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**STRUCTURE, MAGNETISM AND DYNAMICS OF
NANOSTRUCTURED MATERIALS: A THEORETICAL INVESTIGATION**

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ABSTRACT

The present work illustrates how modern atomistic modeling and simulation can supplement the experiments performed in the laboratory by helping to resolve and understand the experimental information, by predicting new phenomena and providing useful hints to guide the development of innovative materials with original, specifically tailored properties. This paper presents our recent theoretical work on nanostructured materials including i) magnetic alloyed CoRh nanoparticles that are good candidates to combine both a large magnetic moment and a high magnetic anisotropy, and ii) nanoscale Mn films adsorbed on W substrates as an example of artificial magnetic material.

1. INTRODUCTION

Motivated by the broad range of technological applications, an intense research field is nowadays concerned by the possibility of generating innovative materials with controlled and adjusted properties to meet specific demands. This is for instance the case in the information storage industry as the rapidly increasing amount of data requires the development of recording media and devices with always bigger storage capacities.

In this context, magnetic nanostructured materials like magnetic nanoparticles and ultrathin films, are extensively studied as potential break-through technologies. Through the enhancement of surface or interface effects, the reduction of dimensionality gives indeed rise to unique properties that are often completely different from those observed in the bulk materials and that may lead to novel materials or devices:

- Recent experiments have demonstrated the interest of alloyed CoRh nanoparticles to combine both a large magnetic moment (stemming from Co) and a high anisotropy (stemming from Rh), while the reduction of size leads furthermore to a strong enhancement with respect to the bulk solids [1].
- The epitaxial growth of nanoscale thin films on appropriate substrates also represents another way to modify considerably the properties of bulk solids through the stabilization of unusual crystalline phases, suggesting hereby the possibility of generating artificial materials. As a representative system, we consider here the case of ultrafine Mn films adsorbed on W substrates that exhibit at room temperature an unusual base-centered-cubic (bcc) structure and are magnetic, whereas this phase in the bulk state is only stable at very high temperature, beyond any magnetic ordering temperature [2].

In such nanoscale systems, understanding the complex interplay between structure, chemical order and magnetism as well as the growth mechanisms in view of controlling and adjusting them, requires atomically resolved information which is often difficult to draw from laboratory experiments only. Many questions remain indeed open and need to be clarified. The lack might be compensated by the use of appropriate computational approaches using state-of-the-art quantum mechanical calculations, and possibly, to get access to larger systems, less-demanding semi-empirical simulations with high-level interaction potentials.

In the following we illustrate our computational approach and its application to the two mentioned examples: small CoRh nanoparticles from atomic clusters to sizes of technological interest, and Mn nanolayers on a W substrate.

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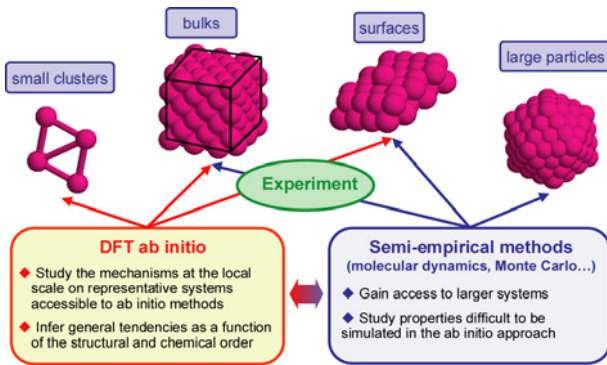


Figure 1: Computational approach used for the study of magnetic bimetallic CoRh nanoparticles.

2. MODELING APPROACH

In nanotechnology studies, atomistic modeling and simulation can fruitfully and economically supplement the experiments performed in the laboratory. They can help to resolve and understand the experimental information, predict new phenomena and provide useful hints to guide further investigations. This is particularly necessary since the quantum behavior characteristic of the nanoscale often escapes to the intuition one can try to infer from the macroscopic world.

A modern and particularly efficient theoretical approach is based first on quantum mechanical calculations to understand and predict from a fully general *ab initio* point of view the interactions between the atoms at the local scale and the inherent quantum effects like magnetism. We used the VASP code [3] that implements in a very efficient way the density functional theory [4], one of the most successful *ab initio* methods able to deal with transition elements in a tractable way. More technical details on our *ab initio* calculations can be found in Refs. 5–9. The code allows to determine many different ground-state properties (optimal structure, magnetic moments, formation energy...) as well as some dynamical parameters (diffusion barriers).

However, the main drawback of *ab initio* methods is their large computational demand, which restrains their use to relatively small or periodic systems. Therefore, our *ab initio* calculations on magnetic CoRh nanoparticles were limited to representative model systems (small clusters with a few atoms up to macroscopic alloyed bulks and surfaces). Then, in a second step the inferred trends were extrapolated to particles of technological size by means of less demanding semi-empirical molecular

dynamics and Monte Carlo Metropolis simulations (Fig. 1). The accuracy of the semi-empirical simulations was ensured by using efficient interaction models specifically adjusted on the *ab initio* results [8].

Our *ab initio* study of Mn/W ultrathin films focused on the first stages of the film growth [9]. The structure and magnetism of compact films were first analyzed, and then the kinetics of the Mn surface diffusion was investigated through the determination of the elementary dynamical events and the associated diffusion barriers. These *ab initio* results bring all ingredients needed to perform a further kinetic Monte Carlo study in the aim of simulating larger time and length scales.

In both studies, the high accuracy of our calculations was checked through extensive convergence studies and is supported by the excellent agreement obtained with previous *ab initio* calculations and with experimental results available for some reference systems (pure clusters, clean surfaces, macroscopic solids).

3. RESULTS

3.1. Magnetic bimetallic CoRh nanoparticles

Between the molecular and metallic states, small alloyed transition-metal nanoparticles of a few nanometer diameter, such as Co_MRh_N , have recently appeared as promising candidates to combine both enhanced magnetization (arising from Co atoms since bulk Rh is non-magnetic) and high magnetic anisotropy (coming from the large spin-orbit coupling in 4d elements like Rh) [1]. From the experimental side, many questions remain open due to the difficulty to get precise atomically-resolved information on such small systems: what is the chemical order within the particles (disordered, core/shell structure...)? What governs their magnetic properties (nature of alloy, size, composition, chemical order...)?

A first insight is given by our *ab initio* investigation of the doping of a non-magnetic Rh surface by magnetic Co impurities (Fig. 2). This demonstrates that two main effects are relevant: i) while they maintain high magnetic moments, Co atoms induce significant moments on the Rh neighbors that increase with Co concentration; ii) the presence of a free surface leads to a further magnetic enhancement for the atoms located in vicinity of the surface. Even at very low Co concentration, giant effective magnetic moments of $4 \mu_B$ can be reached. A tendency to Co enrichment close to the surface is also observed.

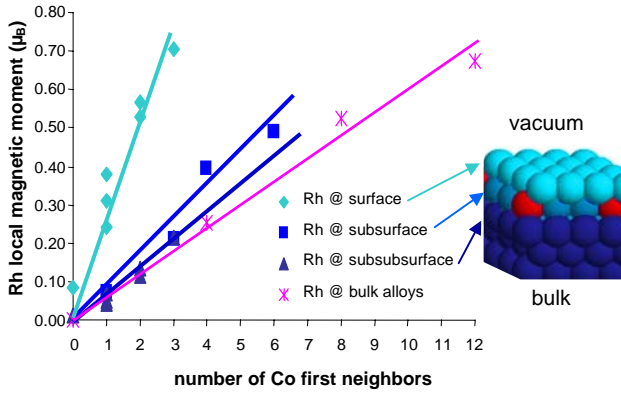


Figure 2: Magnetic moments induced in a Rh(111) surface doped by Co impurities located in the subsurface layer, as a function of the number of Co neighbors and depending on the depth of the Rh atoms in the surface.

These two effects are combined in very small clusters containing a few atoms and generally lead to magnetic moments significantly increased with respect to the bulk alloys. This is in good agreement with the experimental observations. However, in this non-scalable size range there is no simple correlation between magnetic enhancement and Co doping. Our calculations show that the most stable clusters are the most compact structures, but not always the most magnetic ones. They exhibit a strong preference to form mixed Co–Rh bonds (Fig. 3), a tendency which progressively vanishes approaching the bulk state. The magnetic doping is particularly efficient for larger clusters exhibiting a non-magnetic bulk-like core like Rh₃₈ (Fig. 4); in this case, the presence of a single Co atom results in a significant increase of the total magnetic moment by 16 μ_B.

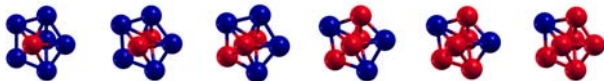


Figure 3: Tendency to form preferentially mixed Co–Rh bonds illustrated on small atomic clusters of increasing Co content.

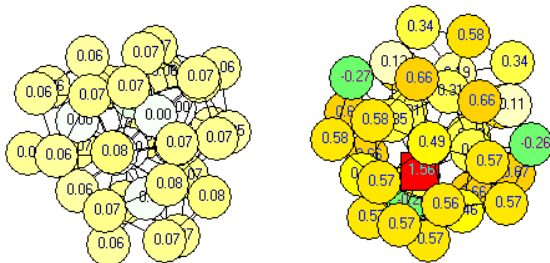


Figure 4: Doping of Rh₃₈ into Rh₃₇Co resulting in a huge magnetic enhancement from 2 to 18 μ_B. The numbers are the local moments in μ_B. The red square is the Co atom.

To investigate nanoparticles with sizes of technological interest, we performed semi-empirical molecular dynamics and Monte Carlo simulations using an efficient interaction model specifically adjusted on the previous *ab initio* results. This enabled us to determine the equilibrium geometry and chemical order as a function of the composition (Fig. 5). Co-rich particles have a glass-like structure resulting probably from the synthesis process, while Rh-rich particles exhibit a crystalline fcc structure. All particles present a Rh-core/Co-shell structure with a few Co atoms accommodated at the center. These results allow to interpret in a very convincing way the wide-angle X-ray scattering (WAXS) experiments (Fig. 6).

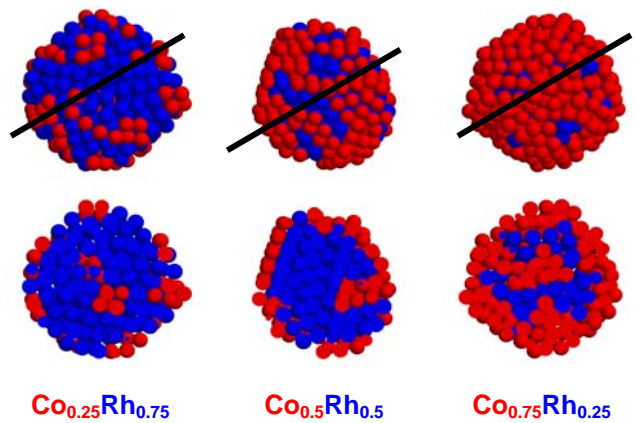


Figure 5: Chemical order within 420-atom particles as predicted by Monte Carlo simulations (top: side view, bottom: cross-sections). Dark and light balls are Rh and Co atoms, respectively.

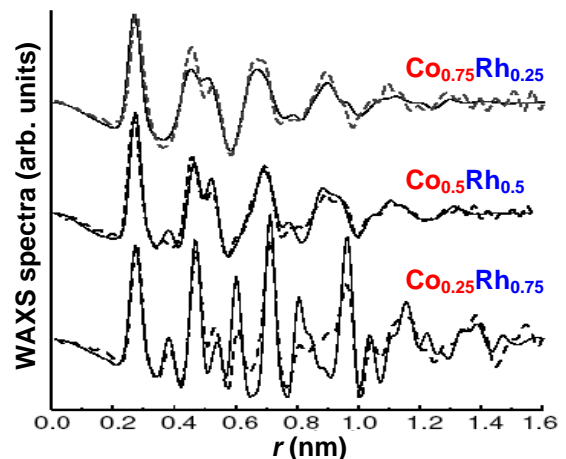


Figure 6: WAXS spectra of mixed particles with various compositions (solid lines: experiments, dotted lines: simulations from the structure of Fig. 5).

3.2. Magnetic Mn nanolayers grown on W substrates

Thin Mn films deposited on W substrates have recently appeared as good templates for the generation of artificial magnetic materials. Recent experiments [2] have indeed demonstrated that upon adsorption, Mn films up to a few layers adopt at room temperature a bcc pseudomorphic structure (δ -Mn) and are magnetic, whereas this structure is stable in the bulk state only at temperatures much higher than any possible magnetic ordering temperature. If an antiferromagnetic (AF) superstructure was observed for Mn deposited on W(110), no quantitative determination of the magnetic moments could be performed experimentally. The origins of the strongly anisotropic growth pattern leading to one-dimensional stripes are still unclear; a thorough understanding of the corresponding mechanisms is essential to be able to control the growth. Moreover, only the W(110) substrate was considered, and the question of magnetism in Mn/W(100) films still remains open.

To get a better insight in the structural and magnetic properties of this intriguing systems, *ab initio* calculations turned out to be very helpful [9]. We first studied compact thin films according several growth patterns on both W(110) and W(100) surfaces (Fig. 7). In good agreement with experiments, our calculations demonstrate that pseudomorphically adsorbed Mn films up to 3 monolayers (ML) are thermodynamically stable despite the huge tensile strain induced by epitaxy (the misfit between δ -Mn and W is about 13 %). The $(\sqrt{2}\sqrt{2})R45^\circ$ reconstruction shown by the clean W(100) surface locally vanishes around Mn adatoms, which partially restores the bcc geometry and thus favors the pseudomorphic growth.

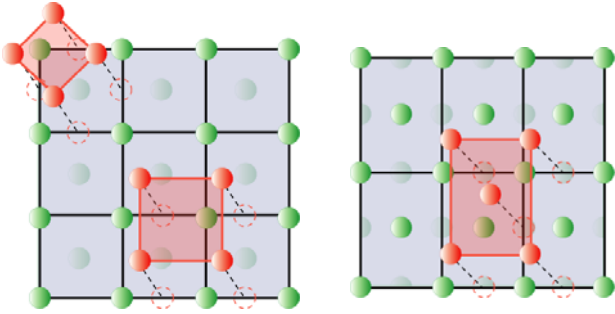
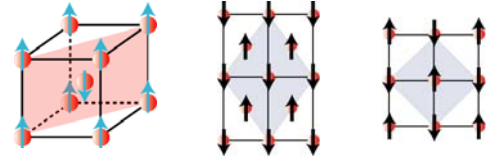


Figure 7: Adsorption of Mn monolayers on W(100) (left) and W(110) (right) surfaces, according different patterns.

For Mn/W(110) we find that in good agreement with experiments, a $c(2\sqrt{2})$ inplane AF order (i.e. a checkerboard arrangement of antiparallel magnetic moments) is stabilized at each film thickness. For Mn/W(100) our calculations predict a ferromagnetic (FM), not yet experimentally observed, arrangement in 1 and 2-ML-thick films, with a transition to a layered AF

order in (100) planes for higher thicknesses. In both cases large Mn magnetic moments reaching typically $3.5 \mu_B$ /atom are obtained in spite of the strong Mn-W interaction, while smaller moments of about 0.1–0.3 μ_B /atom are induced on the W atoms at the interface. In order to estimate the influence of going from a 3D to 2D system, we took benefit of the possibility of computer experiments to investigate strained bulk δ -Mn and free-standing Mn ML. Indeed, as illustrated in Tab. 1, there is a very strong correlation between the local environment (number of first neighbors, interatomic distances/atomic volume) and the magnetic moments, that generally increase as the geometry is expanded and/or the dimensionality is reduced. The simulation also revealed the strong influence of magnetism to the structural properties. It is for example magnetism that stabilizes the pseudomorphic growth of Mn films on W(110).

Geometry of bulk δ -Mn	μ (μ_B)	V_{at}
fully relaxed ($a=2.84 \text{ \AA}$)	1.44	1.00
isostructural to W ($a=3.17 \text{ \AA}$)	3.40	1.44
matching the W(100) surface	2.01	1.15
matching the W(110) surface	2.84	1.17



Geometry of free Mn ML	μ (μ_B)	a (\AA)
Mn(100) ML	fully relaxed	2.55
	expanded	4.35
Mn(110) ML	fully relaxed	3.30
	expanded	3.99

Table 1: Ground-state magnetic moments μ of bulk δ -Mn and free-standing Mn monolayers, either fully relaxed or geometrically constrained: influence of the expansion of the lattice constant a (for bulks, V_{at} is the local atomic volume in unit of the fully relaxed $V_{at}^0=11.091 \text{ \AA}^3$). All configurations are AF.

However, to approach realistic experimental growth conditions, it is important to consider also kinetic effects that may introduce severe limitations. To this aim, we also looked more closely at the elementary dynamical events occurring when Mn atoms diffuse on the surface during the first stages of the growth (Fig. 8).

Basically, atoms can move on the surface by two main processes: hopping from one stable adsorption site to a nearest-neighboring vacant one, or exchange with a surface atom which is pushed out at the surface. Our

calculations of the corresponding energy barriers show that the Mn diffusion is governed by the hopping processes, while exchange with surface atoms is highly disfavored. The substrate nature turns out to have a large influence on the diffusion: hopping is easier on more compact surfaces. Strong Mn-W bonds make the diffusion on clean W surfaces more difficult compared to Mn-covered surfaces where diffusion barriers are generally smaller. However, in this case the magnetic interaction between adatoms and the Mn underlayer – which is strongly magnetic – leads to interesting phenomena: in magnetic calculations, the adatoms are usually located at a larger distance from the substrate than in the non-magnetic one and thus see a flatter surface, which generally reduces the diffusion barriers: this remarkable effect could be experimentally observed if the samples are cooled down sufficiently. In addition, frustration effects due to exchange interaction between the diffusing atom and the substrate may lead in some cases to transient spin-flip or quenching, resulting in higher activation energies.

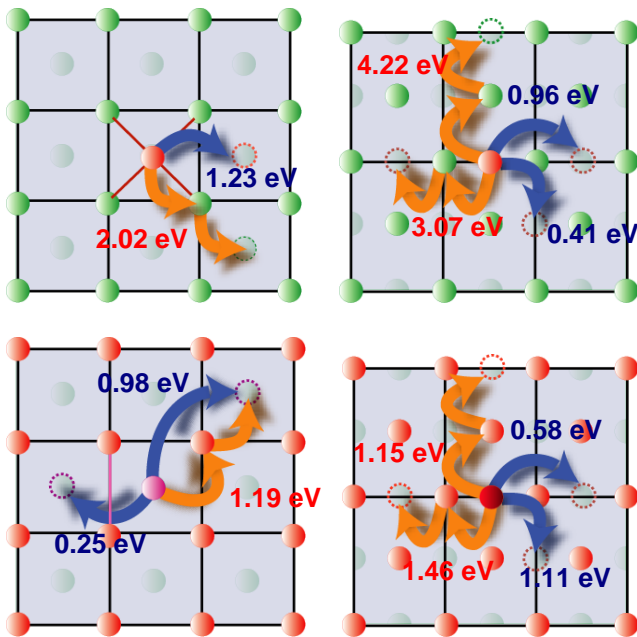


Figure 8: Some diffusion barriers calculated in *ab initio* for the Mn diffusion on clean (top) and Mn-covered (bottom) W surfaces. Blue (dark) and orange (light) arrows depicts hopping and exchange processes, respectively.

Further calculations are currently in progress to investigate the Mn diffusion at stepped surfaces. These *ab initio* results and those of the work reported here will bring all ingredients to perform a further semi-empirical study involving kinetic Monte Carlo simulations, which will allow to gain access to larger time and length scales.

4. CONCLUSION

Taking benefit of the original, unique behaviors characteristic of the nanoscale to design and study new materials or systems generally requires an atomically-resolved information which can be difficult to draw only from real experiments. Moreover, a thorough understanding of the basic underlying mechanisms is essential if one wants to be able to properly control and adjust the properties of the systems under investigation.

In this context we have presented our recent theoretical investigations on nanostructured systems including magnetic bimetallic CoRh nanoparticles and ultrathin Mn films deposited on W substrates. Our approach based on state-of-the-art *ab initio* calculations associated to semi-empirical simulations employing high-level, carefully generated interaction models, has allowed us to gain a better insight in the properties of these systems. Such a computational approach is quite general and can be easily applied to other systems.

Finally, the presented work illustrates how modern atomistic modeling and simulation can fruitfully supplement the experiments performed in the laboratory, by helping to resolve and understand the experimental information, predicting new phenomena and providing useful hints to guide the development of innovative materials with original, specifically tailored properties.

5. REFERENCES

- [1] D. Zitoun *et al.*, “Magnetic enhancement in nanoscale CoRh particles”, *Phys. Rev. Lett.* 89, 037203 (2002).
- [2] M. Bode *et al.*, “Structural, electronic and magnetic properties of a Mn monolayer on W(110)”, *Phys. Rev. B* 66, 014425 (2002).
- [3] <http://cms.mpi.univie.ac.at/vasp/>
- [4] See for instance W. Kohn, “Electronic structure of matter – wave functions and density functionals”, *Rev. Mod. Phys.* 71, 1253 (1999), and references therein.
- [5] S. Dennler, *Structure and magnetism of 3d/4d and 3d/5d alloyed systems: An ab initio study from the macroscopic alloys down to the nanoparticles*, PhD thesis, Université Paul Sabatier, Toulouse, France (2004).
- [6] S. Dennler, J. Morillo, G. Pastor, “First-principles study of binary clusters and alloys”, *J. Phys.: Condens. Matter* 16, S2263 (2004).
- [7] S. Dennler, J. Hafner, M. Marsman, and J. Morillo, “Magnetic doping of 4d transition-metal surfaces: A first-principles study”, *Phys. Rev. B* 71, 094433 (2005).
- [8] J. Morillo, S. Dennler, M.C. Fromen, M.J. Casanove, P. Lecante, and G. Pastor, “Structure, chemical order and magnetism of binary Co-4d(5d) transition metal nanoparticles: Experiment and theory”, *Proceedings of the “Workshop on nanoscale materials: from science to technology ’04*, NovaScience Publisher, New York (in press).
- [9] S. Dennler, J. Hafner, “A first-principles study of ultrathin magnetic Mn films on W surfaces”, *Phys. Rev. B* (in press).