Magnetism at the nanometric lengthscale

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Received el 30 de noviembre de 2006; aceptado el 8 de octubre de 2007

The reduction of dimensions at the nanometric length scale gives rise to new and unexpected physical phenomena. Of special interest is the magnetic behaviour of low dimensional systems, since it can differ from that presented by three-dimensional structures. We review some new magnetic phenomena intimately related to dimensionality. This includes a discussion of singular results on the ground state properties of thin films of ferromagnetic metals, carbon nanotubes and surfaces of non-magnetic ionic crystals. Fully relativistic ab-initio calculations based on the screened Korringa-Kohn-Rostoker method explain the spin-reorientation transitions observed at consecutive atomic Co layers grown on Ru(0001). As the thickness of the cobalt film increases stepwise from one to three atomic layers, the magnetization changes direction twice, by 90 degrees each time. The calculations demonstrate that only for two-monolayer thick cobalt films, the interplay between strain, surface and interface effects leads to perpendicular magnetization. Carbon nanotubes, which constitute a new class of mesoscopic one-dimensional quantum systems, present symmetry dependent intrinsic magnetic properties. We show that in chiral tubes the spin-orbit interaction removes spin degeneracy at the Fermi level in the absence of a magnetic field. This remarkably unusual behavior has a symmetry origin and is due to the absence of spatial inversion symmetry of the crystal potential of chiral nanotubes. Finally, the occurrence of spin-polarization at the surfaces of ionic oxides is proven by means of ab-initio calculations within the density functional theory. Large spin moments develop at O-ended polar terminations of ionic oxides, transforming a non-magnetic insulator into a half-metal. The magnetic moments mainly reside in the surface oxygen atoms, and their origin is related to the existence of 2p holes of well-defined spin polarization at the valence band of the oxide.

Keywords: Magnetism, magnetic anisotropy; thin films; nanotubes; surfaces; ionic oxides; Co; ZrO$_2$.

1. Introduction

Nanostructures are emerging as new fascinating materials that are interesting both from a fundamental point of view and due to the large variety of technological applications they offer. The reduction of one or more dimensions at the nanometric length scale gives rise to new properties and unexpected physical phenomena [1]. At their origin are the crucial role of symmetry or the enhanced effect of surfaces and boundaries. Special interest presents the magnetic behaviour, since it can differ from that shown by three-dimensional (3D) systems. Even non-magnetic materials may develop spin polarization when forming 1D and 2D structures [2]. Understanding the fundamental mechanisms responsible for these unexpected magnetic properties is a main challenge, that requires to explore the role of dimensionality and quantum confinement in determining the magnetic behaviour of low dimensional systems. Further, it would represent a significant step...
in the long-standing search for novel high temperature magnets. We review some recent magnetic phenomena, which may promise emerging directions for the development of new magnetic materials and for the design and implementation of spintronic devices. This includes a discussion of unique results on the magnetic properties of thin films of ferromagnetic metals and on the ground state of non-magnetic materials as carbon nanotubes and ionic crystals [3–5].

The magnetic anisotropy governs the definition of the easy-axis of magnetization in magnetic materials, and thus, it determines how spins orient in thin films of ferromagnetic metals. In general, the anisotropy energy is the result of a delicate balance between different contributions. In thin films, the dominant term is often the dipolar or shape anisotropy, which favors an in-plane orientation of the magnetization. This contribution results from the long-range magnetic dipole-dipole interactions. However, other contributions such as the bulk, interface and surface magnetocrystalline anisotropy energies, as well as magneto-elastic terms, can compete with the dipolar anisotropy to favor out-of-plane magnetization [6, 7]. Therefore, a quantitative knowledge of the various contributions to the anisotropy energy may allow one to control the direction of the magnetization of ferromagnetic films. In particular, magnetization perpendicular to the film plane holds promise for novel information-processing technologies [8].

By means of spin-polarized low-energy electron microscopy (SPLEEM) [9–11], we showed that as the thickness of cobalt films grown on Ru(0001) increases stepwise from one to three atomic layers, the magnetization changes direction twice, by 90 degrees each time [3]. Fully relativistic ab-initio calculations based on the screened Korringa-Kohn-Rostoker (SKKR) method [12] for layered systems. Dipole terms are included in the Madelung constants. The magnetic anisotropy energy (MAE) is obtained as the difference of the total energy for an in-plane and an out-of-plane magnetization, so that a positive MAE corresponds to an out-of-plane magnetization. By employing the force theorem [16], the MAE is defined as a sum of a band energy, $\Delta E_b$, and a classical magnetic dipole-dipole energy $\Delta E_{dd}$ contributions. The value of $\Delta E_{dd}$ is calculated solving the magnetostatic Poisson equation [17], while the band-energy term is obtained from the SKKR calculation. $\Delta E_b$ can be further resolved into contributions with respect to atomic layers that enable us to define surface and interface anisotropies. Moreover, changing the lattice parameters in the calculations allows us to determine how strain influences the magnetic anisotropy.

2. Model and method

2.1. Magnetic anisotropy of Co layers

To establish the orientation of the magnetization of ultrathin Co films, we perform ab-initio calculations based on the relativistic spin polarized screened Korringa-Kohn-Rostoker (SKKR) method [12] for layered systems. Dipole terms are included in the Madelung constants. The magnetic anisotropy energy (MAE) is obtained as the difference of the total energy for an in-plane and an out-of-plane magnetization, so that a positive MAE corresponds to an out-of-plane magnetization. By employing the force theorem [16], the MAE is defined as a sum of a band energy, $\Delta E_b$, and a classical magnetic dipole-dipole energy $\Delta E_{dd}$ contributions. The value of $\Delta E_{dd}$ is calculated solving the magnetostatic Poisson equation [17], while the band-energy term is obtained from the SKKR calculation. $\Delta E_b$ can be further resolved into contributions with respect to atomic layers that enable us to define surface and interface anisotropies. Moreover, changing the lattice parameters in the calculations allows us to determine how strain influences the magnetic anisotropy.

2.2. Chiral carbon nanotubes

Our study of the spin resolved electronic structure of CNTs is based on the Slater-Koster [18] empirical tight-binding (ETB) model including the spin-orbit interaction (SO). The model takes into account the actual discrete nature of the lattice. The unit cell of the CNTs is generated by rolling up a portion of graphene layer. We focus on chiral metallic CNTs, although the SO induced effects are also present in chiral semiconductor tubes. We consider $sp^3$ orbitals, curvature effects [19] are included, and the Tománek-Louie parametrization of graphite [20] is used. The spin-orbit (SO) interaction is caused by the coupling of the spin of a moving electron with an electric field which acts as a magnetic field in the rest frame of the electron. In a crystalline environment, the major internal contribution arises from the electron orbital motion in the crystal potential, and thus its effects are related to the crystal symmetry. Assuming spherical symmetry, the SO interaction can be expressed as $H_{SO} = \lambda \mathbf{L} \cdot \mathbf{S}$, where the SO coupling constant ($\lambda$) depends on the atomic orbital, $\mathbf{L}$ is the angular momentum and $\mathbf{S}$ the spin of the electron.
Within the ETB framework, $H_{SO}$ couples $p$ orbitals on the same atom, and $\lambda$ can be either greater or smaller than the atomic value [21, 22]. The exact value of $\lambda$ in nanotubes is unknown, although low dimensionality, electron-electron interactions and magnetic fields are shown to induce an enhancement of the SO coupling [23–25]. The present calculations have been performed with $\lambda = 0.2$ eV [4] for clarity in the figures, since the SO strength can be controlled by a proper choice of gate potentials [26], as was first proposed for semiconductor heterostructures.

2.3. Polar c-ZrO$_2$ thin films

We have studied thin films of cubic ZrO$_2$, whose structure corresponds to the CaF$_2$ lattice, grown along the low-index directions. For some of these crystallographic orientations, namely (100) and (111), the stacking of atomic planes shows an alternance of O and Zr composition. Our results are obtained from first-principles spin-polarized calculations within the DFT (density functional theory) under the GGA (generalized gradient approximation) for exchange and correlation [27]. We use the SIESTA package [28,29] with basis sets formed by double-zeta polarized localized numerical atomic orbitals. More details about the conditions of the calculations can be found elsewhere [30, 31]. The films are modelled as periodic slabs containing a vacuum region of 10 Å. The width of the vacuum region is enough to inhibit interaction between neighbouring surfaces, while that of the ZrO$_2$ slab is chosen to attain an almost bulk-like behaviour at the innermost central layers. The slabs are symmetric about the central plane, to avoid an artificial divergent Madelung energy. The atomic positions are allowed to relax until the forces on the atoms are less than 0.06 eV/Å.

3. Results and discussion

3.1. Magnetic anisotropy of Co layers

Both Co and Ru crystallize in the hexagonal-close-packed (hcp) structure, although the in-plane lattice parameter of bulk Co in the hcp basal plane is 7.9% smaller than that of Ru. First, we calculate the anisotropy of pseudomorphic one-(1ML) and two-monolayer (2ML) thick Co films, so that Co is under pronounced tensile strain. To release it, we consider uniform contractions of the Co-Ru and Co-Co interlayer distances ($d$) relative to the Ru-Ru interplanar spacing. As shown in Fig. 1a, and 1b, for both Co thicknesses the value of $\Delta E_b$ increases as the interplanar spacing decreases to approach the characteristic Co atomic volume. It becomes positive for contractions larger than 4% for the 1ML film, while for 2ML, it is positive for all the range of $d$. However, due to the negative $\Delta E_{dd}$, the preferred orientation of the magnetization remains always in-plane for 1ML and only above $\Delta d \sim 4\%$, the MAE of the 2ML film favours an out-of-plane magnetization. Interestingly, the change in the MAE is not proportional to the strain and, therefore, simple magnetoelastic arguments do not apply.

Another way to release the strain is to contract the in-plane lattice parameter. We model the in-plane relaxation by contracting the supporting Ru substrate together with the Co film. In the 1ML case, the sign of the MAE does not change (result not shown in the figure). Thus, we conclude that the magnetization of one Co monolayer remains in-plane regardless of strain. For the bilayer, $\Delta E_b$ remains positive, but even under uniform contractions of the Co-Co and Co-Ru interlayer spacings (Fig.1c), it does not compensate the negative $\Delta E_{dd}$. However, the artificial contraction of the in-plane Ru lattice should be corrected introducing a different relaxation of the Co-Co and Co-Ru interlayer distances. An estimation of this difference is obtained assuming that atoms try to maintain the nearest-neighbors (NN) distances of their bulk materials, with Co-Ru distances being an average of the preferred Co-Co and Ru-Ru interlayer separations. This leads to contractions of 7% for the Co-Co interlayer distances and a nearly unrelaxed Co-Ru spacing. As shown by the open symbols in Fig. 1c, such a lattice distortion considerably increases $\Delta E_b$, resulting in a total positive MAE. The surface and interface contributions to $\Delta E_b$ for the contracted in-plane 2ML film are shown in Fig. 1d. With uniform interlayer relaxations, the dominant term is due to the interface Co atoms. However, when Co-Co and Co-Ru interlayer separations are allowed to be different -diamonds in Fig. 1d-, the contribution of the surface Co layer is remarkably enhanced, resulting in the positive value of the MAE (out-of-plane magnetization).

![Figure 1](image-url)  
**Figure 1.** Calculated magnetic anisotropy energies of different Co films on Ru. (a)-(c) Dependence of the calculated MAE (square) and its components, $\Delta E_b$ (circle) and $\Delta E_{dd}$ (up-triangle), on variations of the interlayer distance with respect to the substrate for: pseudomorphic (a) 1 ML and (b) 2 ML Co/Ru(0001) films; (c) in-plane strained 2 ML Co/Ru(0001), with open symbols corresponding to non-uniform contractions of the Co-Co (-7%) and Co-Ru (0%) interlayer separations. (d) Dependence of the surface and interface contributions to $\Delta E_b$ on the interlayer distance for the in-plane strained 2 ML Co/Ru(0001) films of panel (c), diamonds referring to the non-uniform relaxations case, from Ref. 3.
For 3 ML and thicker films, a negative MAE is always obtained for either the ideal or contracted in-plane Ru lattice. The dominance of the increasingly negative $\Delta E_{\text{dd}}$ term associated to thicker films drives the magnetization in-plane.

Experimentally it is found that 1ML films always present a 1×1 LEED pattern indicating pseudomorphic growth, while films thicker than 1 ML are no longer pseudomorphic [3]. From the diffraction patterns, a contracted in-plane spacing of 5±1 % is estimated. Therefore, the most realistic structure for the 2ML Co films is the one represented by the open symbols in Fig. 1c.

In summary, the calculated MAE for consecutive atomic Co layers at the most realistic structures changes sign twice, as observed experimentally. Furthermore, the results highlight that the double spin-reorientation transition is the result of a complicated interplay of structural and interface/surface electronic effects and therefore, the magnetic anisotropy of ultra-thin Co films cannot be simply explained by strain or interface effects alone, but by a combination of both.

### 3.2. Chiral carbon nanotubes

We focus on chiral NTs, which do not have an inversion center and only possess spiral symmetry operations. We have chosen as representative the (9,3) tube. In principle, it presents the band crossing at the Fermi level at $\Gamma$ and only possess spiral symmetry operations. We have considered possibility [32] of spin polarization.

However, for chiral tubes, because of the lack of an inversion center, only the condition imposed by time reversal invariance holds and thus spin degeneracy is removed.

In general, time reversal symmetry only requires that each energy state occurs twice, but not at the same $k$ point in the Brillouin zone. Since the SO interaction preserves time reversal invariance, its role in chiral NTs manifests as an asymmetry in momentum space of the energy branches corresponding to up and down electrons. This is illustrated in Fig. 3, where the spin-resolved dispersion relation for a (9,3) NT around $E_F$ is represented. In this figure, it is also clearly evidenced that electron velocities become dependent on both the spin and the direction of the motion.

#### 3.3. Polar c-ZrO$_2$ thin films

c-ZrO$_2$ may present different surface terminations: polar, both Zr- and O-ended, and non-polar. We have studied thin films ended in all the low-index surfaces including the rarely considered possibility [32] of spin polarization.
Our main result indicates that polar O-terminated thin films of c-ZrO$_2$ present a magnetic ground state, while both the Zr-ended and the non-polar surfaces do not show any spin polarization. Therefore, only the O-rich oxide surfaces are magnetic. The energy reduction due to spin polarization for the low-index surfaces deviates between 0.22 eV/ZrO$_2$ unit for the c-(001) and 0.91 eV/ZrO$_2$ for the c-(111) terminations. These values have been obtained as the total energy difference between the relaxed spin-polarized and non-spin-polarized slabs. They are in the range of those obtained for magnetic bulk oxides [33], and should be taken as the correct order of magnitude more than as an exact prediction.

For all the structures which present a magnetic ground state, magnetic moments (mm) develop at the layers closest to the surface. They reach the largest values at the surface of O plane, and decrease for the layers below. The mm is 0.8 $\mu_B$ at the outermost oxygen layer of c-ZrO$_2$(100) and amounts to 1.6 $\mu_B$ for the O-ended c-ZrO$_2$(111) surface. Although localised, the spin polarization extends to the center of the slab, i.e., for a nine layer symmetric c-ZrO$_2$(100) slab in which O and Zr planes alternate, the mm takes the values 0.82, -0.20, 0.15, -0.03 and 0.07 $\mu_B$ from the surface to the central layer, respectively. Note that the mm in the Zr layers couples antiferromagnetically to the oxygen mm.

All spin moments arise almost exclusively from the $p$ electrons of the valence band of the oxide. Further, the distinct characteristic of the magnetic thin films is the loss of coordination of the outermost O atoms, which already suggests that the O spin polarization can be related to the decrease of the oxygen ionic charge at the surface with respect to the bulk of ZrO$_2$. The correlation is evident comparing the oxygen Mulliken populations at the surface layer, 6.29 and 6.02 electrons for the c-(100) and c-(111) respectively, with that of 6.79 at bulk ZrO$_2$. In both surfaces, oxygen loses ionic charge approaching a charge neutral state. Even more, the smaller the oxygen ionic charge, the larger its associated magnetic moment. Therefore, there is a clear correlation between the reduction of the ionic charge and the size of the magnetic moment. This means that the spin polarization is a response of the system to the loss of transferred charge from the cation to the oxygen. Indeed, for the calculated surfaces with a non-magnetic ground state we obtain O charges close to the bulk ones, which support the origin of the magnetism to be due to the loss of transferred charge. Nevertheless, although the magnetization is a local effect rooted in the lack of donor electrons for the outermost O atoms, the interaction of these atoms with the lower adjacent planes cannot be neglected: the spin polarization at the surface layer induces a magnetic moment at the neighbouring planes, which decays as we deepen into the bulk.

We also found that the (100) and (111) magnetic surfaces of c-ZrO$_2$ are half-metallic. The Fermi level crosses the valence band of the topmost layer, and the bands at $E_F$ always have a well defined minority spin character. The effect of the spin exchange is mostly the shift of the minority spin band. For these surfaces, the majority spin band is full with an almost bulk-like DOS shape, while a deep redistribution of charge affects the partially filled minority spin electrons. The differences between majority and minority spin bands observed in the energy distribution of electron states are also clearly seen in the charge distributions shown on the left and central panels of Fig. 4, which depict the spin resolved charge density differences (CDD, total charge density minus the superposition of atomic charge densities) of the c-ZrO$_2$(100) surface within a plane normal to the surface along the bond direction between a surface O atom and a nearest neighbour at the layer below. For the completely filled majority spin band, the corresponding CDD adopts a charge distribution similar to bulk c-ZrO$_2$. On the contrary, a depletion of charge appears in the minority spin band. This asymmetry between the spatial distributions of the spin states gives rise to the mm. The rightmost panel of the figure shows the corresponding spin density difference (SDD), CDD of majority spin minus CDD of minority spin. Ferromagnetism in thin films of HfO$_2$ and ZrO$_2$ has been measured [34, 35] and very recently it has been demonstrated that it is a universal feature of nanoparticles of otherwise nonmagnetic oxides as CeO$_2$, Al$_2$O$_3$, ZnO, In$_2$O$_3$ and SnO$_2$ [36], which supports the existence of the magnetization mechanism presented here.

4. Conclusions

Fully-relativistic calculations explain why as the thickness of Co films grown on Ru(0001) increases stepwise from 1 to 3ML the magnetisation changes direction twice by 90 degrees, a surprising and rarely observed atomic-layer-stepped spin reorientation transition. They show that the in-plane easy-axis of magnetization of 1 and 3 ML Co films is stable with respect to variations of the strain conditions and demonstrate that only for 2 ML Co films, the interplay between strain, surface and interface effects leads to perpendicular magnetization.

We have also shown that in chiral CNTs, the spin-orbit interaction removes spin degeneracy at the Fermi level in the absence of magnetic field, whereas in achiral tubes, spin degeneracy is preserved. This remarkably unusual behavior is due to the absence of spatial inversion symmetry of the crystal potential of chiral nanotubes, and hence it has a symmetry origin.

Finally, we have proved the occurrence of spin-polarization at the O-ended polar surfaces of thin films of...
Large spin moments are formed due to the lack of donor charge and the subsequent creation of 2p holes in the valence band of the oxide. This leads to a half-metallic ground state, with the majority spin band completely filled and only minority spin states at the Fermi level. The magnetic moments mainly reside in the surface oxygen atoms, although the spin polarization at the surface layer induces a magnetic moment at the neighbouring planes, which decays as we deepen into the film.

Furthermore, they open new routes to the manipulation of spin currents.

Acknowledgments

This research was supported by the Spanish Ministry of Education and Science under Project MAT2006-05122. S.G. acknowledges financial support through a Ramón y Cajal contract of the Spanish Ministry of Education and Science.