Magnetic properties of supported metal atoms and clusters

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Introduction

Storing huge amounts of digital information is still the domain of magnetic storage devices. During the last few decades, enormous progress has been made in increasing the available magnetic storage density. To increase the storage density further, the magnetic particles storing the information have to become smaller and smaller. However, with decreasing size the particles will be superparamagnetic, e.g. the magnetic moments of the individual atoms in the particle are still ferromagnetically coupled, but the resulting total magnetic moment of the particle can rotate freely. The critical parameter to fix the total magnetic moment in space is the anisotropy energy, i.e. the work that is required to rotate the magnetization from the easy axis to another direction. Quite generally, the anisotropy energy can have contributions from shape anisotropy, strain-induced anisotropy as well as magnetocrystalline anisotropy, which couples the magnetic moments to the neighbouring atoms via spin–orbit coupling.

The natural size limit for a magnetic particle is a single atom and several studies have been performed on the magnetic properties of adatoms on different surfaces [1–9]. Large anisotropy energies per atom have been found for some adatoms; however, a stable magnetization of a single holmium atom has only been observed at cryogenic temperatures [2].

To tailor small magnetic particles consisting of only a few atoms with large magnetic moments and anisotropy energies, clusters are very promising candidates. The physical and chemical properties of small clusters can strongly vary with their size, which has been shown for chemical [10, 11] as well as magnetic properties [12, 13]. Small clusters are usually dominated by quantum size effects, i.e. adding or removing a single atom from the cluster can drastically change their properties (‘every atom counts’). Hence, experiments on such clusters have to be performed on mass-selected clusters. From a theoretical point of view, these small clusters are also very interesting as they are large enough to show complex physical properties and yet small enough to use highly sophisticated...
theoretical methods. For larger clusters and nanoparticles in the nm range, the size-dependent effects become smaller, but increased magnetic moments are still found [14].

In this review, we will discuss the magnetic properties of small supported transition-metal clusters in the size range from the adatom up to a dozen atoms per cluster.

1.1. Fundamentals

The critical parameter for the further reduction of the size of magnetic structures is magnetic anisotropy. Magnetic anisotropy energy is the energy that has to be overcome to switch a magnetic nanostructure from one state into another, e.g. from zero to one. It is given by the product of the volume \( V \) and the anisotropy constant \( K \), hence it decreases with smaller structures. To avoid a flip due to a thermal excitation, the magnetic anisotropy energy \( KV \) must be much larger than the thermal energy \( k_B T \). To have a sufficient anisotropy energy with decreasing size, the anisotropy constant has to increase with the decreasing size of the structure. The aim in designing new magnetic materials is now an increase of the anisotropy with a small structure size. How can this be realized? Here, one has to understand, what the microscopic origin of the magnetic anisotropy of a few-atom cluster is. In figure 1, this mechanism is sketched. The total magnetic moment is mostly given by the spin moment of the atoms. However, the spin has no direct coupling to the geometry of the cluster. The coupling of the magnetic moments is mediated via the magnetic orbital moment of the atoms. The coupling to the spin is caused by the spin–orbit interaction. Furthermore, the orbital moment is coupled to the geometry of the cluster via the ligand or crystal field. As the ligand field is, in general, asymmetric, this asymmetry is transferred via the orbital moment to the magnetic spin moment, resulting in the magnetic asymmetry energy [15, 16]. Thus, the asymmetry might be enhanced by an increased spin–orbit coupling, a larger magnetic orbital moment or by a stronger ligand field.

In addition to the atomic origin, the magnetic anisotropy can be strongly affected by the shape of a particle or by strain, e.g. induced in thin films due to a lattice mismatch with the substrate.

In solids, the orbital moment is strongly suppressed; however, it usually slightly increases with a decreasing particle size, e.g. in studies on larger magnetic nanoparticles (usually in the 10–100 nm regime) an increased orbital moment is found [17–22]. The spin–orbit coupling can be somehow influenced by alloying the 3d metals with high Z materials with a much larger spin–orbit coupling as in, for example, the 4d or 5d transition metals.

The relation between orbital magnetic moment and magnetic anisotropy energy per atom has been demonstrated by Gambardella et al [1] for small Co adatoms and non-size-selected clusters on a Pt(1 1 1) surface. Here, a clear correlation between the magnetic anisotropy energy per atom and the orbital magnetic moments of the Co atoms within the cluster is found.

For a detailed understanding of these effects, including the interaction within particles as well as with the substrate, the systems should be studied experimentally and theoretically using sophisticated methods. This is possible only for very small systems containing a rather small number of atoms, which can be realized by clusters in the few-atom limit. Modern DFT-based calculations are able to describe the electronic, geometric and magnetic structure of free clusters in detail, e.g. for Fe3 cluster cations, a decrease of the magnetic moment per atom has been found by an antiferromagnetic coupling of the central atom, which can be well explained by theoretical calculations [23].

The experiments on isolated clusters show clearly the importance of mass selection of the clusters, as adding or removing a single atom from the cluster can dramatically change their properties. This is also well known from studies of the chemical reactivity of clusters by Heiz et al [24], who have shown that ‘every atom counts’ in determining the chemical reactivity.

For possible applications, it is mandatory to deposit the clusters on a surface or to embed them in a host material. The surface can have a tremendous influence on the structure and, hence, also on the functionality of the clusters. An example here is the catalytic activity of small Au clusters on a MgO surface [11].

This review is structured in the following way. In the following section we will first discuss the experimental methods used to produce, prepare and deposit mass-selected clusters as well as to measure their magnetic properties using x-ray spectroscopy. As examples, first the magnetic properties of 3d adatoms on different surfaces and the properties of non-size-selected clusters will be discussed, before the results of different mass-selected clusters and, finally, of alloy clusters will be presented.

2. Experiments

In figure 2 the general setup for a typical experiment on mass-selected clusters is sketched, consisting of cluster production, mass selection and deposition as well as spectroscopic investigation. Metal clusters are produced using, in our case, high-energy sputtering by 30 keV xenon ions from pure target material. The ionic clusters are then extracted from the plasma by an electrostatic extraction lens system optimized for rather low kinetic energies (500 eV) of the cluster ions. The clusters are mass-selected using a dipole magnet. Before deposition on a substrate, the clusters are retarded to a kinetic energy less than 1 eV per atom. To further avoid fragmentation, a soft landing scheme is often used, by depositing the clusters into a rare-gas matrix of argon or krypton.

![Figure 1. Principle of the spin-lattice coupling in clusters and solids.](image-url)
2.1. Cluster production

During the last few decades, a large number of different methods to produce small clusters have been described. To study transition-metal atoms, in particular, laser evaporation and sputter sources are used [25, 26]. Within our setup [27], we use Xe ions with up to 30 keV kinetic energy to sputter a target with the cluster material put on high voltage. In figure 2 a sketch of the complete setup is depicted. Atomic and cluster ions produced due to the sputtering process are accelerated typically to 500 eV kinetic energy and are collimated by an electrostatic lens system.

The advantage of this setup is the robust operation and the small consumption of the target material, also making experiments on rather expensive alloys possible. As the source is operated at a pressure around $1 \cdot 10^{-7}$ mbar, the contamination of the often highly reactive small cluster ions with oxygen can also be largely avoided. However, in contrast to sources using supersonic expansion [25], the cluster size is typically limited from a few atoms up to $10^{-15}$ atoms per cluster. A typical example of the clusters which can be produced by the source are depicted in figures 3 and 4 for a Cr and CoPt alloy target, respectively. With increasing cluster size, the yield strongly decreases. However, special size effects for some specific cluster sizes can increase the yield, e.g. the Cr$^3_7$ yield is higher than the Cr$^2_7$ ion yield. In the CoPt example a Co$^0$Pt$^{18}_n$ cluster always shows a higher yield than the pure Pt$^{18}_n$ cluster.

2.2. Mass spectroscopy

Mass selection of the clusters is typically performed by using a dipole magnet field or a radio-frequency quadruple selector. For bimetallic alloy clusters, in particular, a rather good mass resolution is required to select a specific size and composition. Here, the natural isotope distribution of the elements also has to be taken into account as this can strongly reduce the achievable mass resolution. The density of the clusters on the surface can be calculated from the measured ion current directly, if the size of the cluster spot is known.

2.3. Soft landing and sample preparation

To study the size dependency of the cluster properties, the interaction or the coalescence of the mass-selected clusters have to be avoided. This can be realized by depositing only a very small amount of clusters on the surface. However, for x-ray spectroscopy, discussed in section 2.6, a reasonable number of particles is required for a sufficient count rate. The typical coverage given by the atom density in our experiments is on the order of 3% of a monolayer or below.

Furthermore, the clusters have to be deposited on the surface without fragmentation or changing the surface. Using molecular dynamics simulations, Cheng and Landman [28, 29] have shown that, within a soft landing scheme where the clusters are deposited in a rare-gas matrix, clusters can be landed on a surface without destruction. Within a soft landing scheme, the mass-selected cluster ions are first decelerated to a kinetic energy around 1 eV per atom. By using a rare-gas buffer layer on the substrate of typically 5–10 monolayers, the remaining kinetic energy of the clusters can be efficiently transferred to this buffer layer, which is partially desorbed. In figure 5 the result of a simulation for the soft landing of a Cu$^{147}$ cluster on a Cu(1 1 1) surface is depicted (Cheng and Landman [28]. In several experimental studies [30–34] it has been shown that clusters...
deposited on a surface using this method can be prepared without fragmentation. Finally, the rare-gas layers are desorbed by flash-heating the sample and the deposited clusters are in contact with the surface.

In figure 6 the preparation scheme we have used in our experiments is depicted. In a first step, the Cu(100) single crystal used is cleaned and prepared by sputter and anneal cycles (1). In most of our studies the clusters are deposited on thin magnetic films to align the cluster moments via exchange interaction to the substrate, which are then prepared on the Cu(100) crystal (2). For magnetic films, either thin Fe or Ni films have been prepared. For the magnetic x-ray magnetic circular dichroism (XMCD) studies, a magnetization perpendicular to the surface is favourable, so the film thicknesses have to be chosen accordingly. In a further step, the films are magnetized to the remanence using a small solenoid (3). For soft landing a thin rare-gas layer with typical 5–10 monolayer (ML) of argon or krypton is then adsorbed (4) and the clusters are landed in the rare-gas matrix with a kinetic energy of less than 1 eV per atom (5).

Figure 4. Mass spectrum of a CoPt alloy target recorded with the ICARUS cluster source. A variate of different CoₙPtᵣ clusters can be produced, however, with a strongly decreased intensity at larger sizes.

Figure 5. Simulation of the soft landing process of a Cu₁₄₇ cluster on a Cu(1 1 1) surface taken from [28]. The cluster with a kinetic energy of ≅200 eV (b) is landed in a Xe matrix (c) and stays largely intact. If the cluster is landed without the Xe matrix (a) implantation and mixing with the substrate is found. Reprinted (adapted) with permission from [28] Copyright 1994 American Chemical Society.

Figure 6. Preparation of samples with mass-selected clusters using the soft landing scheme described in the text.
Retardation of the cluster ions is performed by an electrostatic modified einzel lens system with an additional correction potential, resulting in a focal spot size in the order of 2 mm². During the deposition process, the cluster current is monitored to measure the number of deposited clusters, from which the mean cluster density on the surface can be calculated. To avoid interaction and coalescence of the clusters, the atom density is kept below 3% of a monolayer. With typical retarded cluster currents between 10 pA up to 1 nA for the different cluster sizes, the deposition process takes 5–60 min.

Finally, to bring the clusters into contact with the surface, the rare-gas layer is desorbed by flash-heating the sample to 80–100 K (6). The typical size of the cluster spot on the surface is in the order of 1–2 mm², which has to then be aligned to the SR beam.

2.4. Deposition of atoms

For adatoms, in principle, the same method as described for clusters can be used. However, atoms can also be produced much more easily by evaporating the corresponding material from a metal foil or a crucible. In general, no mass selection is necessary and also a soft landing scheme does not have to be used, as the evaporated neutral atoms have only thermal energies and no fragmentation is possible. Nevertheless, the atoms have to be deposited on a cold sample to avoid agglomeration and the coverage of the surface has to be kept below a few % of a monolayer, if only adatoms are to be studied. For larger coverages, clusters with a mean size \( m \) can also be produced.

2.5. Geometry of deposited clusters

In general the exact geometry of the clusters on the surface is not known and cannot be easily obtained. In figure 7 some possible geometric structures for a small cluster with three atoms out of two different elements is depicted. On a (100) surface, two different compact structures are possible, and due to the different arrangement of the two elements, four different cluster geometries are possible in total, which cannot be distinguished by x-ray spectroscopy. For small clusters the number of possible geometries is limited, but it will increase strongly with increasing cluster size. Nevertheless, even with methods that can reach atomic resolution, such as scanning tunnelling microscopy, only the size of a compact cluster can be measured, but not the internal structure. This has been shown by Khajetoorians et al [35] creating a compact Fe₈ cluster out of single atoms by atomic manipulation. Only in a unique experiment on Ag₉ clusters on Pt(1 1 1) was it possible to observe the full geometric structure by decorating the cluster with a rare-gas ‘necklace’ [36].

2.6. X-ray absorption and magnetic x-ray spectroscopy

Due to its element specificity, x-ray absorption spectroscopy (XAS) is ideally suited to study the electronic and magnetic properties of small, deposited clusters. Here, localized core electrons are excited into the unoccupied valence states and, due to the dipole-transition selection rules, first-order valence states with a specific angular moment are excited. In figure 8(b) this excitation is sketched for the 3d metals, where the spin–orbit split \( 2p_{1/2} \) and \( 2p_{3/2} \) core electrons are excited into exchange-split unoccupied 3d states.

Near-edge XAS has been shown to be very sensitive to the electronic structure, and also to the magnetic structure of the excited atoms [37–39] (when using circular polarized light).

To study dilute systems as submonolayer systems, a high intensity, stability and tunability of an x-ray source is required. This can be realized by using undulators at third-generation storage ring facilities such as BESSY II, the ALS or PETRA III. In particular, APPLE II-like undulator sources have been proven to be excellent sources for circular polarized synchrotron radiation over a wide energy range from 100 eV up to more than 1 keV photon energy, especially covering the L-edges and M-edges of the 3d and 4f transition metals, respectively. In figure 8(a) the principle measurement scheme used in our experiments is depicted. The sample with the deposited clusters is magnetized out of plane and x-ray spectroscopy is carried out at normal incidence. The x-ray absorption is measured by recording the total electron yield via the sample current.

2.6.1. Sum rules and magnetic moments

To measure the spin and orbital magnetic moments, XMCD has been shown to be the method of choice. In figure 9 typical x-ray absorption spectra of Fe₇ clusters deposited on a magnetized Ni/Cu(100) substrate are shown. The \( L_3 \) and \( L_2 \) white lines at 708 eV and 720 eV are situated on a slowly varying background from the Ni/Cu substrate. In figure 10 corresponding x-ray absorption spectra using circular polarized light in the range of the Co L edges are depicted for CoPt clusters on an out-of-plane magnetized 3 ML thick Fe film prepared on a Cu(100) substrate. As the Co L edges are energetically above the Fe L edges, the background shows a much more complex structure due to extended x-ray absorption fine structure (EXAFS) oscillation from the Fe film.

Using the sum rules [40, 41] given in equations (1) and (2.6.1) for \( 2p \rightarrow 3d \) transitions, the absolute spin and orbital magnetic moments can be estimated for several elements with an error of around 10%. In particular, for the 3d metals Fe, Co and Ni the sum rules have been proven to be very reliable.
to measure the magnetic moments. For many other element this error for the absolute value can be much larger [42–44]. Especially for the early 3d elements, the error for the absolute moments can be 50% or above, as the $2p$ spin–orbit splitting decreases and the $L_3$ and $L_2$ white lines start to overlap. However, relative changes between different systems, e.g. different cluster sizes, of the magnetic moments can still be obtained.

$\mu_s^\text{eff} = -2\mu_B \cdot n_h \frac{A - 2B}{C} + T_z$  \hspace{1cm} (1)

$\mu_s = -\frac{4}{3} \mu_B \cdot n_h \frac{A + B}{C}$  \hspace{1cm} (2)

with

$C = C_{L3} + C_{L2}$  \hspace{1cm} (3)

Figure 8. Principle of x-ray and magnetic XAS. Exciting the spin–orbit split $2p$ electrons of a 3d metal atom of a magnetized Ni/Cu(100) substrate with left and right polarized light (a) will create spin polarized electrons, which probe the exchange-coupling-split empty $d$ states (b).

Figure 9. X-ray absorption and magnetic circular dichroism (XMCD) spectrum of an Fe$_7$ cluster deposited on an out-of-plane magnetized Ni/Cu(100) substrate. The red and blues curves are the x-ray absorption spectra recorded with the two light helicities. The upper (black) trace is the average absorption spectra corresponding to the absorption of unpolarized or linear polarized light. The low (green) trace is the difference spectra of both helicities, e.g. the XMCD spectrum.

$A$ and $B$ are the integrated dichroism signal at the $L_3$ and $L_2$ edge marked in figure 9, respectively. The normalizing factor $C$ is the integrated intensity $C_{L3}$ and $C_{L2}$ over the $L_2$ and $L_3$ white lines, respectively. Additionally, in the x-ray absorption spectra, the direct nonresonant excitation into $s$-like states is included. This contribution does not contribute to the magnetic properties, shows no resonant feature and can be described by a step function.

The sum rules include the number of holes $n_h$. For bulk materials this number is usually quite well known; however, it is not known for small clusters, where $n_h$ might also change with the size of the cluster. The problem with the unknown $n_h$ can be avoided by always giving the magnetic moments per hole. Furthermore, the orbital-to-spin ratio $\mu_s/\mu_s$ is always independent from the number of holes. The effective spin moment $\mu_s^\text{eff}$ includes, in general, the term $T_z$ which is a magnetic-dipole term and is a measure of the asphericity.
of the spin magnetization. In a cubic symmetry system like bulk transition metals this term is generally negligible, but this does not hold for surfaces \[45\], thin films, monolayers \[38\] or deposited clusters and adatoms \[1, 46\]. Hence, the given spin moments \(S_{\text{eff}}\) always include this usually unknown contribution. For simplicity, in the following we will omit the suffix ‘eff’ and will only write \(S\).

3. Transition-metal adatoms and clusters

In the following sections the results obtained on the magnetic properties of deposited adatoms and clusters will be discussed. This will start with a short summary of 3d metal adatoms and non-size-selected clusters deposited on different surfaces. The importance of size selection will than be demonstrated for size-selected Fe\(_n\) and Co\(_n\) clusters on magnetized surfaces with a ferromagnetic coupling within the cluster and relative to the surface.

The effect of antiferromagnetic coupling, which can result in complex non-collinear coupling schemes, will than be described for the showcase of Cr\(_n\) clusters. In the last part the magnetic properties of non 3d metal clusters, e.g. 4d and 4f metals will be discussed, closing with the effect on the magnetization by alloying 3d with 4d and 5d elements.

3.1. Adatoms

Experiments on adatoms do not require a cluster source or mass selection, as corresponding samples can be prepared by evaporating the adatom material from a crucible or a foil. Nevertheless, low temperatures are required to avoid agglomeration and also low adatom coverages below a few \% of a monolayer are mandatory. Several studies on the magnetic properties of 3d metal adatoms on different surfaces have been performed. The first results were presented by Gambardella \textit{et al} for 3d atoms deposited on different alkali surfaces \[3, 47\]. Depending on the substrate, a multiplet structure similar to that of a free atom \[48\] due to the Coulomb interaction of the 2p hole and the 3d electrons has been observed. The multiplet structure is usually vanishing, if the 3d electrons of the adatom are hybridized with the substrate. As an example, in figure 11 the L-edge x-ray absorption spectra for a free Co atom in the gas phase \[48\] and Co adatoms on Pt(1 1 1) and a K film \[3\].
Nevertheless, the magnetic moments depend on the alkali film (K or Na) [47] used, which already shows the importance of the hybridization with the substrate.

Adatoms have been studied on various other surfaces such as different metals, insulators or graphene to vary the adatom–surface interaction and large effects on the magnetic properties have been found.

The strong influence of the hybridization with the surface has recently been shown for Co atoms deposited on a graphene layer (G) prepared on a Ru(0001) and a Ir(111) surface [49]. For Co/G/Ru(0001) a large total magnetic moment of 3.97 ± 0.27μB is found, which is close to the value expected for the free atom. The X-ray absorption spectra also shows a multiplet splitting, which is in agreement with a mixed d5 + d8 electron configuration. In contrast to this, the magnetic moment of Co/G/Ir(111) is strongly reduced to 0.54 ± 0.04μB and the X-ray absorption shows almost no fine structures and resembles Co metal.

This effect is explained by a different splitting of the degenerate 3d orbitals by the crystal field into an a1 singlet (dxy) and two doublets e1 (dx2−y2,dyz) and e2 (d2−z2,dxz) states. As has been shown by Wehling et al [50], the splitting into the different states depends on the absorption site of the Co atom, resulting in different spin configurations, with different magnetic moments.

Similar effects might also be observed for other adatoms; however, the electronic structure of a specific adatom is very important, which has been shown for Co and Fe adatoms on a MgO(100) surface. For Co atoms deposited on a MgO(100) surface, a very large orbital moment close to that of an isolated Co atom is found [4]. This large orbital moment results in a magnetic anisotropy energy which is close to the limit of a 3d metal atom. In this peculiar case, a Co atom on a MgO(100) surface, the magnetic structure of the Co adatom is protected due to symmetry constraints. For Fe on MgO(100) large magnetic moments (μ = 1.25μB, μs = 3.92μB) are also found, but in comparison to the free atom with a 3F ground state the orbital moment is reduced by 40% [5].

In table 1 the ratio of the magnetic moments of deposited Co adatoms on different substrates are listed. Strongly varying ratios are found ranging from (0.16) for Co on Fe/Cu(100) [51] up to >0.9 per d-hole on the insulating surfaces MgO/Ag(100) [4] and Al2O3/Ni3Al(111) [9], which is close to the value of the free Co atom.

In general, a substrate with an open d shell suppresses the magnetic moment, whereas an sp band or an insulating surface does not affect the moment. Nevertheless, the character of the d band of the substrate also shows a strong influence. For an Fe and Ni substrate with empty 3d states, the ratio μ/μs is reduced by a factor of 3 down to <0.3, while the interaction with a 4d or 5d band reduces the ratio by only ≈40% to ≈0.5.

3.2. Non-size-selected clusters

Additionally, several studies on the magnetic properties of non-size-selected clusters have been performed. In these experiments, the cluster material is deposited by evaporation and the cluster size can be estimated from the deposited amount of atoms. The typical size distribution in these studies is in the order of ⟨s⟩ = m ± √m where m is the mean number of atoms. First experiments have been performed by Gambardella et al [1] for Co30 clusters on a Pt(111) surface. A monotonic decrease of the orbital magnetic moments with increasing cluster size is found, which is converging to the corresponding values of thin films and Co bulk, while the spin moments are rather constant.

Fe clusters on Cu(111) have been studied by Pacchioni et al [55] in a similar way by evaporating small amounts of Fe on a Cu(111) surface from 0.007 up to 0.145 ML. The spin moments of the Fe clusters are almost constant, varying only slightly between 2.0 and 2.2μB per atom, whereas the orbital moment μs decreases from 0.66μB for 0.007 ML, e.g. adatoms, down to 0.32μB per atom for a coverage of 0.145 ML.

As a general trend, a monotonic decrease of orbital moments with the average size of the clusters is observed. As we will see, non-monotonous behaviour becomes visible if the clusters are fully size-selected.

3.3. Mass-selected iron clusters

The first experimental study on the magnetic properties of mass-selected clusters using XMCDB has been performed by Lau et al [12, 13] for iron clusters Fe8 in the size range from 2–9 atoms per cluster. In figure 12 the spin and orbital magnetic moments are given starting from the Fe adatom [56] up to Fe9 clusters [13]. The XMCD spectrum for the case of Fe7 and a thin Ni film is depicted in figure 9. From the sign of the XMCD signal at the L3 edge, a ferromagnetic coupling of the

<table>
<thead>
<tr>
<th>Adatom magnetic moment ratio μ/μs</th>
<th>Substrate</th>
</tr>
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<tbody>
<tr>
<td>0.16</td>
<td>Fe/Cu(100) [51]</td>
</tr>
<tr>
<td>0.30</td>
<td>Ni/Cu(100) [52]</td>
</tr>
<tr>
<td>0.57</td>
<td>Rh(111) [53]</td>
</tr>
<tr>
<td>0.61</td>
<td>Pt(111) [1]</td>
</tr>
<tr>
<td>0.62</td>
<td>Cu2N/Cu(100) [8]</td>
</tr>
<tr>
<td>0.89</td>
<td>K/Cu(111) [54]</td>
</tr>
<tr>
<td>0.91</td>
<td>Al2O3/Ni3Al(111) [9]</td>
</tr>
<tr>
<td>&gt;0.9</td>
<td>MgO/Ag(100) [4]</td>
</tr>
<tr>
<td>0.76</td>
<td>Co/G/Ru(0001), 0° [49]</td>
</tr>
<tr>
<td>0.19</td>
<td>Co/G/Ir(111), 0° [49]</td>
</tr>
</tbody>
</table>

| Table 2. Magnetic moments of small Ru clusters per d-hole n_d on an Fe/Cu(100) substrate in μB. |
|---------------------------------|---------|
| Ru0                             | 0.03    |
| Ru1                             | 0.10    |
| Ru2                             | 0.14    |
| Ru3                             | 0.094   |
| Note: The error of the spin and orbital moment is given by Δμ = 0.05μB. |

The given absolute values are by a factor two smaller as in the original paper of Lau et al, due to an error in the original normalization.
Fe clusters relative to the magnetization of the Ni film can be concluded, which is the case for all Fe clusters.

Both the spin as well as the orbital moment depend on the size of the clusters. The variation of the spin moment is less pronounced with magnetic moments ranging between 0.4\(\mu_B\) and 0.6\(\mu_B\) per d-hole. For the orbital moment, a much stronger variation is found. Adding or removing a single Fe atom from the cluster can change the orbital magnetic moment by a factor of two, as can be seen for the \(\text{Fe}_2\), \(\text{Fe}_3\), and \(\text{Fe}_6\) clusters. The dependency for the orbital and spin moment is also rather different. By adding an atom to \(\text{Fe}_2\), the orbital as well as the spin moment decrease. In contrast, for \(\text{Fe}_3\), the orbital moment decreases by adding or removing an atom from the cluster, whereas the spin moment is increases. Hence, the very strong variation of the ratio of orbital and spin moment can be mainly attributed to the strong variation of the orbital moment with the cluster size. For comparison, in figure 12 the data for non mass-selected \(\text{Fe}_m\) clusters with an average size \(\bar{m}\) deposited on a Cu(111) surface from \cite{55} are also shown. The absolute spin and orbital moments are slightly larger on the Cu(111) substrate, which can be attributed to the smaller hybridization with the surface due to the filled 3d band in Cu. The spin moments also show only small variations, but the orbital moments drop from 0.2\(\mu_B\) for the adatom down to 0.1\(\mu_B\) for an average size of \(\bar{m}\).

This strong dependency of the magnetic moments from the cluster size on the deposited Fe clusters is different from the corresponding dependency observed for Fe cluster cations in the gas phase \cite{57,58}. Here, the orbital and spin moments also show some variations; however, the overall effect is much smaller. Only for the \(\text{Fe}_7\) cluster is a strong drop of the spin

![Figure 12](image12.png)

Figure 12. Spin (■) and orbital (●) magnetic moments of small iron clusters in the mass range from \(n = 1\)–9. Black: mass-selected \(\text{Fe}_n\) on Ni/Cu(100) from \cite{12,13}, Red: \(\text{Fe}_m\) cluster on Cu(111) with a mean size \(\bar{m}\).
moment found due to an antiferromagnetic alignment of the central Fe atom.

A first theoretical analysis of the magnetic moments has been performed by Martinez et al [59] and Robles et al [60]. They performed modified embedded atom model calculations in conjunction with a self-consistent tight-binding method for the geometric structure as well as the spin moments for different structures. Spin and orbital moments were calculated ab initio using the RS-LMTO-ASA method [61–63]. In figure 13 the calculated magnetic moments are depicted. The spin moments are on the order of 0.9µB per d-hole and are decrease monotonously with increasing cluster size. The orbital moments are rather small (around 0.05µB) per d-hole and also slightly decrease with increasing cluster size. Furthermore, the magnetic moments depend only weakly on the geometric structure of the deposited clusters depicted in figure 14. Strong size-dependent variations are not found for the orbital or the spin moments. Hence, the strong size dependency of the magnetic moments found in the experiment is not reproduced by the calculations. Furthermore, the theoretical spin moments are all slightly too large and the orbital moments are much too small.

A theoretical study on the size and shape dependency of the magnetic spin moments of Fe clusters deposited on different surface has been performed by Mavropoulos et al [64] using the Korringa–Kohn–Rostoker (KKR) method. They found a linear decrease of the spin moment of the Fe atoms in the cluster with the increasing number of neighbouring atoms. Similar to the calculation in references [59, 60], the total spin moments of the clusters vary only slightly with the size and are on the order of 0.8–0.9µB per d-hole.

Interestingly the calculated magnetic spin moments are only slightly below the values found for the free cluster cations, where the size dependency is also much less pronounced, but the magnetic spin moments are increasing with the cluster size. This is a hint that the interaction with the surface might be underestimated in the theory. In figure 13 the orbital moments of free Fe clusters [57] are also included. They have a similar magnitude, but the size dependency is different.

An extensive theoretical study of Fe, Co and Ni clusters on the compact surfaces Ir(1 1 1), Pt(1 1 1) and Au(1 1 1) has been performed in the size range from the adatom up to 7 atoms per cluster and for a monolayer [65, 66]. The magnetic spin and orbital moments of all cluster atoms and the spin moments of the nearest-neighbour substrate atoms have been calculated using the spin-polarized relativistic Korringa–Kohn–Rostoker (SPR-KKR) method. For Ir(1 1 1) and Pt(1 1 1), strong induced magnetic moments of the surface atoms ferromagnetically coupled to the cluster moments with spin moments up to 0.15µB are found. For Au(1 1 1) only very small induced moments are calculated, showing a tendency for an antiferromagnetic coupling to the cluster moments. The magnetic spin moments within the cluster decrease with the number of nearest-neighbour atoms. For Fe clusters, the orbital moment varies only slightly for the different atoms of the cluster; however, for Co and Ni clusters the orbital moment strongly depends on the position of the atom within the clusters with variations on the order of a factor of 10. The overall average spin and orbital moments of the cluster atoms, in general, decrease with the cluster size.

3.4. Cobalt clusters

In figure 15 the magnetic spin and orbital moments for Co clusters deposited on a Ni/Cu(100) [52] and a Pt(1 1 1) [1] surface in the few-atom limit are depicted. Size-selected Coₙ clusters with n = 1–3 have been studied on the remanent-magnetized Ni/Cu(100) surface, whereas on the Pt(1 1 1) surface size-averaged Coₙ(3) in a strong magnetic field were investigated.

Spin and orbital magnetic moments are found to be larger on the Pt(1 1 1) surface compared to the Ni/Cu(100) surface. In particular, for the Co adatom on Pt(1 1 1) a giant orbital moment is found, which decreases with increasing size (s). On the Ni/Cu(100) surface the smaller orbital moments show a non monotonic behaviour. They decrease from the adatom to the dimer. However, the largest orbital moment is found for the Co trimer.

Similar to Fe, Co clusters show larger magnetic moments on the more weakly coupling surface Pt(1 1 1). Again, this can be attributed to the effect of hybridization of the 3d orbitals with the substrate, which in this case is smaller with the filled Pt 5d band.

Co adatoms and dimers on a Ni surface show a similar size dependency as the corresponding Fe adatoms and dimers with
Figure 15. Spin (circles $\bigcirc$) and orbital (squares $\square$) magnetic moments of small Co clusters on two different surfaces; filled symbols: mass-selected $\text{Co}_n$ on Ni/Cu(1 0 0); open symbols: size-averaged $\text{Co}_n$ on Pt(1 1 1) taken from [1] with the number of d-holes $n_d = 2.40$.

Figure 16. Schematic illustration of the possible non-collinear coupling of a dimer on a magnetized surface.

Figure 17. XAS spectra for different Cr clusters deposited on an Fe/Cu(1 0 0) and Ni/Cu(1 0 0) surface.
a small increase of the spin moments. The orbital moment slightly decreases from Co₁ to Co₂ and is almost equal for Fe₁ and Fe₂. Adding a further Co atom to the dimer increases the orbital moment strongly by 50% while the spin moment for Co₂ and Co₃ are rather similar. In contrast to this, adding an Fe atom to the Fe₂, the orbital and spin moment drops by 50% and 25%, respectively.

From these results it is obvious that, in order to benchmark theory (particularly if it comes to the calculation of orbital moments) experiments on size-selected clusters are mandatory.

3.5. Chromium clusters

A prototype system for an antiferromagnetic coupling is chromium in the bulk. It is interesting to know how this antiferromagnetic coupling will change, if the structure size is in the order of only a few atoms. In figure 16 the possible magnetic structure for an atom and a dimer deposited on a magnetic surface are depicted. For the atom, an antiferromagnetic coupling can be expected; however, already for the dimer a spin frustration might be found. For small deposited chromium clusters, such an effect should be observable. In figure 17 the XMCD spectra of Crₙ clusters for n = 1–3 deposited on a magnetized Ni film on Cu(100) are depicted [67]. In contrast to iron clusters deposited on this surface [12, 13] for Crₙ only a very weak XMCD signal, if any, is found. In the left part of figure 17 the XMCD spectra for Crₙ (n = 1,3,4) clusters deposited on a three-monolayer-thick Fe film, deposited on Cu(100) and remanent-magnetized are shown. Here, a strong XMCD signal is found, which shows a double peak structure at the L₃ edge. As the positive part is much stronger in total, an antiferromagnetic coupling can be concluded. Interestingly, this double peak structure is identical to the structure found for polarized free Cr atoms in the gas phase [68]. In the gas phase, the two peaks with opposite signs can be easily assigned to two different spin configurations (depicted in figure 18) of the 3d electrons, e.g. a ⁷P and a ⁵P multiplet.

In figure 19, the spin and orbital magnetic moments for the Cr cluster deposited on the Fe surface in the size range from the adatom up to 13 atoms per cluster are depicted. In comparison to the case of Fe clusters, the orbital moment is close to zero and the spin moment strongly decreases from 0.4μₜ for the Cr adatom down to 0.10–0.15μₜ for Crₙ with
This strong decrease can be attributed to the increasing antiferromagnetic ordering of the Cr cluster with increasing size. The almost vanishing orbital moment for chromium can be attributed to the $d^5$ high spin configuration, which will, according to the Pauli principle, have a total angular momentum $L = 0$.

The total magnetic moments for Cr clusters on an Fe(100) surface have been theoretically studied by Robles and Nordstrom [69] using tight-binding calculations for the $s$, $p$ and $d$ valence electrons in a mean-field approximation starting from the Cr dimer up to Cr$_9$ clusters. They calculated the magnetic moments of the individual atoms in the clusters for a Fe(100) bcc surface as well as for an Fe(100) fcc surface, showing a rather different magnetic coupling. In figure 20 the calculated total magnetic moments perpendicular to the surface normal are depicted. The total moment of the clusters is always antiferromagnetically coupled to the surface. For both surface geometries, a collinear and a non-collinear coupling of the individual magnetic moments has been taken into account. For the bcc surface, much larger magnetic moments, depending on the geometry of the cluster on the surface collinear or non-collinear coupling of the Cr moments are found. For the fcc surface, a non-collinear coupling is always observed, which results in a very strong reduction of the total magnetic moment of the cluster, i.e. for Cr$_4$ with a similar geometry, the total moment is decreased by a factor of three from the bcc to the fcc surface.

In the experiments the Cr clusters have been deposited on a thin, three-monolayer iron film, deposited on a Cu(100) crystal. As the iron film is growing pseudomorphically on the Cu(100) surface, it will have an fcc structure. Hence, the experimental data should be compared to the theoretical fcc results. For this direct comparison the total magnetic moment per atom should be known, for which the number of d-holes $n_d$ is required (as has been discussed in section 2.6.1). For the different cluster sizes $n_d$ is not known. In the free atom, the $d^5$ configuration as a high spin state is very stable, hence, for a comparison we assume $n_d \approx 5$ for all cluster sizes. The scaled experimental data for the magnetic spin moments together with the theoretical results of Robles et al [69] and Lounis et al [70] are depicted in figure 20.

Only if the nonlinear coupling due to a spin frustration within the clusters is taken into account can the principle behavior of the experimental data be described.

A detailed theoretical analysis of the non-collinear coupling of Cr clusters on the Fe/Cu(100) surface has been performed by Lounis et al [70] using the SPR-KKR method. To describe the Cr clusters on the Fe substrate, at least two different coupling constants $J_{Cr-Cr}$ and $J_{Cr-Fe}$ for the inter-cluster and the cluster substrate coupling, respectively, are mandatory. The classical spin Hamiltonian is given by
where $e$ is a unit vector defining the direction of the magnetic moment and $i$ and $j$ indicate the cluster atoms and their first Fe neighbours. Taking into account only first-neighbour interactions and neglecting the rotation of Fe moments for the Cr dimer, the Hamiltonian can be described by

$$H = J_{\text{Cr-Cr}} \cos(\theta_1 + \theta_2) - 4J_{\text{Cr-Fe}}(\cos \theta_1 + \cos \theta_2),$$

which $\theta_{1,2}$ the angle of the Cr magnetic moments relative to the magnetization of the Fe substrate (see figure 21). The angle defining the non-collinear solution can be obtained by minimizing the Heisenberg Hamiltonian as

$$\cos(\theta_1) = \cos(\theta_2) = -2J_{\text{Cr-Cr}}/J_{\text{Cr-Fe}}.$$  

If $2|J_{\text{Cr-Fe}}| > |J_{\text{Cr-Cr}}|$, the angle is not defined and the non-collinear solution does not exist. As $2|J_{\text{Cr-Fe}}| = 2 \times 80.8 \text{ meV} > |J_{\text{Cr-Cr}}| = 77.6 \text{ meV}$, this is realized in the case of Cr$_2$ on the Fe substrate.

From figure 16 for a Cr dimer on a magnetic surface a non-collinear spin structure is already expected, which would result in a strongly reduced magnetic moment. However, the exchange coupling of the individual Cr atoms to the Fe substrate is much stronger in comparison to the Cr–Cr coupling which results in a ferromagnetic coupling of the two Cr spins, which are then coupled antiferromagnetically to the Fe surface.

The situation is different for the Cr trimer. Here, a non-collinear coupling depicted in figure 22 is found. The same behavior is also found for the Cr tetramer. Nevertheless, for the Cr$_4$, two different geometrical structures depicted in figure 22 show either a collinear or non-collinear spin configuration. Hence, the geometry of the deposited cluster will have a large effect on its magnetic properties. Starting from Cr$_2$ already, a transition to a more or less antiferromagnetically coupled Cr cluster is found with only weak non-collinear contributions.

From these results one can now understand why only a very weak XMCD signal is found for Cr$_n$ on Ni/Cu(100). In figure 17 for Cr$_1$, a very small positive dichroism signal is found at the $L_3$ edge. From this one can conclude that the coupling constant $J_{\text{Cr-Ni}}$ between the Cr adatom and the Ni surface must be much smaller compared to $J_{\text{Cr-Fe}}$, as the magnetic moment of the Cr adatom is not aligned by the exchange interaction with the magnetized Ni film. Hence, $J_{\text{Cr-Ni}}$ should also be rather small for the dimer and all larger Cr clusters. If $J_{\text{Cr-Cr}}$ on the Ni and Fe film are similar, equation (6) will give $\cos(\theta_1) \approx 0$ and the magnetic moments in the Cr dimer will be oriented almost perpendicular to the Ni magnetization (see figure 23) resulting again in an almost vanishing dichroism signal. This magnetic configuration has already been calculated by Lounis et al [71] using the SPR-KKR method. For the Cr trimer on Ni/Cu(100) they calculated a collinear spin configuration $\uparrow \downarrow \uparrow$ parallel to the Ni magnetization, which should show an XMCD signal in the experimental geometry. Here, as well, a non-collinear solution $\uparrow \uparrow \downarrow \downarrow$ perpendicular to the Ni magnetization as shown in figure 23 and similar to the Cr dimer would explain the experimental result.

An interesting behaviour of the Cr clusters is also found for the orbital moments $\mu_\ell$. In figure 18, the XMCD spectra of the Cr adatom, trimer and tetramer normalized to the $L_2$ dichroism are depicted. In particular Cr$_4$ shows a much weaker positive XMCD signal at the $L_3$ edge, whereas the negative part, which is by comparison to the atomic data assigned to a low spin component, does not show this effect.
Thus, we have the interesting observation, that the negative XMCD signals are almost identical for all clusters even when they belong to different edges ($L_2$ and $L_3$) and only the ratio between the positive and negative intensity varies. This observation can be understood by a comparison of the XMCD spectra with the XMCD signal from the free atom [68]. For the free atoms, the two negative signals are explained due to an excitation into low-spin $^5P$ states, whereas the strong positive XMCD signal results from an excitation into a $^7P$ state. Due to the similarity of the atomic and the cluster XMCD pattern, the negative XMCD signal of the clusters at the $L_3$ edge might also be interpreted as an excitation into low-spin states.

In figure 19 the orbital moments $\mu_\ell$ of the deposited Cr clusters are shown, which have been directly extracted from the orbital sum rule (2.6.1). The sign of the orbital moment is given relative to the spin moment of the Cr$_n$ cluster. Due to the half-filled d shell the ground state of free Cr atoms is $^5S$ and thus the orbital moment $\mu_\ell = 0$. As expected, for the deposited Cr clusters, very small orbital moments $\mu_\ell$ close to zero are found, with a slight trend for a parallel coupling of the orbital and spin moments. This is in contrast to the data of Scherz et al [43, 44], who found, for ultrathin chromium films an orbital moment, $\mu_{\ell,\text{film}} = -0.011 \mu_B$ (the sign is given relative to the spin direction) coupled anti-parallel to the spin moment.

An interesting behaviour is found for the Cr trimer and tetramer. For the Cr$_3$ cluster a very small orbital moment $\mu_{\ell,3} = 0.025 \pm 0.015 \mu_B$ parallel to the spin moment $\mu_S$ is found. However, for the Cr$_4$ cluster an orbital moment $\mu_{\ell,4} = -0.044 \pm 0.013 \mu_B$ with an anti-parallel coupling relative to the spin direction is observed, which is a result of the strong decrease of the high spin component in the XMCD signal as compared to the constant low-spin signal at the $L_3$ edge. For all cluster sizes, an antiferromagnetic coupling of the total magnetic moment relative to the substrate magnetization is found.

According to Hund’s rule, the total magnetic moment of a state $|^{2S+1}L_J\rangle$ for an open-shell atom is given by

$$\mu_J = -\frac{3(J+1) + S(S+1) - L(L+1)}{2\sqrt{J(J+1)}} \cdot \mu_B.$$  

For a $^5D$ state in a free atom for the angular moment $J$ the values between 0 and 4 can be realized by an anti-parallel or parallel alignment of the spin and orbital moments.

For a more than half-filled shell, the ground state of an atom has the maximum possible angular momentum $J$, e.g. for Fe, which is realized by a parallel coupling of the spin and orbital angular momenta. However, for a less than half filled shell the situation changes and an anti-parallel coupling, with the smallest possible $J$ is energetically favoured. The Cr atom with 3$d^5$ has a half-filled shell. From the similarity of the XMCD spectra of the clusters and also the free atom for the Cr clusters, the number of d-holes $n_d$ should be close to 5; however, a small deviation from 5 will result either in a parallel or anti-parallel coupling of the spin and orbital moments. Hence, within this simple atomic model an increase of the number of d-holes, would favour the observed anti-parallel coupling of the orbital and spin moment in the Cr$_4$ cluster.

### 3.6. 4d metals

None of the 4d transition metals shows a magnetic coupling within the bulk, however, Pd metal almost fulfils the Stoner criterion. Nevertheless, in theoretical studies on free 4d metal clusters a superparamagnetic coupling of the atomic moments within the cluster has been predicted for small clusters which has been confirmed for free small Rh clusters by Cox et al [72]. Even a multiferroic behaviour has been reported for free Rh cluster up to 40 atoms per cluster in Stern–Gerlach experiments [73]. The number of core-level studies on 4d metals is rather limited. The $M_{2,3}$ resonances in the soft x-ray regime which would probe the 4d electrons by exciting 3p electrons in unoccupied 4d states are much broader (see figure 24) as the corresponding $L_{2,3}$ resonances, and the 3p hole can decay by a super-Coster–Kronig decay. Also, the dipole matrix element.
for the 3p-4d excitation is smaller, resulting (in sum) in rather weak resonances.

XMCD studies on non-mass-selected Rh clusters embedded in a xenon matrix have revealed magnetic moments of these clusters [74]. The clusters have been grown by evaporating submonolayer amounts of Rh by an e-beam evaporator at 10 K and were aligned by an external magnetic field with up to 6 T. Applying the sum rules, small spin and orbital magnetic moments are found below 0.1 \( \mu_B \) per d-hole, with a rather large and constant orbital-to-spin moment ratio of \( \approx 0.5 \). The magnetic moments depend strongly on the size of the clusters. For a Rh coverage of 0.1 ML, the spin moment has its maximum around 0.08 \( \mu_B \), and decreases strongly for coverages of 0.2 ML down to 0.02 \( \mu_B \) and decreases further, down to 0.01 \( \mu_B \) for large coverages.

Similar XMCD studies have been reported by Honolka et al. [75] on Ru and Rh impurities and non-mass-selected clusters deposited on Ag(100) and Pt(997) surfaces in a strong external magnetic field up to 6 T. For Ru on Ag(100) as well as Rh deposited on Ag(100) and Pt(997) surfaces they observed an absence of local magnetic moments.

In contrast to these results, experiments on mass-selected Ru clusters in the few-atom limit deposited on an out-of-plane magnetized Fe/Cu(100) surface have revealed a ferromagnetic coupling of Ru to the Fe surface with rather small magnetic moments (listed in table 2) of the Ru atoms [76]. The XMCD signal depicted in figure 25 is almost vanishing for the Ru adatoms and has a similar magnitude for \( \text{Ru}_2 \) and \( \text{Ru}_3 \). A peculiar difference between the XMCD spectra of \( \text{Ru}_n \) and the 3d metal spectra is the similar size of the \( M_2 \) and \( M_3 \) XMCD signal; in the 3d metals the \( L_3 \) signal is in general larger than the \( L_2 \) signal. Using the sum rules from the XMCD spectra, the magnetic moments of the Ru clusters have been calculated. For the Ru adatom the magnetic moments within the errors are equal to zero. For the Ru dimer and trimer a small positive spin moment in the order of 0.1 \( \mu_B \) per d-hole is found, indicating a ferromagnetic alignment relative to the Fe magnetization. This value is similar to that of the Ru cluster in a Xe matrix [74]. As
for Ru2, the $M_1$ and $M_2$ XMCD is almost equal to the resulting orbital moment $\mu_\ell$ and is vanishing. This is because $Ru_3 M_2$ is slightly larger than $M_3$ which results in a very small negative orbital moment $0.07 \pm 0.05 B_\mu \mu_\ell$, indicating an anti-parallel coupling of the orbital relative to the spin moment.

3.7 4f metals

The magnetism of the rare-earth elements is characterized by their open 4f-shell electrons, which can give rise to large magnetic moments. Gd is also one of the four elements (Fe, Co, Ni, Gd) which is ferromagnetic at room temperature. As the 4f electrons are localized a direct exchange interaction, as for the itinerant d electrons in the 3d metals, can be neglected and the exchange coupling is mediated by the delocalized 5d and 6s valence electrons. This type of indirect ferromagnetic coupling is called the Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange interaction. In Gd bulk, this coupling results in a ferromagnetic ordering; however, for other 4f materials, such as Ho and Dy, more complicated magnetic ordering with canted spin structures are found [77].

A first study on the magnetic properties of rare-earth metal clusters has been performed on Gd. As Gd clusters can be easily oxidized, these studies are limited to Gd atoms and dimers and their oxides [78]. To study their magnetic properties, they have been deposited on an out-of-plane magnetized three-monolayer Fe film on a Cu(1 0 0) substrate. In figure 26, the x-ray absorption and XMCD spectra of Gd and GdO adatoms and dimers on the Fe/Ni(1 0 0) substrate are depicted. A very strong XMCD signal is found for all clusters and from the positive and negative XMCD signal at the $M_5$ and $M_4$ edge, respectively, from which an antiferromagnetic coupling of the orbital relative to the spin moment for all samples. Additionally, a comparison of the x-ray absorption spectra to gadolinium bulk [82] gives no qualitative differences in the shape and structure of the spectra. Hence, the electronic structure of the Gd 4f states is not affected by the size or chemical composition of the Gd clusters. Therefore, the spin and orbital moments of the Gd and GdO clusters, which can be extracted from the spectra applying the sum rules, are also equal within the error bars for all samples.

Recently, Donati et al studied the magnetic properties of Ho and Er adatoms on a Cu(1 1 1) and Pt(1 1 1) surface [6] in a strong external magnetic field. They found a ferromagnetic coupling of the magnetic moments relative to the applied external magnetic field and large spin as well as orbital moments of the adatoms. For Ho adatoms on both surfaces, similar magnetic moments are found, which are slightly larger on the Cu(1 1 1) surface. For Er adatoms, the situation is different. Both the spin and the orbital moment are strongly reduced from $1.04 s_\mu B_\mu$ down to $0.31 s_\mu$ and $4.49 \mu_\mu_\ell$ to 0.73 $\mu_\mu_\ell$ on the Pt(1 1 1) and Cu(1 1 1) surface, respectively [6]. The effect is attributed to the different hybridization with the surface. On the Cu(1 1 1), the 4f electrons interact with the s and p electrons of the substrate, which act as a uniform charge plane. On the Pt(1 1 1) surface the density of states is dominated by the Pt 5d electrons, which are interacting with a more directional ligand and/or crystal field. This results in different charge distributions of the rare-earth 4f electrons on the two surfaces, influencing the $J_z$ distribution, which is responsible for the 4f magnetic moments.

4. Alloy clusters

For clusters made out of only one element, strongly varying magnetic moments depending on the cluster size have already been found. Additionally, the strong influence of the hybridization with the surface on the magnetic properties has been
shown by comparing the magnetic moments of the clusters on different surfaces. For tailoring the magnetic properties further, clusters consisting of different materials, e.g. alloy cluster, are ideally suited. To increase, in particular, the orbital moment to somehow tune the anisotropy energy, bimetallic alloys consisting of a 3d metal with a large spin moment and a 4d or 5d metal with a larger spin–orbit interaction are highly interesting materials. Such materials as, e.g. Co–Cr–Pt, FePt, and CoPt, are often put forward for use in modern magnetic storage devices [83–85].

The aim of the corresponding investigations on small, size-selected alloy clusters is to understand how the spin and orbital moments, as well as the spin–orbit interaction, of the 3d electrons in the cluster can be increased and how this depends on the size and composition of the clusters. Essential for this effect is the hybridization of the 3d and the 4d or 5d electrons in an alloy cluster.

The spin–orbit interaction of the 3d electrons can be obtained from XAS by evaluating the branching ratio

$$B_r = \frac{C_{L_3}}{C_{L_3} + C_{L_2}}$$

of the $L_3$ and $L_2$ white-line intensities $C_{L_x}$ as has been shown by Thole and van der Laan [86, 87]. In figure 27, the x-ray absorption and the branching ratio for Fe$_n$Pt$_m$ clusters is shown [56]. With increasing Pt content of the FePt alloy clusters the branching ratio $B_r$ also increases, which is attributed to an increased 3d spin–orbit interaction of the Fe 3d electrons by hybridization with the Pt 5d electrons. This is actually what one is aiming for in order to potentially increase orbital moments and, in turn, maybe anisotropy energies/atom.

### 4.1. FePt

3d/5d metal alloy Fe$_n$Pt$_m$ clusters on an out-of-plane magnetized Ni/Cu(100) substrate have been studied. The results for the spin and orbital moments are shown in figure 28. For Fe$_n$Pt$_m$ the orbital moment (square) decreases with an increasing number $m$ of Pt atoms. The spin moment (circle) has a maximum for $m = 1$ and decreases if a second Pt atom is added to the Fe adatom or dimer. Note that this decrease is stronger for the Fe adatom. Hence, there is an optimal number of Pt atoms in the Fe cluster to create the maximum spin moment (see figure 29). This is in contrast to FePt bulk, thin films and nanoparticles [18, 22, 88], where the effective spin moment shown in figure 29 increases with the Pt content up to about 50 at% Pt and is rather constant for larger Pt content [22].

From figure 27 an increase of the Fe 3d spin–orbit interaction due to hybridization of Fe 3d and Pt 5d orbitals with an increasing Pt content has been concluded. For Fe$_n$Pt$_m$ clusters, this increase does result in an increase of the spin moment and a decrease of the orbital moment, in contrast to simple expectations, as we will see below is different from the situation in Co alloy clusters. In principle, an increase of the spin–orbit interaction of the Co 3d orbitals due to the hybridization with Pt 5d and Pd 4f orbitals is to be expected. For CoPt$_n$, this results in an increase of both, spin and orbital magnetic moments, whereas for CoPd$_n$ the orbital moment is increasing, but the spin moment is slightly decreasing.
4.2. CoPt and CoPd

For Co, two different alloy systems, CoPt [52] and CoPd [89] have been studied adding a 5d and 4d element, respectively. In figure 28 the spin and orbital magnetic moments as well as the ratio of these quantities are depicted for CoPd, Co$_2$Pt alloy clusters together with Co$_n$ (n = 1–3) clusters deposited on an out-of-plane magnetized Ni/Cu(100) substrate, as described above. For both alloy clusters, an increase of the orbital moment is found. For Co$_2$Pt the spin moment also increases, whereas for CoPd the spin moment decreases, which results in a strongly enhanced orbital-to-spin ratio for both systems.

As shown for FePt the hybridization of Fe 3d electrons and Pt 5d electrons results in an increase of the spin–orbit coupling. This effect can also be expected for the Co 3d electrons and the increase of the orbital moment in the alloy clusters can be explained by the increase of the 3d spin–orbit interaction. However, this does not necessarily imply an increase of the spin moments, which can be seen in the CoPd example.

Comparing the results for the Co and CoPt clusters to the corresponding Co [19, 20, 90] and CoPt [91] nanoparticles as well as CoPt thin films [92, 93] shows slightly smaller spin moments within the small cluster. However, the orbital moments are strongly enhanced.

One should note, that the chemical reactivity of the Co clusters is also strongly enhanced by alloying with Pt or Pd atoms.

5. Summary

In this topical review we have summarized the current status of experimental studies on the magnetic properties of supported small clusters and adatoms using soft x-rays. These very small particles in the few-atom limit show strong variations of their magnetic properties depending on their size and the substrate. Due to the ability of XMCD to measure the spin and orbital moments of the clusters and adatoms, detailed information on the magnetic moments can be obtained.

For clusters, it has been shown that a size selection is important as both magnetic moments can strongly depend on the size due to quantum size effects and ‘every atom counts’. In general, the variation in the orbital moment is stronger compared to the variation of the spin moment. In particular, for adatoms the orbital magnetic moment can reach values close to the limit given by Hund’s rule for the free atom. Furthermore, the magnetic moments and also the ratio of orbital and spin moment depend strongly on the substrate. Usually, larger moments are found on rather weakly coupled surfaces as insulators or metal surfaces with sp-like bands or a filled d-band. Hence, the magnetic properties are strongly influenced by the cluster–substrate interaction due to the hybridization with the substrate. From the currently available experimental and theoretical data no real trends can be deduced. Hence, further studies on mass-selected clusters on various surfaces are needed. This becomes even more important for alloy clusters, where the magnetic properties of the clusters can be tailored by specifically changing the cluster–cluster interaction by alloying the clusters atom by atom.

To fully understand the variations of the magnetic properties depending on the size and composition of the clusters, a comparison to theoretical studies is mandatory. As the clusters consist of only a small number of atoms, the experimental results are an ideal benchmark for sophisticated theoretical models. Again, the size selection in the experiment is very important. For adatoms on weakly coupling surfaces, rather good agreement between the experimental data and the theory is found already. However, for clusters the agreement is less satisfying. In general, the calculated spin moments are slightly too large and the orbital moments are strongly underestimated. The calculation of the orbital moments is challenging, as usually correlation effects are very important.

The magnetic properties of the clusters is related to the geometric structure of the clusters on the surface which is, unfortunately, usually unknown. To determine the geometry as well, existing experimental methods have to be tested to see whether they work with very dilute samples or even new ones have to be developed. First attempts based on diffraction have been made using x-ray diffraction [94], photoelectron diffraction [95] or reflective high-energy electron diffraction [96]; however, this has always been on nanoparticles in the few-nm size regime, e.g. clusters with typically a few 100 atoms. Recently, Franz et al [97] were able to determine the geometric structure of Pt nanoclusters on graphene/Ir(1 1 1) with only ≅40 Pt atoms per cluster using surface x-ray diffraction. Nevertheless, to the best of our knowledge, none of these experiments have been performed on small or even size-selected clusters.

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