆, 4; △, 5; ●, 6; □, 7. Only the first 100 time steps are shown.

the anisotropy constants, $K_{2,i}$, with respect to the position of the Fe dimer can be related to the different hybridizations between the electronic states of the Fe and the Cu atoms.

4. Finite Co wire at the step edge of a Pt(111) surface

We first performed a calculation treating eight layers of Pt self-consistently, together with four layers of vacuum. Then, a seven-atom chain of Co together with ten empty (vacuum) spheres were embedded into the topmost Pt layer, as schematically indicated in figure 4. Simultaneously, all the nearest neighbours of the Co atoms were re-embedded into the respective Pt or vacuum layers to allow the relaxation of potentials around the Co chain. Therefore, an embedded cluster of a total of 55 atoms was treated self-consistently.

For each Co atom in the chain, in figure 5 the evolution of the θ and ϕ angles is plotted for the first 100 time steps on the artificial timescale mentioned in section 3. Initially, the directions of the atomic magnetic moments were set by a random number generator. It can be seen that after some oscillations both the θ and the ϕ angles for all the Co atoms quickly approach nearly the same value for all the Co atoms, i.e., as in the previous case of Fe dimers at a Cu(111) surface, to a nearly ferromagnetic configuration. The initial rapid oscillations that can be observed in figure 5 are the consequence of the relatively large constraining fields caused by large exchange energies whenever the moments point in very different directions. In about 1000 time steps the ϕ angles converged to 90° , with a spread of less than 1° , i.e.,

Table 2. Calculated magnitudes and orientations of the spin and orbital moments in a seven-atom Co chain along a Pt(111) step edge.

Atom	Spin moment		Orbital moment	
	Moment (μ_B)	Θ (deg)	Moment (μ_B)	Θ (deg)
1	2.23	41.1	0.25	39.1
2	2.18	42.5	0.20	41.5
3	2.18	42.3	0.19	40.1
4	2.18	42.4	0.20	41.3
5	2.18	42.3	0.19	40.2
6	2.18	42.5	0.20	41.5
7	2.23	41.1	0.25	39.1

normal to the chain, and the θ angles converged to nearly 42° . All these results are in excellent agreement with experiment [9].

We also performed MFT calculations with the self-consistent potentials and fields obtained from the SD procedure. The fitted anisotropy parameters $K_{2,1} = -0.16$ meV, $K_{2,2} = -1.06$ meV and $K_{2,3} = -4.81$ meV not only reproduce fairly well the easy axis, $\theta = 38^\circ$ and $\phi = 0^\circ$, but also result in a value of the anisotropy energy (defined as the energy difference between the hard and the easy axes) of 1.42 meV/Co atom that compares satisfactorily with that derived from experiment (2.0 meV) [9].

Extracted from the final (equilibrium) state, the size and the azimuthal angle θ of the spin and orbital moments for each Co atom are shown in table 2. While the calculated spin moments for the inner Co atoms ($2.18 \mu_B$) are in good agreement with the value deduced from experiment ($2.12 \mu_B$) [9] and also with other theoretical studies on infinite wires [19, 20], the edge of the wire is characterized by larger spin (and orbital) moments [21]. Although our calculated orbital moments for the inner atoms (0.19 – $0.20 \mu_B$) are larger than the corresponding values from other LSDA calculations ($0.16 \mu_B$ [19] and $0.15 \mu_B$ [20]), they are still much too small when compared to the experimental value ($0.68 \mu_B$) [9]. Note that on including an orbital polarization scheme or using the LDA + U method, values of $0.92 \mu_B$ [19] and $0.45 \mu_B$ [20] can be obtained.

As can be inferred from table 2, the spin moments of the inner atoms are fairly parallel; those at the end of the chain, however, are off by more than 1° . This can be associated with the anisotropy energy contributions being larger at the end of the chains than inside, as found for finite Co wires deposited on a Pt(111) surface [21]. It can also be seen in table 2 that the orbital moments oscillate more strongly in magnitude and orientation than the spin moments. As pointed out by Jansen [22], within the DFT the spin and orbital moments are required to align only when the ground state relates to a high symmetry direction. This is, however, not the case for the Co wire, since the ground state orientation is not directly induced by symmetry.

5. Summary

In this work we presented calculations of the magnetic ground state of linear atomic chains placed onto surfaces in terms of the magnetic force theorem and an *ab initio* spin dynamics scheme. We found that due to the variation of the anisotropy constants the canted magnetic state obtained for an Fe dimer at a Cu(111) sensitively depends on its position. In excellent quantitative agreement with experiment, we obtained a canted ground state for a finite Co wire along a Pt(111) surface step edge. We also found that this magnetic state is non-collinear: a feature that is expected to play a key role in nanostructures of more complex geometry.

Acknowledgments

Financial support was provided by the Centre for Computational Materials Science (Contract No GZ 45.531), the Austrian Science Foundation (Contract No W004), the Research and Technological Cooperation Project of Austria and Hungary (Contract No A-3/03) and the Hungarian National Scientific Research Foundation (OTKA T046267 and OTKA T037856). The work of BU and GMS was supported by DOE-OS, BES-DMSE under contract number DE-AC05-00OR22725 with UT-Battelle LLC. Calculations were performed at ORNL-CCS (supported by OASCR-MICS) and NERSC (supported by BES-DMSE).

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