



Influence of CO adsorption on the magnetism of small Co particles deposited on Al_2O_3

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Abstract

Ferromagnetic resonance under ultrahigh vacuum conditions was used to study the magnetic properties of small cobalt particles deposited on the reconstructed surface of a sapphire single crystal ($(\sqrt{31} \times \sqrt{31})R \pm 9^\circ \text{Al}_2\text{O}_3(0001)$). The intensity of the resonance line decreases after CO adsorption but the signal is not totally quenched. Therefore, only the atoms in the outer sphere of the cluster are influenced and a magnetic core still remains. STM measurements of Co particles on a thin alumina film $\text{Al}_2\text{O}_3/\text{NiAl}(110)$ support this assumption of three-dimensional growth. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years progress has been made in the investigation of supported small metal particles [1]. This was triggered by the interest in catalytic processes in which supported metals play an important role as reaction centers [2,3]. While the electronic and geometric structure of several metal/support systems has been studied [4], there exists a lack of knowledge with respect to the magnetism of well-characterized supported metal clusters. Therefore we used ferromagnetic resonance (FMR) spectroscopy to gain insight into the magnetic properties and especially to investigate the influence of adsorbed gases. In the past, various techniques have been used to determine the decrease of magnetization during the adsorption of gases, mainly on iron and nickel

samples. Investigations dealing with cobalt are rare, and therefore the data of the other ferromagnetica are used as a reference. For instance, Selwood and co-workers investigated the influence of hydrogen adsorption on several cobalt and nickel samples [5,6] by classical magnetization measurements. Furthermore, spin polarized inverse-photoemission experiments on Ni(110) single crystals as well as FMR experiments on thin Ni films deposited on quartz glass showed that every adsorbed CO molecule quenches the surface magnetism of two Ni atoms [7,8]. A series of investigations based on spin-resolving photoelectron spectroscopy is cited in Ref. [9] concerning the chemisorption of oxygen on different iron and cobalt samples as well as CO adsorption on iron. Non-linear Kerr studies on a 7 ML Co film on Cu(001) have shown that the surface magnetism is sensitive to sub-monolayer coverage with CO [10]. Additionally, the magnetic properties of physisorbed

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Xe on cobalt and iron films have been investigated [11]. Theoretical calculations revealed complete quenching of the magnetic moment of Ni clusters caused by CO adsorption [12,13]. In our experiments we investigated the influence of CO adsorption on the magnetic properties of small cobalt particles. The particles were grown on a sapphire single crystal under ultrahigh vacuum (UHV) conditions and the FMR measurements were carried out in situ.

2. Experimental

The FMR measurements were performed in a specially designed UHV chamber with a base pressure below 2×10^{-11} mbar. Further details about the chamber have been described previously [14] and only the sample holder has been modified to heat the sapphire single crystal with a surrounding loop of tungsten wire to about 1000°C. A new liquid–helium cryostat has recently been installed which allows cooling to about 60 K. The ESR spectrometer from Bruker (B-ER 420) has been improved by means of a new X-band microwave bridge (Bruker ECS 041 XK) and a lock-in amplifier (Bruker ER 023 M). A clean $(\sqrt{31} \times \sqrt{31})R \pm 9^\circ$ -reconstructed sapphire (0001)-surface was prepared by annealing the polished crystal for several minutes to about 1000°C. The temperature was controlled by a thermocouple (NiCr/CuNi) sticking in a small hole near the upper edge of the crystal. The clean surface exhibits neither carbon nor other impurities within the sensitivity of Auger spectroscopy whereas the kind of reconstruction was determined by the LEED pattern. An electron beam evaporator, commercially distributed by Focus (EFM 3), was used to deposit various amounts of cobalt at a low deposition rate of about 0.5 Å/min calibrated by a quartz microbalance and Auger spectroscopy. The pressure during metal evaporation never rises above 1.5×10^{-10} mbar, which is a necessary condition for avoiding the pollution of the freshly prepared Co particles by the residual gas.

The STM measurements were performed in a different chamber equipped with a combined STM/AFM (Omicron) [15]. The metal deposition was carried out with the same equipment and with the same parameters as in the FMR experiment. Instead of the insulating sapphire single crystal a thin

aluminium oxide film grown on an NiAl–alloy single crystal served as substrate. The preparation procedure and the characterization of the well-ordered epitaxial alumina film have been presented previously [16,17].

3. Results

Fig. 1 shows two STM images of cobalt deposits on a thin alumina film. In Fig. 1a, 0.1 Å of Co is

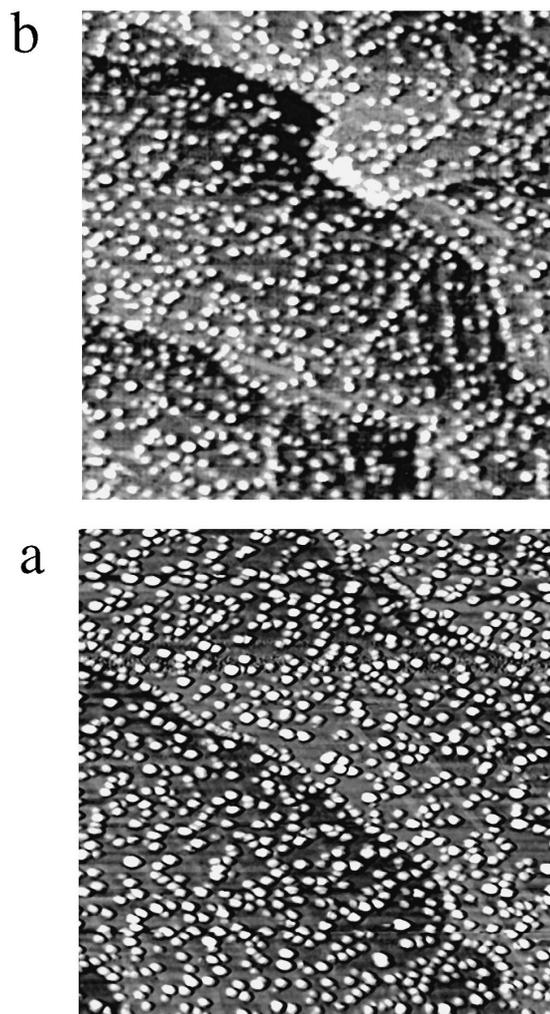


Fig. 1. STM images of 0.1 Å Co/Al₂O₃/NiAl(110). (a) Grown under UHV conditions: 200 × 200 nm², 5.1 V, 0.5 nA. (b) Grown in CO atmosphere: 200 × 200 nm², 8.0 V, 0.6 nA.

deposited at room temperature and nucleates on the terraces of the film exhibiting particle heights of two to three atomic layers. Therefore, even in the limit of small coverages, the Volmer–Weber growth mode is observed. Fig. 1b shows an image of the same amount of deposited cobalt as in Fig. 1a but now deposited in an atmosphere of CO (3×10^{-7} mbar) as in the FMR experiment (see below). In the presence of the gas, nucleation takes place preferably at antiphase boundaries, indicating higher mobility of the impinging moieties, but the shape and number density do not change much. We know from TEM measurements on supported and unsupported Al_2O_3 that the growth mode of particles (Pt, Pd) is not strongly influenced by the supporting metallic substrate in the case of alumina films [19]. Therefore, we conclude from the STM measurements on the supported film that cobalt grows in a three-dimensional way on the reconstructed sapphire surface. However, further transfer of growth properties gained by STM on the alumina film (e.g. the mean particle

diameter) might be difficult due to the fact that the $(\sqrt{31} \times \sqrt{31})R \pm 9^\circ$ -reconstructed sapphire surface is characterized by oxygen deficiency [20–22]. For instance, slightly different diameters of copper particles deposited on the reconstructed and unreconstructed (0001)-surface are reported in the literature [23].

Fig. 2 shows the influence of CO on the FMR spectrum of 2.3 Å cobalt deposited at room temperature. All spectra are measured at 296 K and the direction of the external magnetic field is parallel to the plane of the sapphire single crystal. Spectrum A represents the resonance spectrum of a clean and freshly prepared sample. As a result of the first-derivative detection technique, the characteristic values are the peak-to-peak linewidth (ΔH_{pp}) and the inflection point, i.e. the resonance field (H_0). The resonance line is relatively broad ($\Delta H_{pp} = 1000 \pm 100$ G) compared to those of compact metallic Co layers grown on a tungsten(110) surface. The latter exhibit values of a few hundred gauss [24]. Addition-

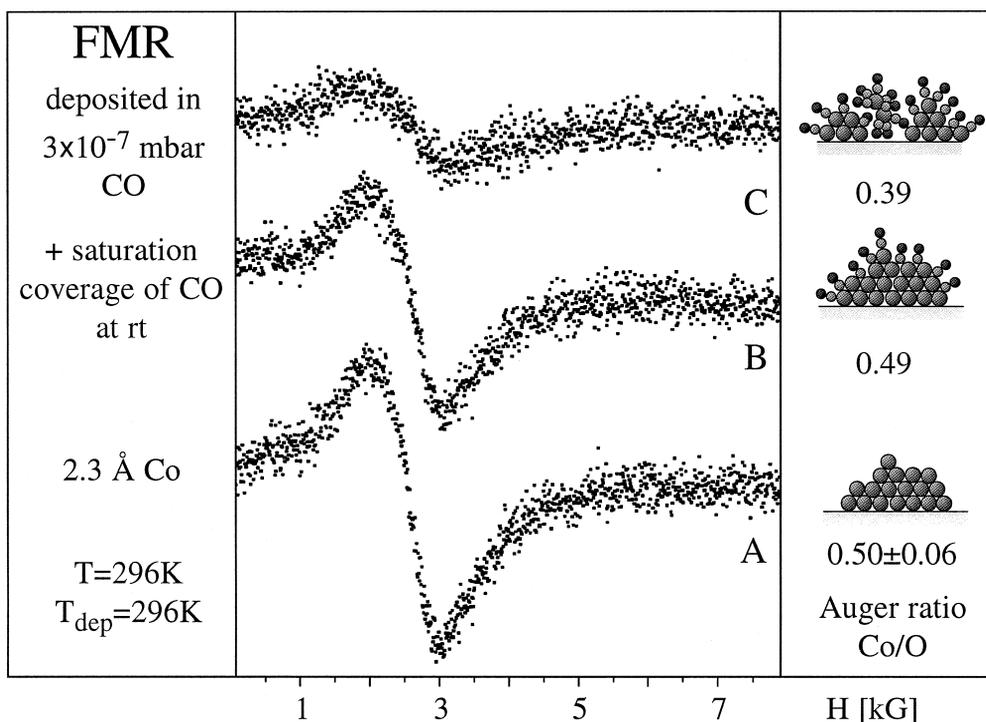


Fig. 2. Influence of CO adsorption. FMR spectra of 2.3 Å Co (A); saturation coverage of CO/2.3 Å Co (B); 2.3 Å Co deposited in an atmosphere of CO (C). Right panel: model concerning the growth and adsorption behaviour, Auger ratio Co/O.

ally, the lineshape is slightly asymmetric and exhibits a shoulder in the low field region. Both linewidth and asymmetry may be due to several causes: one reason could be the particle size distribution leading to a superposition of different resonance lines. Furthermore, inhomogeneities of the magnetization due to misfit dislocations enhances the linewidth. If a magnetic body is not limited by a surface of second degree, the demagnetizing field is a priori inhomogeneous leading to different resonance conditions within the particle. Additionally, we assume that particles of the given size exhibit magnetic behaviour in the border line regime between ferromagnetism and superparamagnetism (SPM) considering the timescale of the experiment [25]. Then, the angular distribution of magnetic moments with respect to the axis of the external field would also lead to different resonance conditions within an SPM ensemble. These points will be discussed in detail elsewhere [26].

The resonance field is located at about 2600 ± 50 G, if the external field is kept parallel to the crystal surface. Since the magnetization lies in plane, as could be shown by angular dependent measurements, the resonance equation simplifies to

$$(\omega/\gamma)^2 = H(H + H_a). \quad (1)$$

The effective anisotropy field H_a can be written as the sum of the demagnetizing field H_d , which is of dipolar origin and a term H_{so} concerning all anisotropies based on spin-orbit interaction ($H_a = H_d + H_{so}$). In the case of the above mentioned two-dimensional compact Co films, the resonance lies much lower than 2600 G due to the large demagnetizing field H_d . This quantity is often calculated by modelling the film by a thin disk within the approach of continuous matter (see Fig. 3) and yields: $H_d = 4\pi M = 18100$ G (with $M = 1440$ G, bulk magnetization). The strong field would shift the resonance from 3035 G, which corresponds to the g -value without any anisotropy ($g = 2.18$) down to about 500 G. Since the assumption of a thin, extended disk does not fit the shape of small Co particles as determined by STM, we calculate the demagnetizing field for small three-dimensional particles evaluating the dipole sum atom by atom. The average number of atoms per island is estimated by STM to be 770

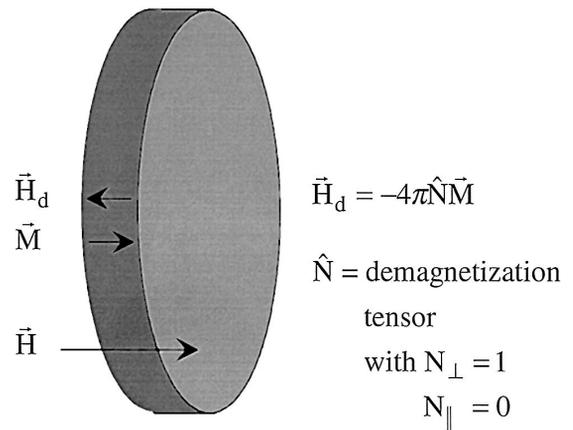


Fig. 3. Demagnetizing field of thin two-dimensional films modelled by a thin disk.

for 2.3 Å Co. As shown in cluster beam experiments free cobalt particles with more than 500 atoms reveal a magnetic moment per atom of $1.72 \mu_B$ [27], which is the bulk value. Assuming a half ellipsoidal shape, the averaged dipole field covers a range from a few hundred to a few thousand gauss depending on the ratio of height and radius [25]. Therefore, the resonance condition can be fulfilled with reasonable values of H_{so} . In line with the STM data, the FMR measurements are consistent with the presence of three-dimensional particles.

Discussing further details which characterize the resonance of small metal particles deposited on an insulating substrate would be beyond the scope of this Letter and will be described elsewhere [26].

If a saturation coverage of CO is offered to 2.3 Å cobalt (A), the spectrum in the middle of Fig. 2, labeled (B), is revealed. The lineshape does not change much and only the resonance position shifts slightly to higher fields (≈ 40 G). Angular-dependent measurements (not shown here) reveal that the effective anisotropy field is reduced after CO adsorption by 18%, indicating that the magnetic part of the aggregate shrinks. This can also be shown by evaluating the FMR intensity. Therefore, it is necessary to double integrate the first derivative spectrum to get a quantitative value for the intensity. Due to the asymmetry of the lineshape and the zero field absorption, it is not possible to do this integration numerically. Since both spectra have almost the same lineshape,

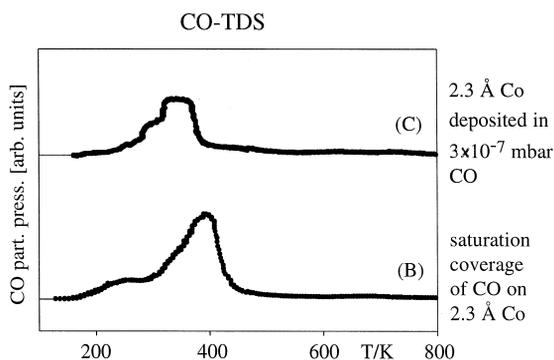


Fig. 4. TD spectra of CO: adsorbed on 2.3 Å Co (B) and from carbonyl-like cobalt species (C).

the quotient of the signal heights gives an estimation of the relative intensities. Thus, CO adsorption leads to a reduction of intensity of about 23%. A titration experiment reveals that saturation is still reached at a coverage of 2 L CO, i.e. further CO adsorption does not influence the spectrum anymore, which is in good agreement with previously mentioned experiments dealing with CO adsorption on copper-sup-

ported Co films [10]. Since a saturation coverage of CO does not quench the magnetism of 2.3 Å cobalt completely, a magnetic core must exist which is not influenced by the adsorbed CO. This is compatible with three-dimensional particles. Otherwise — in the case of two-dimensional islands — one would expect a vanishing signal or at least a stronger decrease in intensity because every Co atom would be accessible for the CO molecules. This assumption has been verified in a third experiment depositing cobalt in an atmosphere of CO (C) making sure that as many Co atoms as possible can be influenced by the CO adsorption. This leads to a much stronger reduction in intensity and will be discussed in detail below.

It is interesting to discuss further the reduction of the signal by only 23% due to the presence of CO. Considering the average number of atoms per island (770) and using various geometrical shapes, the fraction of surface atoms varies between 37 and 44% [28]. Adsorption studies of CO on cobalt single crystals ((0001), (10 $\bar{1}$ 2)) show a saturation coverage of 1/3 [29,30]. This value is only a lower limit for

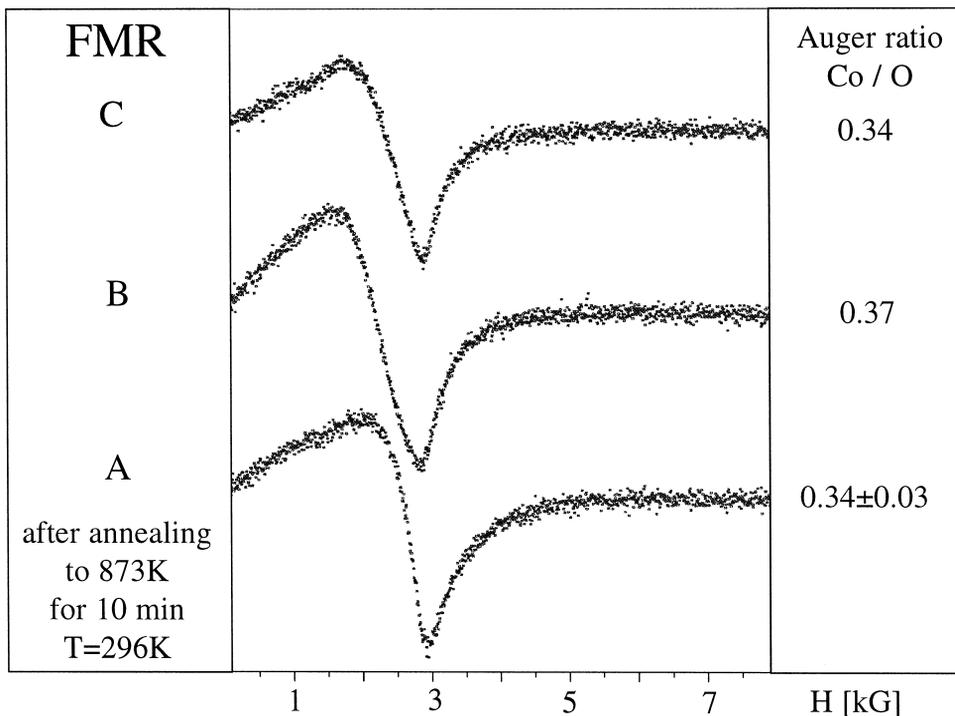


Fig. 5. FMR spectra of samples (A), (B) and (C) after annealing for 10 min to 873 K. Right panel: Auger ratio Co/O.

our estimation since one would expect a higher coverage on more irregularly shaped surfaces of small particles. Assuming that every adsorbed CO quenches the magnetic moment of one cobalt atom completely the magnetic moment of a particle is reduced by at least 12% ($37\% \times 1/3$). Taking into account that the thermal motion of the magnetic moment (i.e. SPM) reduces the magnetization of an ensemble of aggregates the intensity is further decreased, so that our experimental results are quite reasonable.

Coming back to the third type of experiment (Fig. 2C), the CO partial pressure during metal deposition was chosen to be 3×10^{-7} mbar fulfilling two conditions. Firstly, collisions between CO molecules and Co atoms in the gas phase should play only a minor role; secondly, a fast CO saturation of the deposits must be guaranteed. The FMR signal is quenched much more than in the case of subsequent CO adsorption (decrease of 71% versus 23%). This reduction is not the consequence of a smaller amount of metal on the surface as is indicated by the results of Auger spectroscopy. The Auger ratio determined by the quotient of the peak-to-peak heights of the Co peak (778 eV) and the oxygen signal of the sapphire (510 eV) is plotted on the right-hand side. The values for (A) and (B) are almost the same while in case (C) the Auger ratio is slightly smaller, which is due to the effective shielding of Co by the surrounding CO molecules. Therefore, the reduction of intensity must be attributed to a higher amount of Co atoms accessible to CO and to the formation of carbonyl-like species. This assumption is supported by thermal desorption spectroscopy (TDS). The decomposition temperature ($T_{\text{dec}} = 320\text{--}370$ K) revealed by TDS (Fig. 4) is lower than the desorption temperature of CO adsorbed on the small particles (400 K). Comparing this decomposition temperature to the one of diamagnetic stoichiometric cobalt carbonyl clusters, one finds that the conformance is quite good. From dicobalt dodecacarbonyl via the tetranuclear carbonyl cluster to the hexacobalt hexadecacarbonyl T_{dec} rises from 324 K via 333 K to 378 K [31]. Furthermore, complex, non-stoichiometric metal carbonyl aggregates could also be stabilized on a thin alumina film, e.g. carbonyl-like palladium species which do not exist as a pure solid without further stabilization [18,32].

In order to support the above ideas, we performed annealing experiments. The spectra in Fig. 5A–C, which have been taken after annealing to 873 K for 10 min, are nearly independent of the foregoing preparation. In case (B) the CO molecules desorb during annealing at about 400 K (see Fig. 4), while the carbonyl-like species decomposes around 350 K and the Co atoms are then able to build compact particles. At higher temperatures they coalesce to form fewer but bigger islands resulting in an increase of intensity and a strongly asymmetric lineshape. The three spectra show roughly the same intensity which is additionally supported by the Auger data verifying that the same amount of cobalt has been deposited in each case.

4. Conclusion

We investigated the magnetic properties of small deposited Co particles, especially the influence of CO. The magnetic behaviour of the deposited Co particles is compatible with three-dimensional growth on the reconstructed sapphire surface. This is supported by STM investigations. CO quenches or at least reduces the magnetic moments of the surface atoms of the aggregates. The latter conclusion is supported by evaporation of Co in a CO atmosphere which leads to an even more pronounced quenching of the magnetization.

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