Changes in the magnetism of small supported cobalt particles during the oxidation process observed by ferromagnetic resonance

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Abstract

Ferromagnetic resonance (FMR) under ultrahigh vacuum conditions was used to study the influence of oxygen on the magnetic properties of small cobalt particles deposited on the reconstructed surface of a sapphire single crystal $[(\sqrt{31} \times \sqrt{31})R \pm 9° \ Al_2O_3(0001)]$. The combination of FMR-results and thermal desorption spectroscopy shows that at intermediate oxygen dosages only the outer sphere of the particles is oxidized and a magnetic core still remains. These small cores tend to exhibit isotropic superparamagnetic behaviour with decreasing size of the core, i.e. increasing oxygen dosage. At higher dosages the resonance signal vanishes due to the complete formation of cobalt oxide. Additionally, we investigated annealed particles, which possess a higher degree of crystallinity and are larger due to coalescence. The oxidation behaviour of these annealed samples is similar to that of non-annealed ensembles except that a higher dosage of oxygen is necessary to oxidize the larger particles completely. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Small metal particles are of great interest in different areas of current research. One of these fields is heterogeneous catalysis, in which supported metals play an important role as reaction centres [1,2]. Another reason for intense research activities is the interesting properties of magnetic clusters differing from bulk magnetism [3]. Probably, the most spectacular phenomenon in this domain of magnetism is that of superparamagnetism (SPM) [4]. This 'magnetic state' is characterized by the fluctuation of the magnetic moment

of each particle leading to a reduced magnetization compared with ferromagnetic ensembles. In the meantime — from the first description of this phenomenon by Bean and Livingston in 1959 [4] to the present day — many studies have been carried out. Some very precise measurements concerning clusters in the range from a few to a few hundred atoms were performed as cluster beam experiments where particles with distinct sizes can be investigated without any further interaction among the clusters themselves or with any surrounding matrix [5,6]. However, very often much simpler approaches have been chosen to prepare and to characterize aggregates on the nanometre-scale. There are many techniques to generate small particles and to embed them in several kinds of

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matrix to avoid coagulation (for a review see Ref. [7]). However, a severe problem arises in most of these investigations: a possible partial oxidation of the aggregates cannot be excluded. Frequently, complete oxidation can be ruled out owing to comparison with intentionally oxidized samples, but a partial oxidation is difficult to detect and may lead to misinterpretations of the magnetic data. Therefore, we investigated the oxidation process of small cobalt particles to shed light on the influence of oxygen on the magnetic properties. The particles were grown on a sapphire single crystal surface substrate. All experiments were carried out under ultrahigh vacuum (UHV) conditions to protect the magnetic particles from any influence of disturbing gases or matrices. We used ferromagnetic resonance (FMR) spectroscopy to gain insight into the magnetic properties. FMR spectroscopy is a powerful technique for investigating the magnetism of ensembles of small particles since the magnetic properties, such as anisotropy fields and their origin, can be studied.

2. Experimental

The FMR measurements were performed in a specially designed UHV chamber that has been described previously [8]. The sample holder was modified to heat the sapphire single crystal with a surrounding loop of tungsten wire to about $1000°C$. In order to record the FMR spectra, a commercially available electron spin resonance spectrometer was used (Bruker, B-ER 420). The performance of this spectrometer has been improved by a new X-band microwave bridge (Bruker ECS 041 XK) and a lock-in amplifier (Bruker ER 023 M).

A clean $(\sqrt{31} \times \sqrt{31})R \pm 9°$-reconstructed sapphire (0001) surface was prepared by annealing the polished crystal several times for 20 min to about $1000°C$. The temperature was calibrated by a thermocouple (NiCr–CuNi) fastened 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, and the kind of reconstruction was determined by

LEED. Metal was deposited by an electron beam evaporator commercially distributed by Focus (EFM 3). We chose a low deposition rate of about 1 Å/min, calibrated by a quartz microbalance and Auger spectroscopy. The pressure during metal evaporation never rose above 1.5×10^{-10} mbar. A base pressure of below 2×10^{-11} mbar is a necessary condition for avoiding residual gas adsorption onto the freshly prepared Co particles.

The thermal desorption spectroscopy (TDS) measurements were performed in a separate UHV chamber that was also equipped with a LEED/Auger unit. The TD spectra were recorded with a quadrupole mass spectrometer (Vacuum Generators) using heating rates of about 1 K/s. The metal was deposited under the same conditions as in the FMR chamber by an analogous previously calibrated electron beam evaporator.

3. Magnetism of small particles

The magnetic moment of a particle consists of the ferromagnetically coupled moments of each atom. In the case of ferromagnetic solids this large coupled magnetic moment is aligned along certain high symmetry axes of the solid, which are called axes of easy magnetization or easy axes. These energy minima are separated by so-called anisotropy barriers, which can be described by the product of an anisotropy constant K_i and the volume V of the sample. This means that a reduction of the dimensions of a particle leads to a reduction of the anisotropy barrier or anisotropy energy $K_i V$. If the thermal excitation of the particle $k_B T$ is in the order of this anisotropy energy then the magnetic moment of the particle is no longer aligned along the easy axis but fluctuates. This phenomenon is called SPM [4]. In the limit of isotropic SPM the anisotropy barrier is negligible with respect to thermal excitation ($K_i V \ll k_B T$) and the magnetic moment of a particle can rotate freely in space. Therefore, the magnetization of an ensemble of superparamagnetic particles is zero in a vanishing magnetic field. An applied field H leads to a magnetization M described by the

so-called Langevin function $L(x)$ [4]:

$$M(H, T, V) = M_s L(x), \qquad (1)$$

where

$$L(x) = \coth(x) - 1/x \text{ with } x = M_s V H / k_B T \qquad (2)$$

For this case of isotropic SPM Gekht et al. have shown that the resonance frequency ω in the FMR experiment is given by [9]

$$\omega = \gamma H \qquad (3)$$

where γ is the magneto-gyric ratio. Therefore, the resonance field is exclusively determined by the g-factor, which describes the degree of spin–orbit coupling. For cobalt as a solid the g-value equals 2.18 [10] and leads to a resonance field of 3035 G using a representative microwave frequency of 9.261 GHz.

If thermal excitation only leads to a fluctuation of the magnetic moment, but not to isotropic rotation, the quantitative theoretical description is much more difficult. One can say qualitatively that the anisotropy field connected with the anisotropy constants decreases with increasing thermal excitation and with decreasing particle size. Therefore, the resonance equation [Eq. (3)] must be modified by this angular-dependent anisotropy field and the resonance position differs from the above-mentioned value of 3035 G:

$$\omega = \gamma (H + H_{ani}) \qquad (4)$$

4. Results and discussion

The experiments described in this paper were all carried out with a nominal coverage of cobalt of 6.5 Å deposited on the $(\sqrt{31} \times \sqrt{31})R \pm 9°$ $Al_2O_3(0001)$ surface. This means that if it were possible to distribute the cobalt atoms homogeneously on the surface the height would be 6.5 Å. Actually, cobalt grows as three-dimensional islands on alumina, which has been shown by STM experiments reported elsewhere [11,12]. The evaluation of these STM data leads to an averaged number of atoms per cluster of 2170, which corresponds

to a radius $r = 23$ Å considering a half spherical shape. From a detailed analysis of the STM pictures and the FMR spectra it can be concluded that the height of the particles exceeds their radius, which can be modelled by assuming a half ellipsoidal shape. A detailed analysis of these STM data is beyond the scope of this article and is discussed elsewhere [13,14]. The successive oxidation of these small cobalt particles was carried out by dosing oxygen in small amounts. The most obvious result of the oxidation series of a non-annealed ensemble of cobalt particles is shown in Fig. 1: The relative FMR intensity is plotted versus the oxygen dosage measured in langmuirs $(1 \text{ L} = 1 \times 10^{-6} \text{ Torr s})$. The FMR intensity was determined by evaluating the peak-to-peak amplitude, which must be weighted with the square of the line width. This method is only valid if the line shape is purely Lorentzian, but it can also be used as a good approach if the line shape at least does not change as a function of oxygen dosage. At first, one notices that the intensity remains constant after the first two oxidation steps. This means that a total oxygen dosage of 2 L does not influence the magnetism of the cobalt clusters. This is consistent with calculations reported in the literature where Pick and Dreyssé determined that isolated oxygen atoms adsorbed on Co(0001) or Co_{13}-clusters lead to only very small changes of the magnetization [15]. An explanation for this
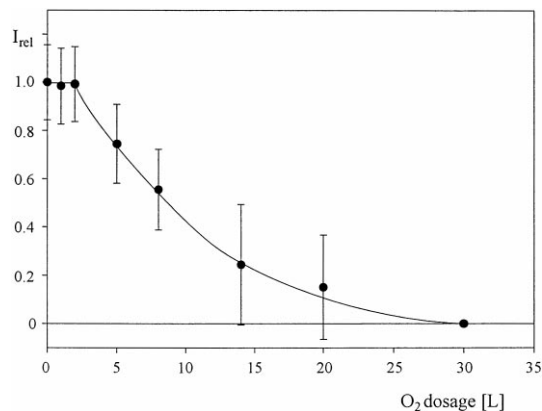

Fig. 1. Reduction of the relative FMR-intensity of cobalt particles (nominal coverage 6.5 Å) as a function of the oxygen dosage.

interesting behaviour may be found on the basis of the results in the literature. Getzlaff et al. [16] have shown by spin-resolved photoelectron spectroscopy that, in the range of atomically chemisorbed oxygen on thin cobalt films supported by a tungsten single crystal [W(110)], the oxygen atoms are spin polarized. Therefore, in this regime of submonolayer coverage the adsorbate does not influence the magnetism of the substrate, but the magnetic sample is able to transfer its magnetism towards the adsorbate. A similar result was obtained by Salvietti et al. [17]: a 10 ML Fe film is able to polarize the oxygen atoms after a dosage of 1 L O_2, whereas an oxygen dosage of 3–4 L forms a non-magnetic oxide layer. The latter can also be observed in the present FMR experiment. For an oxygen dosage larger than 2 L the FMR intensity decreases with increasing dosage. The signal vanishes at a total oxygen amount of 30 L. At this point all the metallic cobalt is oxidized to cobalt oxide, which does not contribute to the FMR signal. More strictly speaking, one would have to argue that the remaining amount of metallic cobalt is too small to be detectable by our spectrometer. Unfortunately, it is not possible to determine whether the oxide formed orders antiferromagnetically like bulk CoO. This is due to the fact that antiferromagnets cannot give rise to any resonance signal in the X-band region because the high field strength — necessary to overcome the exchange fields — is not accessible with the present spectrometer.

We already mentioned that the decreasing FMR intensity is due to the shrinking metallic part of the particles. The question arising immediately is: how does the oxidation process take place in detail? One possibility is the formation of a closed oxide layer at the surface of each particle that grows from the outer sphere to the inner part of the cluster. An alternative is a more irregular oxidation that starts at different points of the particle and leads to the formation of cracks, as reported for small Cu particles [18]. A very sensitive method for investigating whether an oxide film grown on a metallic substrate is closed or not is a titration experiment, e.g. with CO as a probe molecule. Therefore, we performed TDS measurements using saturation coverages of CO adsorbed

at various cobalt samples that were predosed with different amounts of oxygen (Fig. 2). Even the TD spectrum of the pure metallic cobalt particles looks rather complicated and exhibits several desorption peaks. CO desorption starts with a broad plateau at around 250 K labelled β. The maximum of the main desorption peak α_1 is located at about 390 K and shows a shoulder at 330 K (α_2). The desorption temperature of 390 K is comparable to that observed on non-basal planes of cobalt single crystals {Co($10\bar{1}2$): 370 K [19], Co($10\bar{1}0$): 400 K [20]}, whereas the α_1 peak of Co(0001) is located at higher temperature (450 K, [21]). This indicates that the particles are not terminated by flat surfaces, but that they exhibit a rough morphology, which is also supported by the presence of the desorption feature β. This low temperature desorption can be assigned to atoms in highly exposed positions that are coordinated by more than one CO molecule. The resulting intermolecular repulsion leads to a much lower binding energy, which has also been observed in the case of small Pd clusters deposited on a thin alumina film [22]. Additionally, the TD spectra of CO from a stepped nickel surface, e.g. Ni(775), show similar features: a plateau-like desorption at 260 K and an asymmetric, much more intense peak at higher temperature [23]. This represents further confirmation of the assumption that the investigated cobalt clusters exhibit high step densities. Alternatively, the low temperature feature could be explained by desorp-
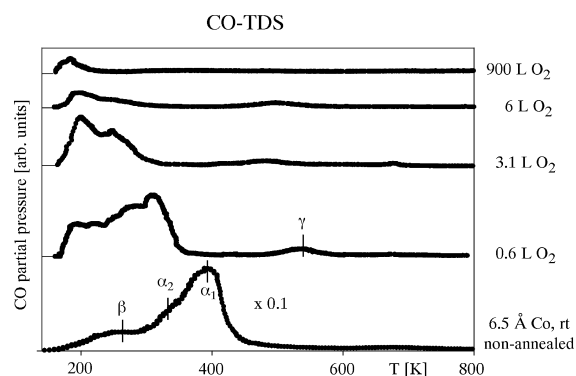

Fig. 2. CO titration experiment: CO-TDS after the cobalt particles had been oxidized with different dosages of O_2. The oxide layer is completely closed after an oxidation with only 6 L O_2.

tion from the interface region of the particles. Several layers of this interface are influenced by the substrate and may be described as partially oxidized (cf. Refs. [13,24,25]). Therefore, simply speaking, within the terms of the Blyholder model, less electrons are available for the back-donation part of the Me–CO bond, which is consequently weakened, and desorption appears at lower temperatures.

After a predosage of 0.6 L O$_2$ the CO desorption spectra change drastically. The intensity decreases significantly to a tenth of the value of the as-deposited particles and the peaks shift to lower temperature. For this coverage the desorption starts at around 200 K and reaches its maximum at 310 K. With increasing oxygen dosage these trends (decreasing intensity and shift to lower temperature) become more pronounced. The decrease of the intensity is due to the coverage of possible adsorption sites by oxygen atoms. This also leads to the desorption at lower temperature: the oxygen atoms attract electronic charge and, therefore, analogously to the above reasoning, the CO molecules are bound more weakly. At an oxygen dosage of only 6 L, CO desorption from pure metallic cobalt can no longer be observed, whereas at this oxidation state the FMR spectrum still shows a rather intense signal. Therefore, only a thin layer of the particles has been oxidized and the inner core remains metallic and thus magnetic. At this point we would like to focus on the small difference between the two TD spectra shown at the top of Fig. 2. In the case of 6 L O$_2$ there is still some CO desorption at about 270 K that vanishes at an oxygen dosage of 900 L. Therefore, CO desorption from the thin oxide layer (6 L) seems to be influenced by the underlying metal atoms, whereas this is not the case for the saturation dosage of 900 L O$_2$ that leads to complete oxidation. Nevertheless, the desorption temperature of 190 K of the completely oxidized samples is relatively high compared with the 125 K obtained from well-ordered CoO films {CO-CoO(111)-Co(0001) [26]}. This is probably due to the high concentration of corners, steps and kinks on such small clusters.

Additionally, the minor desorption γ occurring in the spectrum of 0.6 L O$_2$ at about 550 K must be discussed. This peak can be attributed to either recombinative desorption or associative desorption. Since cobalt is situated between iron and nickel in the periodic table, cobalt is expected to show an intermediate behaviour concerning CO dissociation. Whereas iron is capable of dissociating CO at room temperature, the CO adsorption on nickel is purely molecular. Indeed, carbon monoxide adsorbs molecularly on polycrystalline cobalt surfaces, whereas it dissociates partially at 350 K [27]. An analogous behaviour can be found for some of the non-basal planes of Co single crystals (for a review see Ref. [20]). The only question which arises is: why has this recombinative desorption not been observed in the case of the pure cobalt particles? Presumably, the intensity is too weak compared with the main desorption peak and indeed a small and broad hump can be detected at 680 K — a desorption temperature already reported in the literature for γ-CO [28]. Additionally, the shift to lower temperature in the presence of oxygen from 680 to ∼500 K has been described by Bridge et al. [21].

The essence of these TDS measurements is that the particles are already covered completely with a closed oxide layer at an oxygen dosage of only 6 L. In this oxidation state the FMR intensity is reduced to only 70% (cf. Fig. 1), which means that a large metallic — and therefore magnetic — core still remains. Hence, we postulate that the oxidation process of these cobalt particles can be described by a so called 'shell-to-core' model typified in Fig. 3. In the initial oxidation only the outer sphere of the clusters is influenced and a relatively unchanged magnetic core contributes to the FMR signal. With increasing oxygen dosage
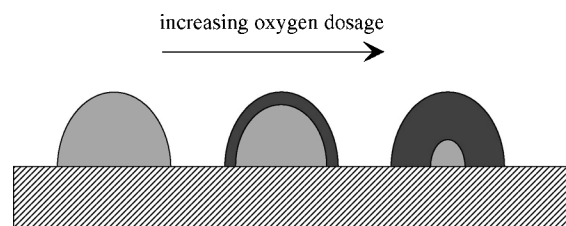

Fig. 3. 'Shell-to-core' oxidation model: already at low oxygen content the particles are surrounded by a completely closed thin oxide layer and in the further oxidation process the metallic core shrinks.

the oxide layer grows from the outer part towards the centre and the metallic core shrinks. According to the discussion above, such a shrinking magnetic core should have a continuously decreasing anisotropy barrier. Indeed the observed increasing superparamagnetic character of the oxidized ensembles provides strong evidence for the validity of the postulated 'shell-to-core' oxidation model, as will be discussed in the next paragraph.

As mentioned above, the resonance field H_0 should be about 3035 G for isotropic superparamagnets. However, the non-oxidized cobalt particles reveal a resonance position of 2580 G, as can be extracted from Fig. 4A. This is due to the
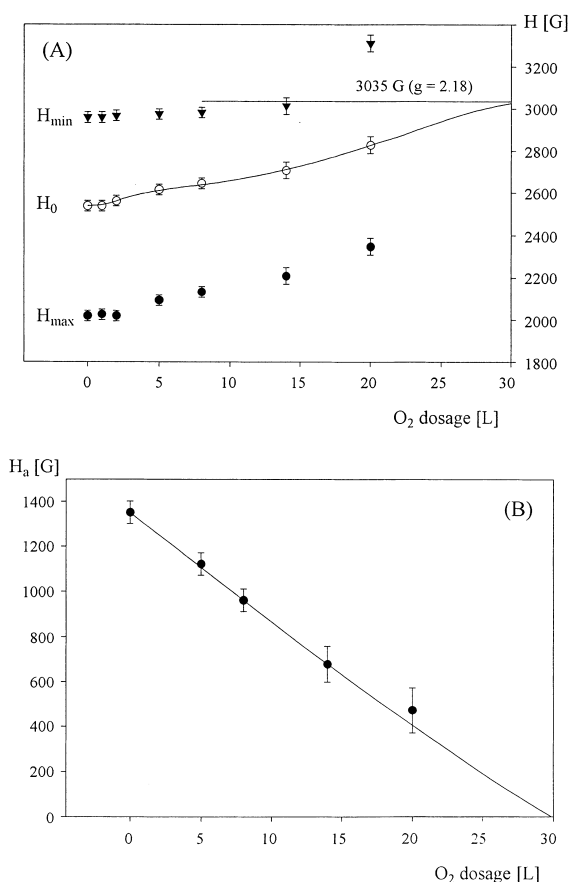

Fig. 4. Changes of magnetic properties during the oxidation series of 6.5 Å Co: (A) resonance field H_0 tends toward 3035 G and asymmetry of the line shape represented by the distances of H_{min} and H_{max} to H_0 remains almost constant; (B) effective anisotropy field H_a decreases. Solid lines are guides to the eye.

anisotropy field, which is not averaged out as in isotropic SPM. We have shown that the shape anisotropy in the case of these small cobalt particles leads to this shift [12,13]. With increasing oxygen dosage, not only does the FMR intensity change, but also the resonance position shifts to higher values and tends towards the upper limit of 3035 G. Therefore, with progressing oxidation the anisotropy field decreases (Fig. 4B). In Fig. 4B the so-called effective anisotropy field H_a is plotted versus the O_2 dosage. The effective anisotropy field is a measure for the anisotropy often used in FMR spectroscopy and is defined as $H_a = H_0(\theta = 0°) - H_0(\theta = 90°)$. Here, the angle θ is the polar angle between the normal of the substrate surface and the direction of the applied magnetic field. The data points in Fig. 4B are thus results of measurements at two different angles. We conclude that the anisotropy field decreases with increasing oxygen dosage, which means that the superparamagnetic character of the ensemble increases. This is due to the shrinking metallic core and, therefore, is fully consistent with our suggested oxidation model.

In a second experiment we investigated the oxidation behaviour of an annealed ensemble of cobalt particles. For that purpose, a coverage of 6.5 Å Co was annealed to 873 K for 10 min. This leads, on the one hand, to crystallization of the aggregates and, on the other hand, to coalescence of the particles. Consequently, the particles are larger than in the non-annealed sample and their crystalline structure shows the formation of ordered, low index surfaces with relatively high packing density compared with the non-annealed samples. More oxygen is needed to oxidize the clusters completely. This is shown in Fig. 5 where, analogously to Fig. 1, the relative FMR intensity is plotted against the oxygen dosage. Up to a dosage of 40 L one finds a linear decrease, whereas at larger amounts of O_2 the curve flattens out. Obviously the oxidation process is slower in the latter region. This is due to the initially generated, possibly crystalline, oxide layer, which makes further oxidation difficult. Similar behaviour was reported by Görts et al. [29] for the oxidation of a cobalt single crystal surface Co($10\bar{1}0$): a combination of ellipsometry and high-energy ion scatter-
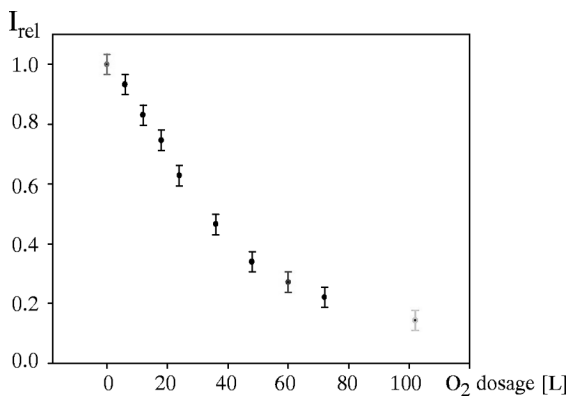
Fig. 5. Reduction of the relative FMR intensity of annealed cobalt particles (10 min, 873 K, nominal coverage 6.5 Å) as a function of the oxygen dosage.

ing detected that, after a steep initial phase, the oxygen uptake decreased until the oxidation rate merged into saturation at a dosage of 100 L. This reduction of the oxidation rate is caused by the increasing diffusion path of the Co atoms through the oxide layer towards the gas–oxide interface where the oxidation takes place [30]. The linearization of the oxygen uptake beyond 100 L observed in the cited literature cannot be verified in the present experiments because the particles are almost completely oxidized at a total oxygen dosage of 102 L. This final value of 102 L is much larger than in the case of the non-annealed sample due to the larger size of the particles and the hindered oxidation of deeper layers.

Additionally, coalescence leads to an asymmetric particle size distribution because the smaller aggregates are more mobile and, therefore, bigger clusters are formed at the expense of smaller ones. This growth behaviour can often be described by a log-normal distribution [31,32]. Since the particle size distribution is not uniform the observed line shape consists of many resonance lines, each corresponding to a given particle size. The resonance position of these single lines depends on the corresponding anisotropy field, as shown in Eq. (4). Since the anisotropy field depends on the particle size [13], the observable line shape envelope reflects the particle size distribution. Thus, the asymmetric size distribution leads to an asymmetric line shape, which has been evaluated in Ref. [13]. The result-

ing FMR spectrum is shown in Fig. 6 together with two further representative ones recorded at different oxidation states. The asymmetry of the resonance signal belonging to the pure cobalt particles is directly visible and is depicted in Fig. 7A. In addition to the resonance field H_0, which is represented by the inflection point of the signal measured as the first derivative of the magnetic field, both the maximum and the minimum of the resonance line are plotted as H_{max} and H_{min} (cf. Fig. 6). The different distances from H_{max} and H_{min} to H_0 reflect, in a simple way, the asymmetry of the line shape, which does not change during the first 25 L of oxygen. This is due to the formation of the oxide layer reducing the magnetic part of each particle by almost the same amount independently of their size. This leads to a shift of the size distribution towards lower diameters without changing its general shape. Since the shape of the size distribution stays almost unaltered, the line shape does not change. In the range from 30 to 70 L O_2 the line shape symmetrizes. The symmetrical line shape observed for dosages above 70 L looks like that of the non-annealed Co
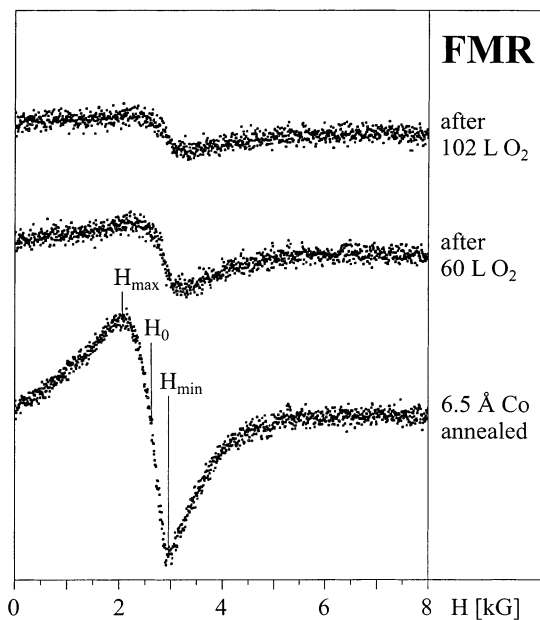

Fig. 6. FMR spectrum of cobalt particles (nominal coverage 6.5 Å, annealed at 873 K for 10 min): as annealed and after different dosages of oxygen.
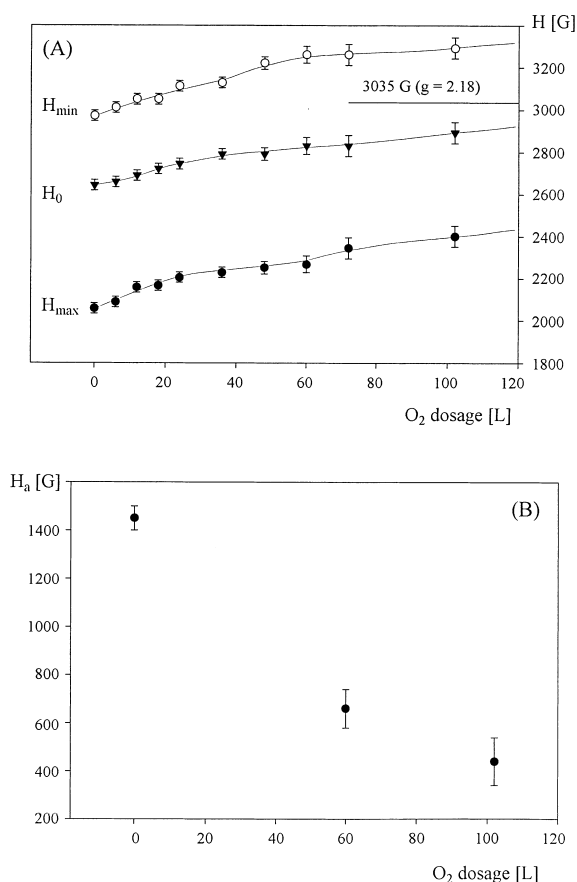
Fig. 7. Changes of magnetic properties during the oxidation series of 6.5 Å Co (annealed): (A) resonance field H_0 tends toward 3035 G and asymmetry of the line shape represented by the distances of H_{min} and H_{max} to H_0 decreases; (B) effective anisotropy field H_a decreases. Solid lines are guides to the eye.

Table 1
Comparison of FMR spectra measured in the last step before complete oxidation

6.5 Å Co	O_2 dosage (L)	H_{max} (G)	H_0 (G)	H_{min} (G)	H_a (G)
Non-annealed	20	2347	2829	3311	472
Annealed	102	2401	2893	3292	438

the size of the aggregates: a small metallic core showing almost isotropic SPM, surrounded by a more or less thick FMR-inactive oxide layer. The thickness of the oxide layer depends on the original size of the corresponding particle. This is additional confirmation of our suggested 'shell-to-core' oxidation model.

5. Conclusion

We have investigated the influence of the interaction of oxygen with small supported Co particles. In the initial state of the oxidation process the magnetism of a sample with a nominal coverage of 6.5 Å is not influenced. But at dosages of 6 L O_2 a formation of an FMR-inactive oxide layer was observed that grows during the further oxidation process from the outer part to the inner core. The shrinking volume of the metallic core leads to a reduction of the magnetic anisotropy and, therefore, to an increasing superparamagnetic character. This 'shell-to-core' oxidation model was verified by an additional experiment with a sample of larger Co particles that leads to the same results. Hence, the magnetic response of the remaining metallic core does not depend on the thickness of the oxide layer formed.

samples. It seems interesting to compare both the annealed and non-annealed systems further, because the principal trends are very similar. In Fig. 7 the same tendency is shown as for the as-deposited samples in Fig. 4: the anisotropy decreases with increasing oxygen dosage, which leads to the already known shift of the resonance field towards 3035 G. The spectra gained in the last step before complete oxidation of both series are almost identical. This is shown in Table 1, where the characteristic parameters of the resonances are listed. Therefore, we have demonstrated clearly at this point that the oxidation of cobalt particles leads to the same product independent of

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