

# INVESTIGATION OF MAGNETIC ATOMS AND NANOPARTICLES BY POLARIZED X-RAY ABSORPTION SPECTROSCOPY



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To be awarded the Latsis Prize for research carried out at the Ecole Polytechnique Fédérale de Lausanne in 2003 is a great encouragement for a young researcher. I wish to thank the Latsis Foundation for this honor and the EPFL research commission for the positive evaluation of the work presented here.

There has always been a spell in magnetic phenomena, starting from the invisible and yet powerful attraction of two magnets brought close to each other that we first observed as kids. There is much more than that in our daily life : magnets are used to drive electric motors, transformers, telephones, and to store digital information on credit cards and computer hard disks. Despite this broad range of applications, however, our understanding of magnetism, even in the simplest materials, is still incomplete. This needs not be discouraging ; on the contrary, as the status of our knowledge advances, we may be able to artificially produce and exploit novel magnetic structures whose properties are still to be discovered.

Most elements in the periodic table are magnetic as free atoms. However, only iron, cobalt, nickel, a few rare-earths and their alloys exhibit ferromagnetic properties in bulk compounds. The evolution of the atomic magnetic moments, their mutual coupling (which ultimately produces macroscopic magnetism), and the appearance of magnetic anisotropy in molecules, nanosized aggregates, and solids are the subjects of intense investigation. Besides being of fundamental interest, such questions bear on the design of novel magnetic devices with one or more dimensions reduced to the length scale of interatomic cooperative magnetic behavior. History shows that from the invention of the compass to the electric motor and the computer, advances in magnetic materials have paralleled the commercial, industrial, and information revolutions of the past centuries. Understandably, we have good theoretical models and plenty of experimental data that tell us how magnetism works in free atoms and crystalline solids. However, as we explore the realm in between these two limits, we face a remarkable paucity of experimental information. The relevant length scale of the exchange interaction in most magnetic materials is only a few atomic spacings. This is the reason why the exploration of magnetic nanostructures has traditionally lagged behind the semiconductor field. Whereas in semiconductors the dimensions of the system influence the

charge carriers behavior already for typical lengths of tens of nanometers, magnetic materials must be engineered down to the Angstrom scale. It is only in the last two decades that advances in growth and characterization methods have allowed us to investigate and produce artificial structures with magnetic properties controlled with nanometer precision. Such progress has given rise to a wealth of technological applications, of which the most relevant are giant magnetoresistance, currently used in sensors and in the read-heads of computer hard disks, spin-based electronics, of great promise for integrated memory and electronic devices, and the conception of new magnetic media. Presently, we are concerned with fundamental issues that govern the magnetic behavior of nanostructured materials as well as that of bulk magnetic alloys. The first step in assembling either of these is the deposition of a magnetic atom on a nonmagnetic substrate or matrix. From this premise starts our investigation.

### **Magnetic Atoms on Nonmagnetic Surfaces**

The experimental approach is based on the extensive use of synchrotron radiation in the soft x-ray range, which represents one of the most powerful spectroscopy techniques with magnetic sensitivity available to date. Scanning tunneling microscopy (STM) was also used to relate the atomic-scale morphology of metal particles with their magnetic properties. Atoms in the gas-phase are (para)magnetic when the sum of the spin (**S**) and orbital (**L**) magnetic moments of its electrons is nonzero. The bar graph in Fig. 1 (a) shows the magnitude of **S** and **L** for a free Co atom with  $d^7$  electronic configuration as given by the Hund's rules. In a solid, however, band-structure and hybridization effects, by modifying the local  $d$ -electron configuration strongly affect or even completely quench the atomic magnetic moment. This is shown in Fig. 1 (b)-(d) to be a gradual process that starts as soon as a magnetic atom is brought into contact with a nonmagnetic surface. At the same time, magnetic anisotropy appears as a result of the broken spherical symmetry of the free atom.

In alloys with nonmagnetic metals, the extent to which the  $d$  electrons of transition-metal (TM) atoms mix with the conduction  $sp$  electrons governs fundamental macroscopic properties such as the resistivity,

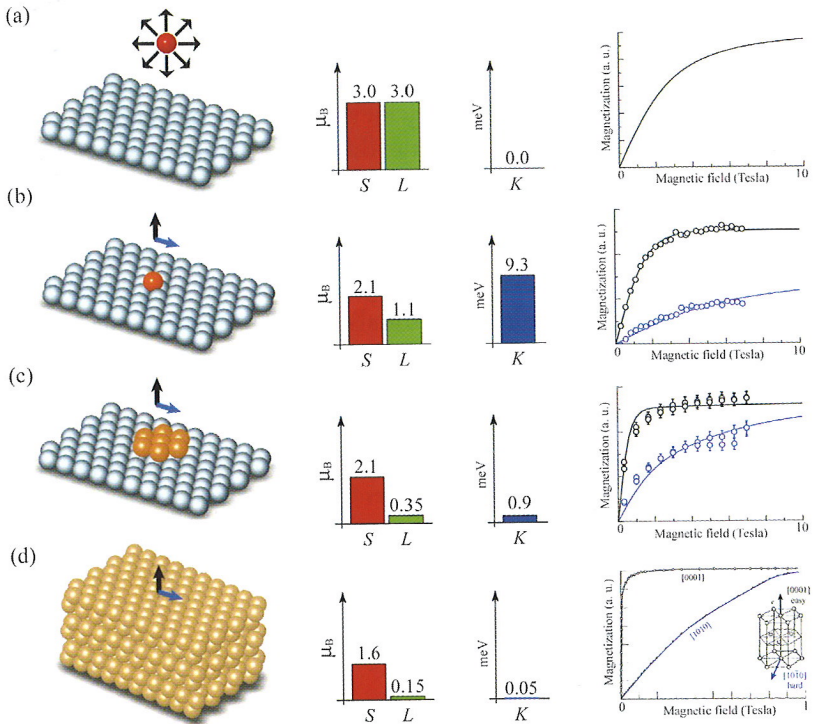


Fig. 1 : The bar graph shows the magnitude of the spin (**S**) and orbital (**L**) magnetic moments and the magnetic anisotropy energy (**K**) for a Co atom in the gas-phase (a), on a Pt surface (b), in a particle consisting of 7 atoms on a Pt surface (c), in the bulk hcp phase (d).

magnetic susceptibility, and specific heat. In this context, we set about a conceptually simple but experimentally challenging problem, that of determining the modifications of the magnetic moment of a TM atom on metal surfaces of different type. The experimental challenge lies in the extremely reduced amount of TM atoms that can be probed together as isolated entities on a two-dimensional surface. To achieve the required sensitivity and to obtain simultaneous information on the electronic structure and magnetic state of the deposited atoms, we employed x-ray absorption spectroscopy (XAS) with circularly polarized x-rays. The lineshape and relative strength of the XAS spectra due to excitation of

the  $2p$  to  $3d$  electronic transitions are fingerprints for the  $d$ -state configuration of the probed atoms. As the absorption depends on the orientation of the sample magnetization relative to the x-rays polarization direction, magnetic sensitivity is achieved by x-ray magnetic circular dichroism (XMCD), i.e., by taking the difference of the XAS spectra for parallel and antiparallel orientation of the light helicity with respect to an externally applied magnetic field that defines the sample magnetization (see Fig. 2). The size of the XMCD signal allows to determine the magnetic moment of a given element. In Fig. 2, we can observe that the coupling between the  $d$  electron orbitals and the substrate conduction states changes substantially (XAS shape), reducing the atomic magnetic moments (XMCD) going from Cs to Li in the Alkali group in the periodic table. The substrate free-electron density turns out to be the crucial parameter that determines the extent to which the magnetic  $d$ -states mix with the host conduction electrons and therefore governs the

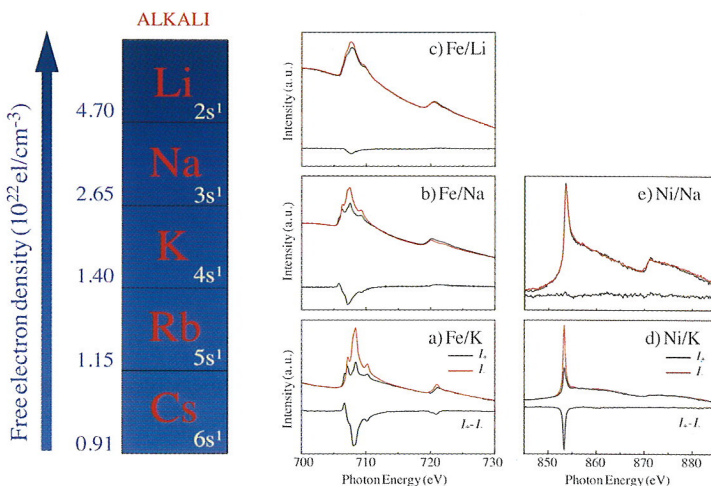


Fig. 2 : Magnetic moment of Fe and Ni atoms on substrates with increasing free-electron density (left) as given by the XMCD magnitude. XAS spectra recorded with parallel (black lines) and antiparallel (red lines) polarization relative to a 7 Tesla applied magnetic field at 10 K and corresponding XMCD for (a) Fe/K, (b) Fe/Na, (c) Fe/Li, (d) Ni/K, (e) Ni/Na. Note that the absence of XMCD for Ni/Na indicates that the Na substrate ‘kills’ the Ni magnetism.

magnitude of the atomic magnetic moment. Such effects have been predicted in the framework of the Anderson model, where the covalent admixture of free-electron states with a  $d$ -state is shown to reduce the number of spin-up electrons and increase the number of spin-down electrons.

### The Rise and Fall of Magnetic Anisotropy

A fundamental question concerns the origin of magnetic anisotropy, its correlation to the atomic magnetic moments, and how both evolve from single atoms to finite-sized magnetic particles and bulk compounds. The magnetic anisotropy energy (MAE) describes the tendency of the magnetization to align along specific spatial directions rather than randomly fluctuate over time, thereby determining the stability of the magnetization in bulk magnets as well as nanoparticle systems. By controlling the energetic hierarchy of the different diffusion and association/dissociation processes of atoms at surfaces, we can study isolated magnetic atoms deposited on an atomically ordered metal surface and subsequently increase the particle size almost in an atom-by-atom fashion, as shown in Fig. 3. The experiment, of course, is carried out in ultra-high-vacuum conditions.

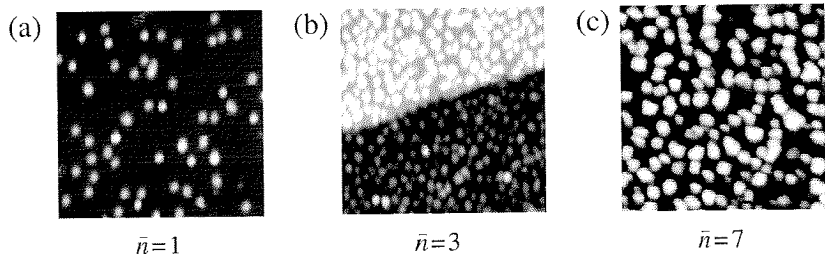


Fig. 3 : Scanning Tunneling Microscope images of Co particles grown on Pt(111) with average size  $\bar{n}$ . All images  $180 \text{ \AA} \times 180 \text{ \AA}$  ( $1 \text{ \AA} = 10^{-10} \text{ m}$ ).

The observation of the MAE of single surface atoms and small particles in this reduced size range is reported here for the first time. The MAE for single Co atoms on a Pt(111) surface is about 9 meV, which is exceptionally large compared to the hardest magnetic bulk compounds

such as  $\text{SmCo}_5$  (1.8 meV/Co atom) and CoPt alloys (0.8 meV/Co atom). Different effects combine in establishing the huge MAE of Co atoms on the Pt surface. (i) The broken symmetry of the Co atoms as compared to the gas phase constitutes the necessary condition to exhibit anisotropic behavior. (ii) The reduced coordination leads to  $3d$ -electron localization (band narrowing), which augments the spin-orbit energy due to increases in the local density of states near the Fermi level and the spin magnetic moment. (iii) The strong spin-orbit coupling of the Pt  $5d$ -states results in additional MAE of the induced magnetization, an effect common to CoPt compounds. While (i) determines the angular dependence of the MAE, (ii) and (iii) determine its magnitude. Measurements on larger Co particles further reveal the predominant influence of (ii) on the MAE. Figure 4 shows that the MAE is rapidly quenched with increasing average particle size  $n$ . Remarkably, drastic changes of the MAE are observed for one-atom variations of the particles size, showing that the coordination of the magnetic atoms is the key parameter that determines both the angular dependence and magnitude of magnetic anisotropy.

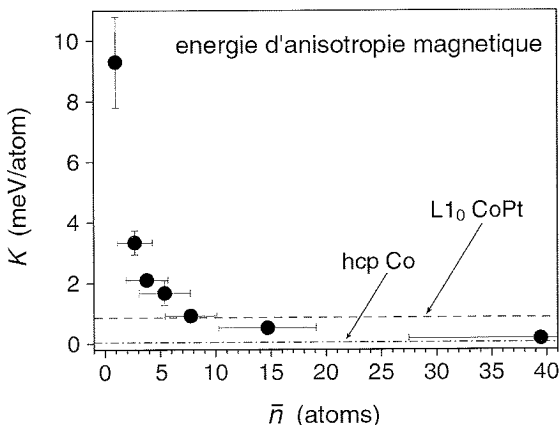


Fig. 4 : Magnetic Anisotropy Energy ( $K$ ) as a function of the average size of Co particles on a Pt surface. For comparison, the dashed and dashed-dot lines show  $K$  per Co atom of a CoPt alloy and bulk hcp-Co, respectively. The error bars on the horizontal scale represent the standard deviation of the particle size distribution determined by STM.

## Conclusions

The use of synchrotron radiation spectroscopy and high magnetic field facilities, coupled to the ability to arrange one or more atoms at a time into structures of designed shape, size, and chemical composition has allowed us to elucidate the rich magnetic behavior of atoms and nanometer-sized particles on nonmagnetic surfaces. In the quest for novel physics, I believe that there are two converging directions of research. On the one hand, we must develop new tools that combine structural, chemical, and magnetic sensitivity at an atomic level in order to fully understand all the processes that contribute to magnetism. On the other hand, the principles and observations reported in the previous sections can be used a guide to create novel magnetic structures. These include metal nanoparticles, magnetic semiconductors, and supramolecular assemblies of metal-organic magnets at surfaces. Ultimately, I believe that only the coordination of ideas and expertise from different domains can lead to substantial progress in the field of magnetism and magnetic materials.

To conclude, I would like to gratefully acknowledge the many experimental groups that contributed to this work, in particular the staff at the *Institut de Physique des Nanostructures, Ecole Polytechnique Fédérale de Lausanne*, the *Institut für Festkörperforschung, Forschungszentrum Jülich*, the *ID08 beamline at the European Synchrotron Radiation Facility* in Grenoble, the *Max-Planck-Institut für Festkörperforschung* in Stuttgart, the *Istituto di Struttura della Materia* of the *Italian National Research Council* in Trieste.