



Gold atoms and clusters on MgO(100) films; an EPR and IRAS study

M. Yulikov, M. Sterrer, T. Risse*, H.-J. Freund

Fritz-Haber-Institut der Max-Planck Gesellschaft, Department of Chemical Physics, Faradayweg 4-6, 14195 Berlin, Germany

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ABSTRACT

Single gold atoms deposited on single crystalline MgO(100) films grown on Mo(100) are characterized by electron paramagnetic resonance spectroscopy as well as IR spectroscopy using CO as probe molecules. In this article we describe the first angular dependent measurements to determine the principal hyperfine components of a secondary hyperfine interaction, namely, with ^{17}O of the MgO. The values determined here are in perfect agreement with theoretical expectations and corroborate the previously reported binding mechanism of Au atoms on the oxygen anions of the MgO terrace. The temperature dependent EPR data reveal an onset of Au atom mobility at about 80 K while the formation of Au particles occurs only above 125 K. By an analysis of the EPR line width in combination with STM measurements it is possible to deduce an increase of the interatomic distance above 80 K. The Au/CO complexes show a somewhat smaller temperature stability as compared to the Au atoms. The observed thermal stability is in perfect agreement with theoretical predictions for CO desorption.

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1. Introduction

A detailed understanding of the properties of oxide supported metal atoms and clusters is of paramount importance for a variety of technological aspects such as heterogeneous catalysis. About a decade ago it was found that highly dispersed gold supported on oxides exhibits high chemical activity in an increasing number of chemical reactions [1,2]. These properties of gold have stimulated a huge number of studies in catalysis, photonics and biology. In spite of the enormous interest and enhanced activities worldwide, a complete atomistic understanding of these systems is still lacking. To this end model studies of metal particles supported on planar oxide substrates under well-controlled conditions were envisioned to provide fundamental insights into the relationships between the atomic structure and the physical and chemical properties of supported gold atoms and clusters (e.g. [3–5]). Even for the simplest system, namely supported Au atoms, experimental characterization of the electronic structure and binding mechanism is rather scarce [6–8] while theory has investigated these systems extensively (e.g. [9–12]). In this respect electron paramagnetic resonance (EPR) spectroscopy is a powerful tool to elucidate the electronic and geometric properties of paramagnetic species which has been shown for a variety of problems in physics, chemistry and biology (e.g. [13–16]). EPR spectra of single gold atoms on a single

crystalline MgO(100) surface have been reported recently. It was shown that EPR spectroscopy can provide insight into the binding site and, together with appropriate theoretical support, into the electronic properties [17].

This article will focus on two main aspects: first we will discuss the structure and the electronic properties of Au atoms on MgO using EPR spectroscopy. In particular, we will elucidate the impact of the terrace size on the properties of supported Au atoms by comparing the published results on well annealed MgO(100) films on Mo(100) [17] with non annealed, so called pristine, films which exhibit a significantly smaller island size. With respect to the electronic properties of the Au atoms we will report the first angular resolved measurement of a secondary hyperfine interaction (Mg ^{17}O -film; $I(^{17}\text{O}) = 5/2$), which allows the determination of the hyperfine coupling tensor and its spatial orientation. These values provide additional information on the binding of Au atoms and will be compared with theoretical predictions. Secondly, we will explore the thermal stability of Au atoms and compare the bare atoms with the behavior of Au/CO complexes. The latter will be investigated using IR spectroscopy. In order to interpret the temperature dependent data it is important to know the properties of Au atoms as a function of coverage. Thus, the article is organized as follows: after some remarks about experimental details and theoretical aspects of the data analysis we will first discuss EPR data of Au atoms on pristine films and the angular dependent measurements to determine the ^{17}O hyperfine tensor. The following sections describe EPR and IR measurements as a function of Au coverage and as a function of temperature, respectively. Subsequently,

* Corresponding author. Tel.: +49 30 84134218.

E-mail address: risse@fhi-berlin.mpg.de (T. Risse).

these results are discussed and the paper concludes with a summary.

2. Methods

2.1. Experimental details

The experiments were performed using a UHV apparatus described in detail elsewhere [18]. The base pressure during experiments was below 1×10^{-10} mbar. A liquid He cryostat allowed cooling of the sample down to approx. 30 K. Thin MgO films were grown on Mo(100) surfaces using established procedures [19]. In brief, the Mo crystal was cleaned by oxidation with O₂ at 1500 K and subsequent flashes to 2300 K prior to the preparation of the MgO films. The sample temperature was monitored by a type C (W-5%Re/W-26%Re) thermocouple spot-welded to the upper edge of the Mo crystal. Mg was deposited on the clean Mo surface in an oxygen ambient (1×10^{-6} mbar) and a temperature of 600 K. For all experiments MgO films with a thickness of 20 ML were used. The MgO growth rate was 1 ML/min. Two types of MgO films were studied: so called pristine films were prepared according to the above mentioned procedure, whereas annealed films were heated to 1100 K for 10 min. after film preparation. The annealing results in an increase of the terrace size and a reduction of defects such as steps and corners. This can be verified using low energy electron diffraction (LEED) as well as IR and TPD measurements using CO as a probe.

The cw-EPR spectra of Au atoms were measured at X-band (microwave frequency approx. 9.6 GHz) with 20 mW microwave power using a TE₁₀₂ cavity. A modulation amplitude of 4 G was used for all measurements. Angular dependent measurements were performed by rotating the Mo crystal around the x-axis of the TE₁₀₂ mode. The angle θ is given as the angle between the surface normal and the static magnetic field B_0 oriented along the y-axis of the TE₁₀₂ cavity. Infrared spectra were taken with a spectral resolution of 4 cm^{-1} and 1000 scans were accumulated to obtain a reasonable signal-to-noise ratio.

2.2. Simulation of EPR spectra

The components and orientation of the magnetic interaction matrices were determined by spectral simulations using the Easy-Spin package [20]. In case of an axial symmetric hyperfine matrix \hat{A} the interaction between electron and nuclear spin is given in the molecular framework as [21]

$$\hat{A} = \begin{pmatrix} A_{\perp} & 0 & 0 \\ 0 & A_{\perp} & 0 \\ 0 & 0 & A_{\parallel} \end{pmatrix} = a_{iso} \cdot \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + B \cdot \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \quad (1)$$

The first term on the right hand side represents the isotropic (Fermi contact) and the second term represents the anisotropic (dipolar) part of the hyperfine interaction. To account for small changes in the local environments of the Au atom on the MgO surface a strain of the isotropic hyperfine interaction a_{iso} was modeled by a Gaussian distribution according to

$$W(A_{iso}) = \frac{1}{\sqrt{2\pi} \cdot \Delta A} \cdot \exp\left(-\frac{(a_{iso} - a_{iso}^0)^2}{2 \cdot \Delta A^2}\right) \quad (2)$$

The hyperfine and g-matrix components as well as their orientation with respect to the surface were derived from a least squares fit to the angular dependent data.

3. Experimental results

3.1. Spectroscopic parameters of adsorbed Au atoms

The EPR spectrum of individual Au atoms on MgO(100) surfaces has recently been published [17]. The spectra are characterized by a quartet of lines due to the hyperfine interaction of the unpaired electron with the nuclear spin of ¹⁹⁷Au ($I = 3/2$; natural abundance 100%). Based on the EPR spectra it was concluded that the Au atoms are located on top of oxygen anions of the MgO terraces. These spectra were obtained on 20 ML thick annealed MgO(100) films which are characterized by relatively large MgO terraces. It would be interesting to compare the properties of Au atoms on terraces with those on low-coordinated sites such as steps. However, on annealed films the number of low-coordinated sites is too small to allow for an observation by EPR. Therefore experiments were performed on pristine MgO(100) films which are characterized by a larger amount of low coordinated sites [22]. Fig. 1a shows the EPR spectrum of Au atoms adsorbed on a pristine MgO film taken at an angle $\theta = 90^\circ$ between the static magnetic field and the surface normal. Qualitatively, the spectrum is identical to the one

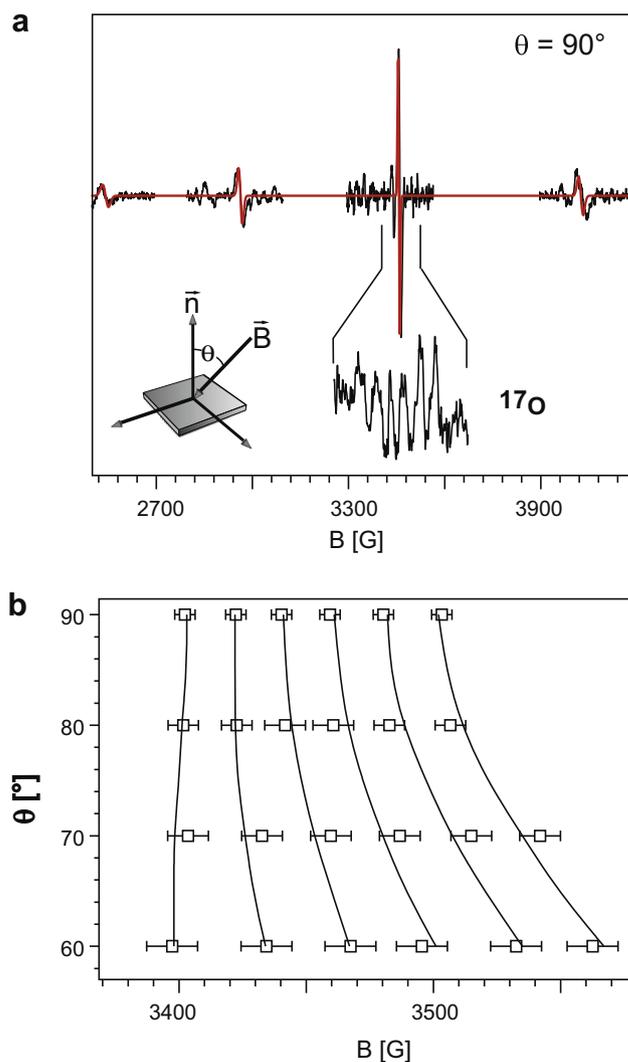


Fig. 1. (a) EPR spectrum of 0.005 ML Au on "pristine" MgO(100) film, the inset shows a smaller field region of the EPR spectrum of 0.005 ML Au on an isotope-enriched "pristine" Mg¹⁷O(100) film; (b) angular dependence of the six ¹⁷O hyperfine components for an annealed Mg¹⁷O-film. All the spectra were measured at 30 K.

observed on the annealed film. It consists of a quartet of lines whose line width varies from 20 G for the outermost components to 6.5 G for the line at around 3400 G. This variation in line width of the hyperfine components can be understood by *A*-tensor strain caused by a distribution of magnetically non equivalent sites. Due to the non-linear dependence of the resonance position on the hyperfine coupling constant for different nuclear spin states in the general Breit–Rabi case [23], the outermost components are affected most while the 3-rd line of the manifold is almost unaffected by the distribution for the given *g*- and *a*_{iso}-components. The fit to the experimental spectrum reveals a ΔA of 21 G (Fig. 1a). Angular dependent measurements can be used to deduce the components and the orientation of the *g*- and *A*-interaction matrices (data not shown) [17]. The fit reveals that one component of the coupling matrices is oriented along the surface normal while the other two, degenerate components are oriented in the surface plane. As discussed previously [15], the orientation of the coupling matrix requires Au adsorption sites with a symmetry axis along the surface normal. Among the expected sites on the MgO(100) surface this orientation is only compatible with terrace sites of the MgO surface. Thus, it is concluded that the spectra observed on the pristine film are indicative for Au atoms adsorbed on terrace sites and no indication for Au atoms on low coordinated sites can be found.

Additional information can be gathered from the hyperfine interaction between the Au atoms and the substrate. In case of MgO films grown with ¹⁷O enriched O₂ (enrichment 90%), an additional hyperfine coupling of the unpaired electron with an ¹⁷O nucleus (*I* = 5/2) is observed. The corresponding spectrum for the field range around the position of the 3-rd Au hyperfine component is presented in Fig. 1a. The observed hyperfine manifold consists of 6 approximately equally intense lines separated by 21 G, which indicates hyperfine interaction with one oxygen nucleus. Because of the enrichment factor of 90% an additional line is found in the center (overlapping with the inner hyperfine components), which is due to Au nucleating on ¹⁶O sites. This is in line with the observations for the annealed film and proves the nucleation of the Au atoms on top of the oxygen sites [17]. Furthermore, the principal tensor components as well as their orientation with respect to the surface can be obtained by analyzing angular dependent measurements as mentioned above. In case of the ¹⁷O enriched films angular dependent measurements on the pristine MgO films suffer from the low signal to noise ratio of the peaks due to the comparatively large line width. Therefore, the resonance positions were extracted from spectra taken for annealed films and are shown in Fig. 1b. The analysis of the spectra reveals an axial symmetric hyperfine tensor with the parallel component being oriented along the surface normal. This is in line with expectations for Au nucleated on ideal terrace sites. The magnetic parameters obtained by fitting the angular dependent spectra are compiled in Table 1 for both the pristine and the annealed films [17]. From this qualitative discussion of the spectra it can already be concluded that the adsorption site of Au atoms on the pristine film observed by EPR is on-top of the O anion on regular terrace site of the MgO (100) surface. Together with the close resemblance of the magnetic parameters found for both systems one can conclude that the properties of Au atoms on terrace sites are very similar for the pristine and the annealed films [17]. It is important to note that this does not imply that Au does not nucleate on steps or other structural defects. In fact, STM investigations show that nucleation at low coordinated sites occurs [24]. However, these atoms are not monitored by EPR, because the total number is significantly smaller as compared to the amount of atoms on the terrace. In addition, the EPR spectra of these sites are expected to be significantly broadened due to a tilting of the magnetic tensors with respect to the surface normal and the corresponding superposition of structurally equivalent, but magnetically inequivalent sites.

Table 1

The comparison of the EPR parameters for individual Au atoms on MgO(100) as extracted from fits to experimental spectra with those obtained from the DFT calculations for Au atom on regular terrace adsorption site.

	Fit of exp. data (pristine)	Fit of exp. data (annealed)	O ₂₁ Mg ₂₁ ZORA(PW91) [25]
<i>g</i> _⊥	2.0690	2.0652	2.0759
<i>g</i> _∥	1.9911	1.9904	1.9680
<i>A</i> _⊥ (¹⁹⁷ Au) [G]	508.5	500.5	605.5
<i>A</i> _∥ (¹⁹⁷ Au) [G]	495.5	503.4	613.3
ΔA (¹⁹⁷ Au) [G]	21 ± 2	12.5 ± 1	–
<i>A</i> _⊥ (¹⁷ O) [G]	21 ± 2	21 ± 2	16.2
<i>A</i> _∥ (¹⁷ O) [G]	–	61 ± 10	56.7

Additional insight into the physics of the system can be obtained by comparing the values of the magnetic parameters with calculated ones presented in Table 1 [25]. The calculated *g*- and hyperfine-components show a qualitative agreement with the experimentally determined values. Experiment and theory determine the parallel and perpendicular *g*-components smaller and significantly larger than the free electron value, respectively. While the experimental *g*-components show only a slight increase of the anisotropy and the isotropic value for the pristine as compared to the annealed film, the anisotropy of the components is overestimated by the calculations, in particular as far as the parallel component is concerned. In terms of the hyperfine interaction, the calculations nicely reproduce the dominating isotropic hyperfine component for the interaction with the Au nucleus, which is reduced by about a factor of 2 (~1400 MHz vs. 3053 MHz [26]) as compared to the free atoms. However, the absolute value of the isotropic hyperfine coupling constant is overestimated by about 15% in contrast to the free atom where the theoretical approach is significantly more accurate [17,25]. In contrast to that the dipolar part of the hyperfine interaction is very small, both in experiment as well as in theory. The small differences in the magnetic parameters of the two films can be understood in terms of their structural differences such as the smaller terrace size. The increased number of Au atoms close to structural defects (steps, edges etc.) leads to an inhomogeneity of adsorption sites and can explain the slight differences in the magnetic parameters.

An analysis of the calculations reveals that the reduction of the isotropic hyperfine interaction observed for the Au atom is mainly due to a polarization of the unpaired electron away from the MgO surface. The adsorbed Au atoms are essentially neutral. The polarization leads to a reduced *s* contribution of the unpaired electron wave-function. Consequently, the spin-density on the Au nucleus is reduced, which is reflected by a smaller isotropic hyperfine interaction [17,25]. The absence of a significant charge transfer between the Au atoms and the MgO surface implies that the spin density is almost completely on the Au atoms. Therefore, the hyperfine interaction with the oxygen atom of the film is rather small. Theoretically, the isotropic hyperfine coupling constant was predicted to be about 30 G with a comparatively large dipolar part (*B*) of 13.5 G. This is in close agreement with the experiment which finds a slightly higher isotropic value (34 G) and the same dipolar component (13.3 G). This further confirms the abovementioned interpretation of neutral, polarized Au atoms.

3.2. Coverage-dependent measurements

Fig. 2a shows the third line of the gold quartet at about 3450 G for different amounts of Au deposited on a pristine MgO (100) film. The amount of single Au atoms was deduced from the EPR data by double integration of the spectra shown in Fig. 2a. The values are compared to the nominal amount of deposited Au atoms as measured by a quartz micro-balance (Fig. 2b). For very small coverage

and low temperatures ($T_{\text{dep}} = 30$ K) it is expected that most of the Au is adsorbed as single atoms. Unfortunately, it is not possible to calibrate the EPR intensity with sufficient accuracy to determine the absolute number of Au atoms on the surface. Therefore, the EPR intensity has been scaled such as to match the nominal amount of Au atoms for the lowest coverage of 5×10^{-4} ML.

With increasing Au coverage it is seen that the EPR intensity grows slower than expected for exclusive nucleation as isolated atoms. This can be understood by the formation of Au clusters due to nucleation and growth. For a Au coverage below 0.01 ML the deviation between the nominal Au coverage and the EPR signal intensity is noticeable but rather small. Thus, Au nucleates preferentially as individual atoms under these conditions. With increasing Au coverage the difference between the deposited amount and the amount detected by EPR increases and above 2% coverage the EPR intensity decreases as expected for an increasing fraction of Au clusters. Concomitantly, the width of the EPR line increases from approximately 5 G for the lowest coverage to about 10 G for 0.05 ML (Fig. 2c). It is interesting to note that the system with 0.05 and 0.005 ML nominal Au coverage have about the same signal intensity, which implies that the number of Au atoms is comparable. On the other hand the line width is significantly increased for the higher coverage situation pointing to considerable differences in the magnetic properties of the two systems.

The same system was investigated by IR spectroscopy using CO as a probe molecule. The IR spectra taken for different amounts of deposited Au are shown in Fig. 3. The spectra were taken after saturating the surface with CO at 30 K and subsequently annealing the system to 60–65 K to remove CO molecules adsorbed on regular terrace sites of MgO [27]. The spectra are characterized by three signals. The first band around 2170 cm^{-1} corresponds to CO bound to defects sites of the MgO films such as corners or steps [28,29].

The second band at 2120 cm^{-1} is indicative for CO bound to neutral Au clusters [30–32] on the MgO surface while the signal at 1852 cm^{-1} has been identified as CO bound to Au atoms adsorbed to the MgO surface [27,33]. The Au–CO complex has a one-to-one stoichiometry as inferred from isotope mixing experiments [27]. The intensity of the signal at 1852 cm^{-1} shows the same behavior as found for single Au atoms by EPR. The signal intensity increases up to a coverage of about 1% of a monolayer and decreases afterwards. On the other hand the signal of CO bound to Au clusters grows monotonously with coverage indicating an increasing fraction of Au clusters in this coverage range.

Formally the Au–CO complex has an odd number of electrons and should give rise to an EPR signal. Theoretical calculations show that about 60% of the spin density is located on the CO molecule due to an intra-complex charge transfer from Au to CO, which is due to the strong polarization of the Au atoms. This transfer of spin density gives rise to a reduction of the isotropic hyperfine interaction with the ^{197}Au nucleus to 304 G [33]. The partially negatively charged CO molecule has a tilted adsorption structure with a tilt angle of 46° with respect to the linear adsorption geometry [33]. However, no EPR signal was detected after CO adsorption. The reason for the absence of an EPR signal may be found in the geometry of the Au/CO complex. The tilted geometry has important consequences for the orientation of the g -tensor with respect to the surface. While one of the tensor components is oriented along the surface normal for Au atoms adsorbed on the terrace sites due to symmetry reasons, this does no longer hold true for the Au/CO complex. Even though the precise orientation of the tensor is not known, a substantial tilt of the principal components away from the surface normal is expected. Because the Au/CO complexes have no preferred azimuthal orientation with respect to the laboratory framework the expected signal is a superposition of spectra for

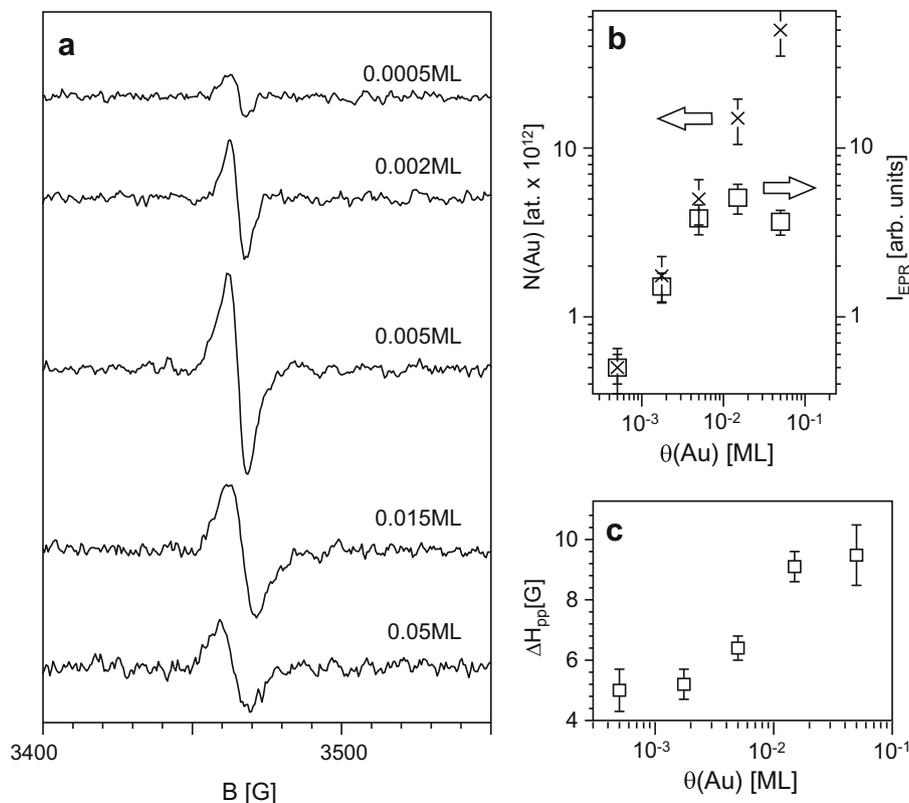


Fig. 2. (a) 3-rd hyperfine component of the EPR spectrum of Au on 20 ML “pristine” MgO (100) film for different Au coverages; (b) Comparison between the integral EPR intensities derived from spectra in a) (right scale) and the number of deposited Au atoms as measured by quartz microbalance (left scale); (c) EPR line width as a function of coverage taken from the spectra shown in a). All the spectra were measured at 30 K.

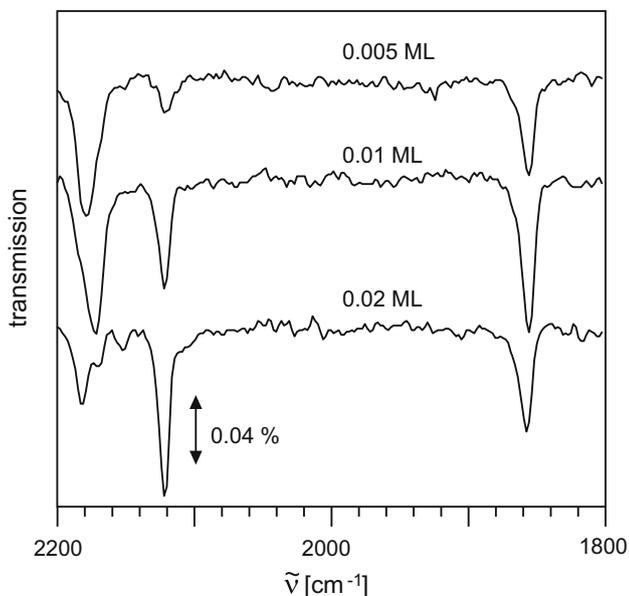


Fig. 3. IR spectra of adsorbed CO molecules for different Au coverage on the annealed MgO(100) thin film. CO adsorption and IR measurements were done at 30 K.

all azimuthal orientations. This gives rise to a spread of the signal due to the superposition of species with different orientations, thus, different resonance fields. It is important to bear in mind that the energy barrier for rotation around the surface normal is ex-

pected to be low, which will influence the apparent g -anisotropy due to motional averaging. A more quantitative estimation of the expected spectra is hampered by the unknown rotational correlation times of this motion. In conclusion, the absence of the EPR spectra is explained by a spread of the signal over the field which renders an observation of the signal impossible.

3.3. Thermal stability of Au atoms and Au/CO complexes

Fig. 4 shows the dependence of the EPR signal of single Au atoms upon annealing for 0.05 ML Au on a pristine MgO (100) film. Au was deposited at 30 K and subsequently annealed to different temperatures. The corresponding EPR spectra for each annealing step were again measured at 30 K. Upon annealing the signal amplitude first increases up to a temperature of 125 K and, subsequently, decreases rapidly at higher annealing temperature. After annealing to 180 K the signal has completely vanished. This reduction of the EPR intensity can be understood as a direct consequence of Au cluster formation. Concomitant to the increase of the signal amplitude the line width of the spectra decreases which leaves the EPR intensity unchanged up to annealing temperatures of 125 K (see **Fig. 5**). This shows that the number of individual Au atoms on the surface remains constant. On the other hand the reduction of line width shown in **Fig. 4a** implies that Au atoms start to rearrange on the MgO surface well before they start to aggregate.

A similar series of annealing experiments was performed monitoring the IR line of Au–CO complexes as shown in **Fig. 4b**. The IR intensity drops considerably above 85 K and vanishes completely at 180 K. To compare the temperature behavior of the IR and EPR

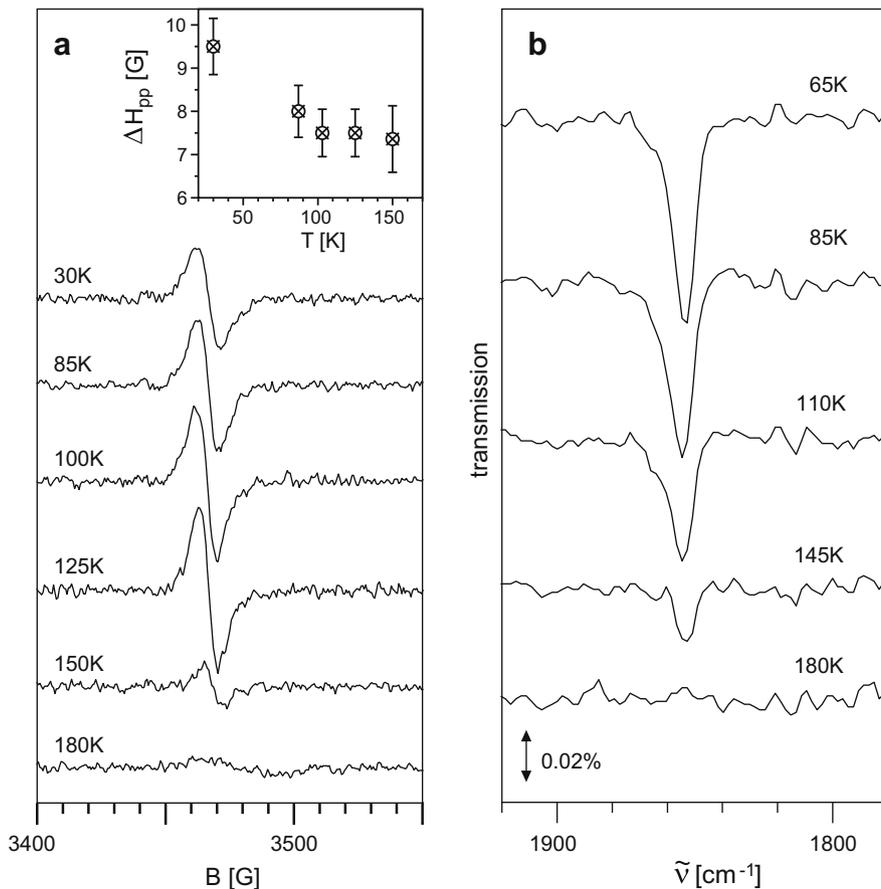


Fig. 4. (a) EPR spectra of 0.05 ML Au on a 20 ML MgO (100) film as a function of annealing temperature. The inset shows the corresponding dependence of the line width. (b) IR spectra of adsorbed CO molecules on 0.05 ML Au on a 20 ML MgO (100) film as a function of annealing temperature. All spectra were measured at 30 K.

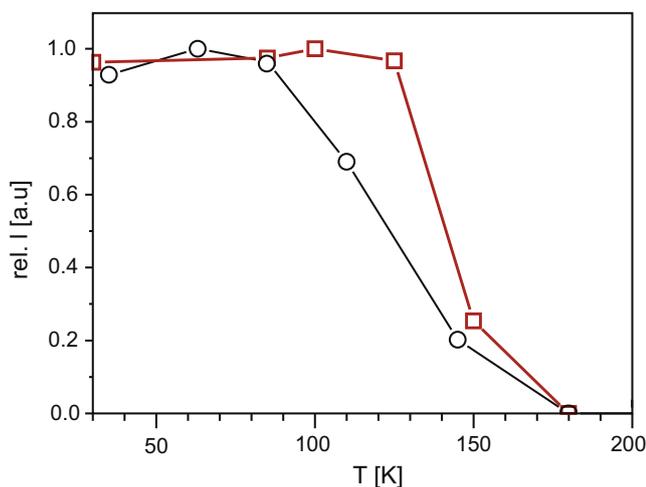


Fig. 5. Comparison of EPR- (squares) and IR (circles) signal intensities as a function of annealing temperature. The intensities were derived from the spectra shown in Fig. 4.

data the normalized intensities of both measurements are plotted against annealing temperature as shown in Fig. 5. One can clearly see that the IR intensity (circles) remains stable up to 85 K and decreases for higher temperatures. In contrast to that the intensity of the EPR signal (squares) remains constant up to 125 K and decreases rapidly for higher annealing temperatures. This indicates that the stability of the Au/CO complex is slightly smaller than that of the Au atoms on the MgO terrace.

4. Discussion

The experiments convincingly show the presence of Au atoms on the terrace of the MgO(001) surface as well as the formation of Au clusters for higher Au coverage. The latter was inferred from the signal intensity of the EPR line corresponding to Au atoms and corroborated by IR spectroscopy. It is important to note that the properties of the Au atoms on the terrace are very similar for pristine and annealed films. The first additional result that can be deduced from the temperature dependent EPR line width is a rearrangement of the Au atoms below 85 K. However, this temperature is not sufficient to induce the formation of Au clusters as seen by the constant EPR intensity. The temperature found for the rearrangement is well in line with calculations for the diffusion barrier of Au atoms on the MgO surface which was found to be around 0.2 eV [10,34]. On the other hand it is interesting to note that the energy required to form Au particles is about 0.2 eV higher than the barrier for the onset of mobility as estimated from the temperature dependence of the EPR signal. In case the diffusion barrier for Au atoms is correct this implies that there is a barrier to form a Au dimer or add a Au atom to a particle which corresponds to approximately 0.4 eV. The origin of such a barrier is unclear at present.

What dynamic processes lead to the reduction of the EPR line width observed after annealing the system to 85 K? This question is intimately connected to the observation of an increased line width for 0.05 ML Au coverage as compared to 0.005 ML Au coverage while the EPR intensity, thus, the number of Au atoms on the surface, is very similar. The main difference between these two systems is the number of Au clusters on the surface. While this number is rather small for the 0.005 ML case, only about 10% of the nominal coverage is found as Au atoms by EPR spectroscopy for 0.05 ML Au coverage. In this respect it is important to notice that the intensity behavior observed by EPR is reflected nicely by IR spectroscopy. A possible scenario to explain this phenomenon

is a different distribution of the Au atoms on the surface. For small Au coverage and large MgO terrace sizes low temperature STM experiments on 8 ML thick MgO films have shown that Au atoms form ordered structures which is a direct consequence of a repulsive interaction between the Au atoms [24]. This results in a relatively large distance between the Au atoms. For 0.005 ML Au coverage STM investigations on an 8 ML MgO film shows that more than 90% of all pair distances are larger than 22 Å (data not shown). In the presence of Au particles the available area for the Au atoms shrinks leading to a reduction of the interatomic distance. More importantly, the lateral order of the atoms breaks down. This leads to the formation of Au atom patches and more open areas as demonstrated by the STM image shown in Fig. 6. As a consequence the interatomic distance is significantly reduced in the presence of Au clusters. It is important to note that such a configuration is kinetically controlled. The atoms repel each other (as shown previously [24]), but a configuration with a maximized distance between the Au atoms cannot be achieved in the presence of immobile particles during the low temperature deposition process.

As soon as the interatomic distance becomes smaller than about 25 Å the magnetic dipole–dipole interaction will lead to a broadening of the EPR line. Due to the cubic distance dependence of the dipole–dipole interaction the closest pair will dominate the broadening. Based on the STM data a system with 0.005 ML Au coverage and a Au–Au distance larger than 22 Å should not show dipolar broadening of the EPR line. To elucidate the distance of Au pairs necessary to account for the broadening of the spectrum, model calculations using a distance distribution of azimuthally disordered pairs of point dipoles have been performed. For the given geometry (magnetic field in the surface plane) the calculations show that a distance distribution with a lower cut off at about 17 Å is sufficient to account for the observed broadening. This would imply that the Au–Au distance has to shrink by about 5 Å.

Annealing of the low temperature deposits above 85 K allows lateral rearrangements of the atoms and relaxes the kinetically controlled configuration prepared at low temperature. In particular it should lead to an increase of the Au–Au distance due to the repulsive interaction between the atoms as shown by STM. This increase of Au–Au distance leads to a reduction of the EPR line width. It is worth noting that the line width observed after annealing remains consistently larger than the one observed for the 0.5% coverage case (6.3 G vs. 7.5 G). The observed reduction corresponds to an increase of the distance by about 2–3 Å which is easily to be accommodated in terms of the available area as seen from Fig. 6.

With respect to the Au/CO complex, DFT calculations predict a CO binding energy of 0.35 eV for an isolated CO/Au complex on the terrace of MgO [33]. This corresponds to a desorption temperature of around 130 K which is in good agreement with the IR data.

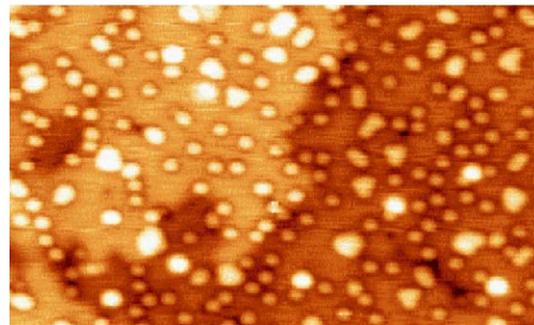


Fig. 6. Low temperature STM image ($30 \times 18 \text{ nm}^2$, 5 K) taken for about 0.005 ML nominal Au coverage on 8 ML MgO film on Ag(100).

The rather broad temperature range for the disappearance of the IR signal of at least 50 K suggests a broad desorption peak, hence, a distribution of binding energies. This can be rationalized by the size of the Au/CO complexes which are rather big entities. The size together with the electronic properties renders it likely that there are repulsive interactions between adjacent Au/CO complexes at higher coverage which lower the binding energy.

5. Conclusions

It was shown that Au atoms are preferably adsorbed on top of oxygen anions of the MgO terraces for both pristine and annealed films. The ^{17}O hyperfine interaction tensor determined here is in perfect agreement with the theoretical prediction which further corroborates the binding mechanism published earlier [17]. The amount of Au atoms drops with increasing Au coverage as expected due to the formation of Au clusters. However, the EPR line width increases significantly with increasing coverage. Significantly different line widths were found for the same amount of Au atoms. This can be understood as a reduced Au-Au distance caused by a change in Au atom distribution in the presence of Au particles.

Based on temperature dependent EPR data it is possible to show that the onset of Au atom mobility at about 80 K is considerably lower than the temperature necessary to form Au clusters. Together with the calculated barriers of diffusion it is possible to understand the reduction of the EPR line width above 80 K as a consequence of lateral rearrangements which lead to an increased Au-Au distance. Au clusters are formed above 125 K and the EPR signal disappears at 180 K. The onset of depletion for the Au-CO complex is found above 85 K. The temperature range of the depletion is rather large. Only after annealing above 150 K the IR signal of the Au-CO complexes is completely gone. The temperature dependence of the IR data is in good agreement with the calculated stability of the Au/CO complex on the MgO terrace towards CO desorption. Thus, there is no indication from the experimental data that the Au/CO complexes show an enhanced mobility as compared to bare Au atoms.

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