Chapter 2 Atomic Scale Characterization of Defects on Oxide Surfaces

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Abstract The physics and chemistry of oxide surfaces cannot be recognized without taking into account the variety of lattice defects. Defects largely govern the electronic and optical properties of oxides, they offer potential binding sites for atoms and molecules, and serve as charge centers that control the donor or acceptor character of the material. In this contribution, we demonstrate how the nature of surface defects on oxides can be probed in an ensemble but also on the level of individual defects, focusing on defects on the surface of thin, single-crystalline oxide films of MgO and CeO₂ as prototype examples for non-reducible and reducible oxides, respectively. Scanning probe techniques play a fundamental role in this respect, as they enable direct visualization of surface defects and provide insight into the electronic structure of defects and local potential modulations in their vicinity.

2.1 Introduction

Heterogeneous catalysts are often based on oxide supported metal nano particles. This is one important reason why several groups around the world have started to work on understanding the interaction of metal particles with well-ordered oxide surfaces [1–4]. Wide varieties of metals and oxide surface combinations have been studied. It has been realized that there are crucial factors influencing the interaction

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of metal nano particles with oxide surfaces [5]. The most important one is the nature, i.e. point and line defect, abundance and chemical identity of defects on such surfaces. In order to investigate defect containing surfaces, one needs to know the reference system, i.e. the defect free surface, in detail. Also, since defects are atomically small chemical entities, it is necessary to apply local probe techniques in combination with ensemble averaging spectroscopic techniques to fully treat the problem. This asks for samples, which allow us to apply such methods. One strategy to realize such an approach is to use thin oxide films grown on metal single crystals [6]. This has the pronounced advantage that the systems may be prepared in a well-ordered manner so that it is possible to know where the atoms are! We review in the following chapter our approach by concentrating on two case studies, i.e. the MgO(100) surface and its interaction with Au [7], as an example for a nonreducible support, and the $CeO_2(111)$ surface interacting with Au [8, 9] as an example where the oxide support itself may be involved in redox processes. Those case studies have been chosen because Au shows pronounced interaction with oxide substrates, and it is known that Au, dispersed into small nano particles, shows interesting structure-reactivity relations. Haruta [10] had demonstrated at the end of the eighties of the last century that Au nano particles, with diameters below 3 nm, oxidize CO into carbondioxide at temperatures below room temperature, which might become very important if one needs low temperature catalysis, as, for example, in the case of fuel cell processes. Consequently, understanding the influence of the metal oxide interfaces on the electronic properties is of key importance and may be exemplified on the basis of the two systems.

2.2 Point Defects

2.2.1 Non-reducible Oxides: MgO

2.2.1.1 Defects on MgO Surfaces—A Brief Overview

A prototypical example of a non-reducible, ionic oxide is magnesium oxide (MgO). Because of its simple geometric and electronic structure (fcc lattice, 7–8 eV band gap), MgO has been and still is a benchmark system for, both, experimental studies regarding surface/defect structure of, and adsorption on a variety of morphologically different samples, and corresponding computational investigations. For a long time it has been assumed that the surfaces of MgO microcrystals consist mainly of (100) terminated planes, which is the most stable surface termination. In the 1970s, mainly due to observations of photo-luminescence spectra which could not be interpreted in a straight forward way, Coluccia followed the terrace-step-kink approach and proposed a model for the MgO surface including a series of geometrical features of differently coordinated anions and cations [11] (Fig. 2.1a). This model has become a fundamental basis for further investigations concerning defects on the surface of MgO.



Fig. 2.1 a Model of the MgO surface according to Coluccia and Tench [11]. b Diffuse reflectance UV/Vis spectrum of nanocrystalline MgO

Early experimental studies regarding defects in MgO mainly concerned bulk defects in single crystals. In recent years, growing interest aimed at determining in more detail the nature and properties of oxide surfaces, as there is growing evidence that chemical and spectroscopic properties of surface sites depend on their local coordination. Early UV diffuse reflectance (DR) studies have shown that highly dispersed alkaline earth metal oxides have optical absorption bands which are not characteristic of pure single crystals and need, therefore, be attributed to surface features involving low coordinated ions.

A detailed analysis of the DR spectra of alkaline earth metal oxides has been undertaken by Garrone et al. [12], who satisfactorily explained the experimental results by using the approach of Levine and Mark [13], where ions located on an ideal surface are treated like bulk ions, except of their reduced Madelung constants. They suggested, that the experimentally observed absorption bands (Fig. 2.1b) correspond to electronic excitations of low coordinated surface oxygen ions: the lowest in energy for 3C, the next highest for 4C. The assignment of the two minima in reflection (maxima in absorption) which are observed in the DR spectra of MgO between 200 and 300 nm (Fig. 2.1b) to the excitation of 4 coordinated (at 225 nm) and 3 coordinated (at 270 nm) oxygen ions, respectively, is now well-established.

Furthermore, a comparison of the energies of the surface bands in the series of the alkaline earth metal oxides with those of the respective bulk exciton and bulk band gap values corroborated the assumption of the excitonic nature of the transitions, since the values of the surface bands correlate better with the bulk exciton than with the bulk band gap values. Garrone et al. were also the first who, by applying the Mollwo-Ivey relation [14], provided theoretical evidence for the mobility of the excitons. With a free exciton, the excitation travels through the crystal as a whole, whereas the excitation of a bound exciton is localized (typically at an internal point imperfection). According to the findings of Garrone et al. the mobility of excitons decreases in the series $6C \rightarrow 5C \rightarrow 4C \rightarrow 3C$. This goes along with the bonding

character of the differently coordinated states, which were assumed to become more covalent going from 6C to 3C. Therefore, it was concluded that an exciton at a 3C site is strongly localized (bound) there, whereas at higher coordinated sites (4C and 5C), an electron is transferred from the surface anion to the next nearest cation neighbors. The general trend of decreasing excitation energy for oxygen ions with lower coordination was corroborated by calculations performed by Shluger et al. [15]. In this work, the authors also considered the localization of the excited state and found good agreement with the qualitative statement given by Garrone et al. [12], i.e. excitons on 3C corner sites are strongly localized, whereas excited states at higher coordinated sites tend to be more delocalized.

Photoluminescence is a process that is ultimately connected with light absorption on MgO. The first who reported photoluminescence spectra from high surface area MgO degassed at high temperatures were Tench and Pott [16]. More detailed studies about the photoluminescence properties of powdered alkaline earth metal oxides were then reported by Coluccia et al. [17], Shvets et al. [18], Anpo et al. [19], Che et al. [20–22] and Diwald et al. [23–25].

In the case of MgO, the photoluminescence is sensitively quenched by oxygen [16], which is an indication that the light emission process is a surface phenomenon. The photoluminescence excitation bands observed for small MgO crystallites in vacuo were essentially identical with the surface absorption bands, which were measured under oxygen atmosphere [17]. Since the adsorption of oxygen does not modify the levels responsible for the absorption of light, Coluccia et al. concluded that absorption and emission of light might take place at different sites on the surface. The very complex luminescence spectra observed for the alkaline earth metal oxide samples also led to the assumption that the different spectral components are most likely the result of differences in the environment of the emission sites, such as changes of the coordination state of the neighboring ions, which renders a detailed assignment of emission sites a difficult task. A first attempt to solve this problem by quantum-mechanical calculations was given by Shluger et al. [15]. They showed, that even the second coordination sphere of the emitting sites strongly influences the luminescence energy. This result clearly demonstrates that the simple surface picture of low coordinated ions (at perfect corners and edges) for powdered MgO samples does no longer suffice. More complex surface features involving differences in the second coordination sphere of an anion need to be taken into account as well. Examples of the structures described by Shluger et al. [15] are shown in Fig. 2.2.

In the case of the *regular edge* site, the 4C oxygen ion is surrounded by two 4C and two 5C Mg ions, respectively, whereas the 4C oxygen ion at the *step edge* is surrounded by two 4C, one 5C and one 6C Mg ion. A *regular corner* oxygen ion has three 4C Mg neighbors, at the *step corner*, one of the three Mg neighbors is 6 coordinated and at the *kink corner*, all three neighbors are differently coordinated (4C, 5C and 6C, respectively).

The electronic and optical properties of such surface geometrical features are influenced also by their strong relaxation from ideal geometries. Recent quantum-chemical calculations demonstrated that the relaxation of steps and corners tends to round these features by displacing the low coordinated ions inside the surface [26, 27],



Fig. 2.2 Different geometrical features of low coordinated (LC) oxygen ions in edges (4C) and corners (3C) on MgO according to Shluger et al. [15]

leading to a redistribution of the electron density and, therefore, to differences in the ionization potentials and electron affinities of the corresponding surface sites.

Vacancies

Vacancies, especially anion vacancies, are by far the most studied defects in alkaline earth metal oxides. Historically, vacancy defects have first been studied in single crystal samples, where optical absorption bands in the UV/Vis region were observed, which are not characteristic for the bulk absorption band edge [28]. The growing interest in high surface area powdered oxides forced the study of vacancies in such samples, as they were believed to be the main chemically active surface defect. A direct spectroscopic access to vacancy defects is in most cases not possible, as their concentration is too low and/or they are spectroscopically inactive. Therefore, most experiments concerning the characterization of vacancy sites require a pretreatment of the oxide sample, which leads to the creation of vacancies or transforms existing electron traps into spectroscopically active surface species.

Anion Vacancies

Defect centers on MgO, which have been widely studied both experimentally and computationally, are the "color" or "F" centers, which are electrons trapped in an anion vacancy. Historically, the reference to the word "color" goes back to the observation of similar defects in alkali halides, giving the normally transparent crystals a specific color. A nomenclature for surface anion vacancies was introduced by A.J. Tench, on account of which they are described as F_S^{n+} centers. The subscript "S" denotes the location of the vacancy in the surface and "n+", with n = 0, 1, 2, refers to the charge of the vacancy [29]. The removal of O^{2-} results in unbalanced charge, the corresponding anion vacancy is designated as F_S^{2+} .

The removal of an O^- ion or a neutral O atom results in F_S^+ and F_S^0 centers with one or two electrons trapped in the vacancy, respectively.

From an energetic point of view, the formation of F_{s}^{0} and F_{s}^{+} vacancy defects is more favorable than the formation of the F_s^{2+} center. Calculated formation energies for anion vacancy defects on a MgO(100) surface plane range from 7 to 10 eV for the F_8^0 center, 10–13 eV for the F_8^+ center, to 30 eV for the F_8^{2+} center [30, 31]. In a classical description, the surface F centers have been located at the terrace plane [32]. However, calculations [33] and experiments [34] have shown that oxygen vacancies may be also formed on less coordinated sites like edges and corners (Fig. 2.3a). In fact, the calculated formation energies for anion vacancy defects at low coordinated sites are significantly lower than for the classical terrace center. The fact that anion vacancies, F_{s}^{2+} , at low coordinated sites also have a high electron affinity makes them likely candidates for electron trapping centers. Analvsis of the charge distribution of the paramagnetic F_s^+ center shows a strong localization of the spin density in the center of the vacancy for the 5 coordinated terrace site. Going further to step and corner vacancies, the spin density gets more diffuse inside the cavity with a significant amount also being localized at the neighboring Mg ions [26] (Fig. 2.3b). This is also reflected in the calculated hyperfine coupling constants for the neighboring ²⁵Mg ions, which increase with decreasing coordination of the Mg ions constituting the vacancy [33]. The larger electron affinity of low coordinated Mg ions is also responsible for the anomalous trend observed for the ionization potentials of differently coordinated F_8^+ centers: IP(corner) > IP(step) > IP(terrace) > IP(bulk) [33].

As an alternative to the classical single vacancy centers, the cation-anion divacancy [35–37] has been considered. Ojamäe and Pisani [36] calculated the properties of divacancies located at the (001) surface of MgO and found that the neutral divacancy is a relatively stable defect, which may be formed through the recombination of isolated cation and anion vacancies, and tends to migrate to the surface.



Fig. 2.3 a Schematic representation of F centers at various sites of the MgO surface: terrace, edge and corner (from [33]). b Spin density plot for the F_S^+ center at the corner of MgO (from [26])

The calculated electron affinity is very high suggesting that this type of defect may also serve as potential electron trap and for the formation of color centers. Going from the extended (001) surface plane to the more reactive low coordinated sites, Ricci et al. [37] calculated the electronic properties of divacancy defects located on steps, edges and corners. The electron affinities of these defects amount to about 0.6-1.1 eV, depending on the coordination of the site. The calculated ionization potentials of the trapped electron state of 1.4-2.0 eV implies that trapped electrons are strongly bound by divacancies and stable at room temperature. The location of the spin strongly depends on the electrostatic potential around the divacancy, which in turn is correlated to the coordination of the ions constituting the defect. For example, at the terrace divacancy, the trapped electron occupies the vacant oxygen site. On the other hand, at the step divacancy, the spin density is localized mainly on the 3C Mg²⁺ ion [37].

In general, the description of vacancy defect sites on the surface of MgO from experimental data only is a difficult task. The support by quantum-chemical calculations has opened new insights on the complexity of these defects and also revealed some discrepancies with the models, which were proposed from experiments. Recent calculations support the assumption that apart from classical vacancies also other local surface structures (Fig. 2.4) exhibit electron affinities, which could account for the formation of color centers [38, 39].

A detailed understanding of these surface defects is highly desirable not the least because of the suggested role of color centers as active sites in catalysis. This fact was boosted by studies, which, from a combination of indirect experimental evidence and theoretical calculations, infer the involvement of color centers for the enhanced catalytic activity of deposited metal particles [40]. Despite the debate on a possible role of color center defects in catalysis, the geometric and electronic details

	H H	Mg ²⁺	R	FR	F
	single anion vacancies	anion/cation divacancies	reverse corner	step edge	low coordinated Mg sites
calculated EA (IP) in eV	4.5-5.8 (5.6-6.6)	0.6-1.1(1.4-1.5) 3.1 (4.8)	0.7 (1.7) (3.7)	0.6-2.0 (3.7) plus O²⁻H⁺	
calculated electronic transition energy in eV	<u>5C 4C 3C</u> y 3 2.4 2.1		2.0	1.8, 2.4	2.0, 2.4 plus O ² H

Fig. 2.4 Models, calculated electron affinities [EA], ionization potentials (IP), and electronic transition energies of electron traps on the surface of MgO (single anion vacancies [41]; divacancies [37]; reverse corner and step edge [38]; LC Mg sites [39]) adapted from [189]

of surface color centers are widely discussed. In particular, the electronic properties of electron trapping sites at various surface locations (e.g., anion vacancies on a terrace, step, or corner as well as divacancies and kinks) are now accessible from calculations [27, 31, 38, 39, 41]. However, detailed experimental investigations to corroborate these results are scarce [42]. This is due to the fact that the manifold of sites located at different positions and exhibiting different charge states leads to highly convoluted signals for most spectroscopic methods, which are often difficult to disentangle.

2.2.1.2 MgO Model Surfaces

From the considerations above it is clear that insight into the properties of specific defects on MgO surfaces cannot be obtained without careful control over the morphology of the samples. To this end, a number of MgO model systems have been introduced, examples of which are presented in the following (Fig. 2.5).

The upper panel of Fig. 2.5 displays transmission electron micrographs of various MgO powder samples. MgO smoke particles (Fig. 2.5a) are perfectlyshaped, almost defect-free cubes with edge-lengths of more than 100 nm [43]. Chemical vapor deposition, on the other hand, produces high surface-area (HSA) material consisting of well-shaped MgO cubes with edge-lengths of a few nanometers (Fig. 2.5b), with a strongly enhanced fraction of edge and corner sites relative to MgO smoke particles [44, 45]. Finally, the thermal decomposition of Mg $(OH)_2$ yields aggregates of interpenetrated MgO cubes with additional structural irregularities such as inverse corners and steps (Fig. 2.5c).

Vacuum-cleaved single-crystal MgO surfaces (Fig. 2.5d) have wide terraces and a number of defects such as monolayer deep rectangular holes and string-like ad-species of unknown origin that are formed during the cleaving process [46, 47]. Alternatively, single-crystalline MgO thin films can be grown on metallic substrates, which allow electron spectroscopies and scanning tunneling microscopy to be routinely applied for surface characterization.

Extensive investigations into the growth and properties of MgO thin films started around 25 years ago with reports from Goodman's group on MgO(001)/Mo(001) samples [48]. Detailed investigations into the structural and electronic properties of MgO films grown on Mo(001) from the ultrathin regime up to thick layers have later been undertaken by our group in cooperation with Valeri's group [49, 50]. In particular in the ultrathin regime, the MgO growth on Mo(001) is significantly affected by the Mo(001) substrate. The rather large lattice mismatch between Mo (001) and MgO(001) (5.3 %) leads to the formation of a dislocation network. We will discuss the properties of the dislocation network and its role in electron trapping further below (Sect. 2.3.2). In terms of lattice mismatch, Ag(001) is a more suitable substrate than Mo(001) and first studies of the growth mode have been reported by Wollschläger et al. [51]. First scanning tunneling microscopy (STM) data from surfaces of ultrathin MgO(001)/Ag(001) thin films were reported by Schintke et al., which demonstrated that large MgO(001) islands with a low density



Fig. 2.5 MgO model systems. *Upper panel* Transmission electron micrographs of MgO particles: **a** MgO smoke [57]; **b** CVD-MgO [45]; **c** MgO prepared by thermal decomposition of Mg(OH)₂ [57]. *Middle panel* Single-crystalline MgO(100) surfaces: **d** AFM image of the surface of vacuumcleaved MgO [46]; **e** room-temperature STM image of 15 ML MgO(100)/Mo(100) thin film (+4 V, 0.15 nA) [49]; **f** low-temperature STM image of 4 ML MgO(100)/Ag(100) (+3.5 V, 0.2 nA). *Lower panel* **g** Atomic resolution STM images of a regular terrace (*left*; +0.02 V, 3 nA), a regular step (*middle*; large scale image: +3.5 V, 0.2 nA; atomic resolution image: +1.2 V, 0.15 nA) and an irregular step (*right*; large scale image: +3.5 V, 25 pA; atomic resolution image: +0.1 V, 25 pA) taken from a 4 ML MgO(100)/Ag(100) sample [53]

of defects grow on the Ag(001) surface [52]. Examples of STM images from a 15 ML MgO(100)/Mo(100) and 4 ML MgO(001)/Ag(001) thin film are shown in Fig. 2.5e and f, respectively. These images show that terrace sizes on MgO thin films are in general significantly smaller (20–40 nm) than on cleaved single-crystals and the fraction of low-coordinated sites (steps) is correspondingly larger. Examples of atomic resolution STM images of the surface of 4 ML MgO(001)/Ag(001) films are

shown in Fig. 2.5g. In general, only one ionic sublattice of MgO can be resolved in STM, as shown in the left panel of Fig. 2.5g, which displays atomic resolution obtained on a regular (100) terrace and the corresponding model of the atomic arrangement of the ions. The middle and right panel of Fig. 2.5g shows large scale and atomic resolution images of regular and irregular step features observed on these surfaces [53]. As expected, the most common step direction is the lowest energy MgO [100] direction. On the irregular steps, a large fraction of kink sites is seen. Recently, the possibility of controlling the shape and size, and thus the defectivity of MgO islands on Ag(001) by variation of the growth conditions has been demonstrated [54].

2.2.1.3 Adsorption on Low-Coordinated Sites

Mg²⁺-CO Interaction

The various geometries of the model systems presented in the previous chapter represent an ideal playground for studying the adsorption properties of different surface morphologies, in particular the different bonding of molecules to terrace and low-coordinated sites. Studies of carbon monoxide adsorption on MgO turned out to be ideal in this respect, both for experiment and for theory. Early infrared spectros-copy studies related to CO adsorption on HSA MgO powder at room temperature have shown that both, the strongly basic low-coordinated oxygen anion sites and the acidic magnesium cation sites interact with CO [55, 56]. The formation of polymeric species upon interaction of CO with the oxide anions is rather complex and shall not be further discussed here. Instead, we focus on the properties of CO adsorbed to cation sites, which is characterized by a rather weak interaction and requires low sample temperatures to be studied, but allows, according to distinct CO frequency shifts and interaction strengths, Mg sites of different coordination to be distinguished [57].

A comparison of infrared spectra from different MgO substrates taken at saturation coverage of CO at low temperature is shown in Fig. 2.6a. Nearly identical IR spectra consisting of three sharp IR bands at 2151, 2137, and 2132 cm⁻¹, respectively, are observed in the case of CO adsorption on cleaved single-crystal [58] and on the MgO smoke particles [59], resembling the similar surface morphologies of these model systems (Fig. 2.5a, d) [57, 59]. According to low-energy electron diffraction and helium atom scattering studies [60, 61], which both indicated the formation of a well-ordered $c(4 \times 2)$ CO overlayer on extended MgO(100) surfaces, and polarization dependent IR studies on MgO single-crystals [58], the bands have been assigned to perpendicularly oriented CO molecules adsorbed on regular terrace sites (2,151 cm⁻¹), and the in-phase (2,737 cm⁻¹) and out-of-phase (2,732 cm⁻¹) vibrational excitation of tilted CO in the ordered overlayer.

Significant broadening of the IR bands is evident from the corresponding IR spectrum of CO adsorbed on the high-surface area powder sample. In particular, a clear shoulder is seen at the high-frequency side of the main band, which can be assigned to CO adsorption on low-coordinated Mg^{2+} sites [56]. A similar shoulder appears also in the IR spectrum taken from CO adsorbed on the surface of MgO thin films [62]. The appearance of the high-frequency shoulder on HSA and MgO



Fig. 2.6 a Infrared spectra of CO adsorbed at low temperature on a MgO(100) single-crystal surface [58], MgO smoke [57], high surface area (HSA) MgO powder [57], MgO(100)/Mo(100) thin film surface [62]. **b** Determination of the heat of adsorption of CO on MgO powder samples from the dependence of $\ln(K_{ads})$ on 1/T for CO adsorbed on Mg²⁺ step and terrace sites [57]. **c** Temperature-programmed desorption traces for CO adsorbed at 30 K on pristine and annealed (1,200 K) MgO(100)/Mo(100) thin film surfaces [66]. **d** CO desorption energy E_{des} as a function of CO coverage on MgO thin films determined from TPD data by inversion of the Wigner-Polanyi equation. Data for CO on terrace sites from [65], for steps from [62]

thin film samples is consistent with the higher abundance of low coordinated sites on HSA compared to MgO smoke, and MgO thin films compared to cleaved MgO single-crystal samples. CO coverage-dependent IR studies reveal shifts of the CO stretching frequency with CO coverage (not shown), which are the result of dipolar interaction between the adsorbed CO oscillators [63]. It should also be mentioned that another high-frequency CO vibration has been detected on HSA-MgO samples at ~2,200 cm⁻¹, which has been assigned to CO adsorbed on the lowest-coordinated Mg corner sites, $Mg^{2+}(3C)$ [56].

Zecchina et al. determined the enthalpy of adsorption from optical isobars for CO on 5C terrace and 4C edge sites (Fig. 2.6b) of MgO powder samples and obtained values of 12.5 kJ/mol (5C) and 22.6 kJ/mol (4C) [57, 59]. The value for 5C sites is in good agreement with desorption energies derived from CO-TPD studies of vacuumcleaved MgO single-crystals, where CO was found to desorb in a single peak at 57 K, yielding $E_{des} = 15.2$ kJ/mol by using the Redhead analysis [64]. Different to MgO (100) single-crystals, the CO-TPD data for as-deposited MgO(100)/Mo(100) thin films exhibit two distinct desorption maxima of almost equal intensity at 52 and 68 K, and further desorption signals extending up to $\sim 100 \text{ K}$ [62, 65–67], suggesting a high abundance of low-coordinated sites on the surface (Fig. 2.6c). A CO-TPD taken after annealing to 1,200 K shows that the high-temperature desorption signals can be significantly reduced by thermal ordering of the thin film surface [66], providing support for the assignment of these desorption features to more strongly bound CO on low-coordinated sites. An analysis of the desorption energy of CO on MgO(100) thin film surfaces based on inversion of the Wigner-Polanyi equation is presented in Fig. 2.6d [65]. The data were taken for CO dosed at different substrate temperature, which allows, according to the TPD data, the contribution of terrace sites and lowcoordinated step sites to be separated. In the case of CO adsorbed on terrace sites (data taken from [65]), E_{des} is 17 kJ/mol in the limit of monolayer saturation (0.8 ML) coverage. E_{des} increases linearly with decreasing CO coverage due to decreasing lateral interactions within the adsorbed layer, and can be estimated by linear extrapolation to be 20 kJ/mol in the limit of zero coverage. Similarly, a strong coverage dependence of E_{des} is seen for CO on step sites, ranging between 20 kJ/mol at high CO coverage, and 25 kJ/mol in the limit of zero CO coverage (data taken from [62]).

The experimental results presented in Fig. 2.6 clearly indicate that CO adsorption studies allow the properties of samples with different surface morphologies surface science model systems as well as powders with different morphological characteristics—to be compared with each other. The values obtained for desorption/adsorption energies and CO vibrational shifts for the various samples are comparable in absolute terms and represent, therefore, benchmarks for computational studies addressing this weakly interacting adsorption system.

It is not the purpose of this chapter to provide a review of the various computational approaches used to model CO interaction with MgO surfaces and we refer, therefore, to previous review papers [68, 69]. In short, it is now well-established that CO binds with the carbon end down to the surface Mg cations and that the bonding is to a large extent dominated by electrostatic interactions. The stronger bonding to low-coordinated sites was shown to result from the larger electrostatic field generated at these sites, which, in addition to a contribution from the "walleffect", is also responsible for the blue-shift of the CO vibrational frequency compared to the CO gas-phase value. Recently, interest in computational modeling of CO adsorption on the MgO surface has found a new impetus with the advent of methodologies aiming to correctly account for dispersion interactions with density functional methods [69–71].

Metal Nucleation at MgO Step Sites

Steps are the most obvious defect sites on MgO(100) single-crystal surfaces and their importance, not only in the adsorption of molecules as shown above, but also as nucleation sites for metal nanoparticles on MgO(100), is well-documented. For example, TEM and AFM investigations of Pd deposition on MgO(100) surfaces of cleaved single-crystals have shown that steps are preferentially decorated with Pd particles in the initial stages of nucleation and growth [72-74]. This behavior is in line with the calculated higher adsorption and adhesion energy of Pd adsorbed on low-coordinated step and corner sites compared to those adsorbed on regular terraces [75]. An example that demonstrates the diffusion of Pd to, and preferential nucleation of Pd at step sites of MgO thin film samples is presented in Fig. 2.7. Figure 2.7a displays a low-temperature STM image obtained from the surface of a MgO(100)/Ag(100) thin film, onto which Pd has been deposited at a substrate temperature of 5 K [76]. This temperature is low enough to prevent diffusion of Pd on the surface such that the majority of the features seen in this image can be assigned to single Pd atoms randomly distributed on the MgO(100) terraces, and only a small fraction forms aggregates, seen as the brighter spots. This sample has subsequently been warmed to room temperature to activate diffusion of Pd atoms (Fig. 2.7b). An STM image taken afterwards shows a significantly reduced number density of bright features, indicative of Pd cluster formation, and the preferential location of the clusters at the step edges (A number of Pd clusters remain on the terrace sites and most probably nucleated at defects on the terraces).



Fig. 2.7 Low-temperature STM images of a MgO(100)/Ag(100) thin film surface with deposited Pd. **a** Pd atoms imaged directly after deposition at 5 K (30 nm x 24 nm, +0.3 V, 0.01 nA). **b** Pd clusters formed by warming the surface to room temperature (30 nm x 24 nm, +1.0 V, 0.01 nA). **c** Pd atom and MgO defect at a step (9.8 nm x 5.3 nm, +1.0 V, 0.01 nA). **d**-**e** Detail of the Pd atom and the defect before and after trapping of the Pd atom at the defect (3.7 nm x 2.7 nm, +0.2 V, 0.01 nA) [77]

The step edges on the surface of MgO thin films are only in rare cases absolute perfect MgO(100) steps, but may exhibit a number of defects such as kinks (see above), or vacancy sites, which could act as even deeper traps for deposited metal atoms than regular step sites. The STM images in the lower panel of Fig. 2.7 serve to illustrate the strong attractive potential of defects on a step. Figure 2.7c, d display a large scale STM image and a close-up, respectively, of a surface region of a MgO (100)/Ag(100) thin film, where a single Pd atom attached to a step is located close to a step defect. By application of a bias voltage larger than the imaging bias voltage the Pd atom was activated to move and spontaneously got trapped at the defect (Fig. 2.7e). Further attempts to manipulate the Pd atom at the defect site led only to a slight modification of the Pd atoms' location at the defect, but the Pd atom could not be pulled back out of the defect (Fig. 2.7f), which suggests the formation of a very strong bond between the defect and the Pd atom [77]. Although the exact structure of the defect cannot be straightforwardly determined from the STM images, this example demonstrates the outstanding role of surface irregularities for the nucleation of metals on MgO surfaces.

2.2.1.4 Identification of Color Centers on MgO Thin Films

The formation of trapped electron states (color centers) on the surface of MgO powders using ionizing radiation has been known for a long time. First reports providing indication for the formation of color centers on the MgO(100) singlecrystal surface appeared in the early 1980s, when Henrich and coworkers identified a low-energy excitation at ~ 2.3 eV in electron energy loss spectra of electronbombarded MgO(100), which could be quenched by adsorption of oxygen [78]. Later, an electronic excitation with a transition energy of 1.15 eV was detected on thermally activated MgO(100)/Mo(100) thin films and assigned to surface color centers [79]. A band-gap state located about 2 eV above the top of the valence band of electron bombarded MgO(100)/Mo(100) thin film as detected with metastable impact electron spectroscopy and ultraviolet photoelectron spectroscopy has been attributed to the electronic ground state of color centers [80]. A more detailed experimental study of the electronic excitations of color centers created by electron bombardment was reported by Pfnür et al. for MgO(100)/Ag(100) thin films [81], which showed generally good agreement with the optical transitions of color centers formed on MgO powders and corresponding calculated transition energies for defects located at steps and terraces [34, 82]. In order to discriminate between electronic transitions resulting from defects located at steps and terraces, Pfnür et al. compared EELS spectra of electron-bombarded MgO films grown on Ag(100) and Ag(1,1,19), which provide surfaces with different step densities [42, 81]. Sterrer et al. concluded from angular dependent ESR measurements of electron-bombarded MgO(100)/Mo(100) thin films that the paramagnetic F_{s}^{+} centers are preferably formed on step sites [83].

A combination of microscopic and spectroscopic information, which is accessible with scanning tunneling microscopy (STM) [84] and atomic force microscopy

(AFM) [85], has the potential to reveal differences in the properties of color centers located at different sites on the MgO surface on a local scale. According to theory, the electronic ground state of color centers containing one (F_S^+) or two (F_S^0) trapped electrons is located within the band-gap region of MgO, close to the valence band on-set [26]. This opens the possibility for selective imaging of color center states by a proper choice of the bias voltage in STM on MgO thin films [84, 86].

Figure 2.8a shows an STM image of a 4 ML MgO(001)/Ag(001) thin film sample taken at a sample bias voltage of +3.5 V, corresponding to electron tunneling from the tip into the conduction band states of MgO, which provides an image of the overall morphology of the MgO surface. The very same surface was subsequently imaged at a bias voltage of -3.5 V, which corresponds to an energy within the band-gap of MgO, close to the valence band onset (see below). In addition to the general morphological features of the MgO islands, some bright spots located at the step edges of the islands can be seen in this image, indicating the presence of localized defect states within the band gap of MgO. The local electric field between the STM tip and the sample is sufficiently large to mediate surface charging, as demonstrated by Fig. 2.8b, c, which present STM images from the same surface area obtained after repeated scanning at high bias voltages, where the successive generation and stabilization of defects on the island edges can clearly be seen [84].

Two types of defects can be distinguished in the STM images shown in Fig. 2.8b–d: rather dim and pointlike states (Type 1), and large bright protrusions (Type 2). Moreover, both types of defects can be stabilized on the very same surface location (indicated by arrows in Fig. 2.8c, d), which suggests that the two different defect appearances are caused by different charge states of one and the same defect, as expected for F centers.

Detailed information about the electronic states of the defects and the sitespecific electronic structure could be obtained by employing tunneling spectroscopic [84] measurements. Figure 2.8e shows constant-current and corresponding conductance images taken at different bias voltages from the edge of an MgO island where Type 1 defects were formed. In constant current mode, the integral density of states from the Fermi level ($E_F = 0$ V) to the selected bias voltage (V_S) contributes to the image, whereas, in the differential conductance mode (dI/dV_S) , the local density of states at the particular energy is imaged. The maximum conductance of different defects clearly depends on the applied bias voltage, being lowest for the defects located on the left-hand step edge (-2.5 V, defect 1) and highest for the step corner (-3.2 V, defect 4). The tunneling spectra (Fig. 2.8f) of the individual defects are in perfect agreement with the conductance images, exhibiting peaks between -2.5 and -3.2 V with respect to the Fermi level. Additionally, the spectra provide information about the location of the defect energy levels within the band gap (the onset of the valence band is at about 4.5 eV below $E_{\rm F}$ and the onset of the conduction band at about +2.5 eV above E_F). The energy levels of Type 1 defects are located about 1-2 eV above the valence band of MgO. Their position depends on the location of the defect on the surface and shifts toward the valence band when going from the edge (higher coordinated) to the corner (lower coordinated) site.



Fig. 2.8 a STM images $(25 \times 25 \text{ nm}^2)$ of a MgO island on 4 ML MgO(001)/Ag(001) imaged at $V_S = +3.5 \text{ V}$, **b** $V_S = -3.5 \text{ V}$; **c** and **d** images taken at $V_S = -3.5 \text{ V}$, after subsequent scanning at high positive bias voltages; a Type 1 and Type 2 defect located at the same surface site is indicated by *arrows*. **e** Constant current and conductance images of Type 1 defects located on the edges of a MgO island at different V_S (image size: $5 \text{ nm} \times 5 \text{ nm}$). **f** dz/d V_S spectra taken at the defects (*1*-4) indicated in (**e**). **g** dz/d V_S spectrum of a Type 2 defect. From [84]

A typical tunneling spectrum of a Type 2 defect is shown in Fig. 2.8g. In contrast to the results in Fig. 2.8f, two peaks are observed within the band gap of MgO, at around -1 and +1 V. The peak at negative bias voltage originates from tunneling out of occupied defect states and is located in the middle between the valence band and the conduction band, and higher in energy than the corresponding filled state of the Type 1 defects.

A qualitative comparison of the experimental data with the calculated groundstate energy levels of F_S^+ and F_S^0 centers on MgO shows very good agreement, both with respect to the energies of defects exhibiting different charge states, and with respect to the variation of the position of the defect energy levels as a function of local coordination [84]. Therefore, Type 1 defects were assigned to F_s^+ centers, while Type 2 defects show characteristics typical of F_s^{0} centers [84]. The same defects were identified on surfaces of electron-bombarded MgO(100)/Ag(100) films [87].

Some concerns have been raised as to what extent the metallic substrate underneath the thin oxide film could influence the charge state of the defects, since the Fermi energy of the Ag substrate is located above the defect levels. This could lead to spontaneous electron donation into the traps. A discussion about this topic including detailed computational results can be found in [88, 89].

2.2.1.5 Interaction of Gold with Color Centers

The identification of color centers on the surface of thin MgO films based on ESR spectroscopy and scanning tunneling microscopy opened the door for studies of another topic of relevance—their interaction with metal atoms and clusters. Numerous computational studies pointed out the relevance of F centers in metal nucleation on MgO surfaces, where the adsorption energies of metals were found to be on the order of 2–4 times larger than on regular surfaces sites (e.g. [90–94]). Experimentally, direct proof for the enhanced interaction was provided in a non-contact AFM study on MgO thin films, where the interaction energy between the metallic AFM tip and the F^0 defect was found to be more than four times larger as compared to the interaction of the tip with the regular surface [95].

As an example, Fig. 2.9 shows results of calculations addressing the bonding of Au atoms on regular O^{2-} surface sites, and F_S^0 and F_S^+ centers, respectively, displaying the structure (a) and the charge density difference maps (b) [92]. Bonding of gold to the regular sites is dominated by intraunit polarization with only little contributions of covalent bonding. Correspondingly, the interaction is weak and the calculated adsorption energy is ~80 kJ/mol. The adsorption of gold atoms on F_S^+ and F_S^0 centers leads to the formation of a strong covalent bond between Au and the defects with adsorption energies 3–4 times larger than for gold adsorbed on O^{2-} terrace sites, and significant charge transfer from the defects into the gold atoms. Notably, the bonding of Au to F_S^+ is stronger than to F_S^0 because of the coupling of the unpaired electron in the vacancy with the single 6s valence electron of Au, which leads to accumulation of charge between the Au atom and the vacancy. As a consequence of the closed-shell nature of the Au- F_S^+ system, the energy gain for the formation of Au dimers at these sites is small, which suggests that F_S^+ defects are, in contrast to F_S^0 centers, not likely nucleation sites for gold on the MgO surface [92].

By a combination of STM experiments, ESR spectroscopy and IRAS measurements using CO as a probe for the charge state of Au, the preferential nucleation of gold atoms on color centers and the charge transfer from the defects into adsorbed gold could unambiguously be verified [96]. The experimental results are presented in Fig. 2.10. The top STM image in Fig. 2.10a displays the surface of a 4 ML MgO (100)/Ag(100) film, which has been electron-bombarded to create color centers. At the selected imaging bias voltage (-3.0 V), F_S^+ (dim spots) and F_S^0 (bright protusions) defects can be identified according to their distinct appearance and electronic





structure as shown above [84]. Upon deposition of gold, Au atoms are found on the terraces of the MgO film (Fig. 2.10a, bottom; bias voltage: +1.3 V). In addition, some larger clusters exhibiting an internal structure (see inset), which is attributed to delocalized states within the Au clusters [97], are formed. These larger clusters are not formed when Au is deposited on pristine (defect-free) MgO thin film surfaces [98], which suggests that they arise from nucleation of gold at F center defects, most probably at F_S^{0} . The STM image in Fig. 2.10a, bottom, provides, however, no direct evidence for Au- F_S^+ adsorption complexes. This is most probably related to the fact that the corresponding electronic state is located deep in the band gap of MgO and, therefore, not accessible at the imaging bias voltage of +1.3 V.

Evidence that F_S^+ centers are preferred adsorption sites for gold atoms comes from the ESR data shown in Fig. 2.10b. The topmost spectrum is the ESR signal corresponding to the paramagnetic F_S^+ centers created on MgO(100)/Mo(100) films by electron bombardment [83]. Stepwise deposition of gold results in quenching of the F_S^+ signal, showing that Au atoms adsorb on the defects, and finally, when almost all defects have been consumed, the appearance of the ESR signal characteristic of single neutral Au atoms [99].



Fig. 2.10 a Low-temperature STM images (30 nm \times 30 nm) of electron-bombarded MgO(100)/Ag (100) (*top*, -3.0 V, 0.008 nA) and after subsequent deposition of Au atoms at 5 K (*bottom*, +1.3 V, 0.017 nA). **b** From *top* to *bottom*: electron spin resonance spectra of F_s^+ centers created by electron bombardment on MgO(100)/Mo(100) thin films, and after subsequent deposition of Au at 30 K, which results in the quenching of the F_s^+ signal and the appearance of an ESR signal of Au atoms. **c** IRAS spectra of CO adsorbed on large, neutral Au particles (*top*) and on negatively charged Au particles obtained by deposition of Au on MgO(001) films containing color center defects. From [96, 101]

The STM and ESR results have provided relevant new experimental information about the preferential adsorption of gold on F_S centers on the MgO(001) surface. However, an important piece of information, namely whether or not charge is transferred from the defects into Au, cannot be deduced from those results. The strong dependence of the stretching frequency of CO on the charge state of gold [100] should, however, allow us to directly confirm charge transfer by infrared spectroscopy. Indeed, the infrared data presented in Fig. 2.10c shows that the stretching frequency of CO adsorbed on gold nucleated at color centers is significantly red-shifted (due to CO adsorption on negatively charged Au) compared to that of CO adsorbed on Au nucleated on the regular MgO surface [96]. The topmost spectrum in Fig. 2.10c was obtained from large, neutral Au particles. The stretching frequency of CO adsorbed on these particles is $v(CO) = 2,100 \text{ cm}^{-1}$. Depending on the number of defects created and the Au coverage, CO bands extending from $2,080 \text{ cm}^{-1}$ down to $1,923 \text{ cm}^{-1}$ were observed (lower three spectra in Fig. 2.10c) [96, 101]. The broad variation of v(CO) on the defective MgO surface simply reflects the broad size distribution of Au clusters and particles formed on top of the color centers and the corresponding distribution of the charge (in larger clusters the charge is distributed over more atoms, hence the shift of v(CO) is smaller). The sharp band at 1,923 cm⁻¹ seen in the bottom spectrum of Fig. 2.10c can, in agreement with calculations, be assigned to CO adsorbed on a single, negatively charged Au atom at a color center [101]. Note that the IR signal characteristic of neutral Au atoms $(1,852 \text{ cm}^{-1} \text{ [101]})$ can only be observed on a surface with low defect density (bottom spectrum in Fig. 2.10c), underlining the strong attraction of Au atoms to, and their preferred nucleation at color center defects.

2.2.2 Reducible Oxides

The properties of non-reducible oxides, in particular MgO, have been in the focus of the preceding sections. This class of materials is typically characterized by a large band-gap and a simple electronic structure, consisting of an empty conduction band governed by the metal *sp*-states and a valence band dominated by the filled O 2p orbitals of oxygen. The dominant point defects in these oxides are oxygen vacancies that appear in the form of color centers and are able to trap zero, one or two electrons. Most non-reducible oxides are chemically inert, and adsorption energies for simple molecules and metal adatoms are well below 1.0 eV. Stronger binding only occurs to defects in the oxide surface, where the interaction energy may exceed 3.0 V and adsorption is often accompanied by charge-transfer processes.

The second group of materials discussed in this chapter is the one of the reducible oxides that comprises either a transition or rare-earth metal in combination with oxygen [102]. The main difference to non-reducible oxides lies in the chemical variability of the oxide cations that may bind the oxygen anions in different geometries and can thus adopt more than one charge state [103]. Moreover, while ionic binding dominates in non-reducible materials, a covalent interaction between cations and anions is more common in reducible oxides. The fundamental reason for the different behavior of reducible oxides is the thermodynamic stability of transition and rare-earth metal ions in various oxidation states, which reflects the efficient internal screening of their *d* and *f* orbitals [104]. As a consequence, most transition and rare earth metals are able to form numerous oxide phases, with manganese (five compounds from MnO to Mn_2O_7), [105, 106] vanadium (four compounds from VO to V_2O_5) [103, 107, 108] and cerium (two phases from Ce₂O₃ to CeO₂) being typical examples [109, 110]. Not surprisingly, the number of understoichiometric and specific surface phases is even higher for the reducible oxides.

The different chemical nature of reducible oxides becomes evident also from their defect landscape. As for non-reducible oxides, oxygen vacancies are the dominant defect type, which occur however in a distinctively different manifestation [104]. While in non-reducible oxides, electrons that remain in the lattice upon oxygen removal get trapped in the vacancy site, they tend to move to adjacent cations in the case of reducible materials. As a consequence, two cations of lower oxidation state emerge for each O defect introduced in the lattice, for example two Ti⁴⁺ ions transform into Ti³⁺ species when an O atom leaves a TiO₂ surface. The deviating electron-localization behavior has a major impact on the chemistry of reducible oxides [111, 112]. Reducible oxides are characterized by formation energies for O vacancies that are lower than for non-reducible oxides, as concomitant excess electrons are readily stored in adjacent cations at low energy costs [113]. Moreover, those electrons are easily released from the lattice again, which enables facile re-oxidation in the presence of O₂ and makes reducible oxides to an ideal oxygen-buffer in chemical reactions.

2.2.2.1 Characterization of O-Vacancies in CeO₂(111) Films

The archetypical reducible oxide is ceria (CeO₂). It features an exceptionally low formation energy for O vacancies, hence a particularly high reducibility. Consequently, ceria is widely used as support in heterogeneous catalysis, e.g. for the watergas-shift and NO_x reduction and the oxidation of methanol [114–116]. In the following chapter, we will demonstrate how non-local (XPS) and local techniques (STM conductance spectroscopy) can be combined to explore the properties O vacancies in ceria, providing general insight into reduction pathways in reducible oxides.

On the non-local scale, the reduction of ceria can be conveniently followed with photoelectron spectroscopy (PES) [117]. Here, the gradual filling of the Ce 4f states just below the Fermi level and the characteristic shifts of the Ce 3d core levels are the typical signatures of a subsequent reduction [118]. Whereas valence-band spectroscopy directly visualizes the effect of electron localization in the formally empty 4f band, the evaluation of shifts in the Ce 3d levels is more complex. Early interpretations assigned the evolution in the Ce 3d state manifold to the formation of mixed valence Ce-O states upon oxide reduction. In later experiments, different final states after the photo-excitation were made responsible for shifts of the 3d states, and especially the occupancy of the 4f states was found to induce different screening scenarios of the core hole [119]. Although PES provides quantitative insight into the number of Ce³⁺ ions in the ceria lattice, hence on the global reduction state of the oxide, no insight into the spatial distribution of the associated O defects and the localization of the extra electrons can be obtained.

Such information may be generated, however, with scanning tunneling and atomic force microscopy [120, 121]. Individual O vacancies were visualized by Esch and coworkers on the surface of bulk ceria, employing high-temperature STM in order to enhance the intrinsic conductivity of the material [122]. The authors were able to distinguish between surface and sub-surface O vacancies, exploiting the contrast-fingerprint predicted by DFT calculations. At higher degrees of reduction, also vacancy clusters with characteristic 1D shapes were found on the surface. These cluster geometries were rationalized by the energetic preference to localize the Ce³⁺ ions along the vacancy edges instead of incorporating them into the unperturbed CeO₂ lattice [123]. Ceria single crystals of higher reduction states were investigated with AFM in the Reichling group [124]. The experiments revealed a number of well-ordered arrangements of O defects, with a 2 × 2 superstructure of subsurface vacancies being the most stable one. This unexpected ordering phenomenon was explained later as a strain effects, triggered by the Ce³⁺ ions. In addition to the 2×2 configuration, other superstructures have been predicted by theory [125].

Despite a large number of well-resolved STM and AFM images of CeO_2 surfaces and interfaces [122, 124, 126, 127], the fundamental question of electron localization in the vicinity of an O vacancy remained unsolved. Whereas first theoretical studies indicated electron transfer from the vacancy site to adjacent Ce cations [104, 128, 129], more sophisticated calculations performed with hybrid-functional DFT approaches suggested a slight preference for more distant Ce ions to act as electron acceptors [123, 130]. In ceria nano-clusters, the Ce³⁺ ions were even

found to develop exclusively at low-coordinated edge sites, even if the corresponding O vacancy was far away [131, 132].

An unambiguous answer to the problem of electron localization became possible only after identifying the Ce³⁺ ions directly in the lattice via their distinct spectral signature in STM conductance spectroscopy. The issue of insufficient conductivity of bulk CeO₂ was overcome in those studies by growing the oxide in the form of thin films of five to eight trilayer thickness on Ru(0001) supports [133, 134]. After annealing to 1,000 K in O₂, the films developed a sharp, hexagonal LEED pattern, indicative for a CeO₂(111) termination. The film morphology, as seen in STM, was governed by atomically flat terraces of triangular/hexagonal shape and more than 50 nm diameter (Fig. 2.11a).

Well-resolved STM images were acquired mainly at positive sample bias, when the unoccupied Ce⁴⁺ states are responsible for the image contrast [135]. At negative bias, the filled O 2p orbitals provided most of the initial states for tunneling, however atomic resolution was more difficult to obtain due to the low hole-mobility of ceria at low temperature. Point defects have been generated in the film, either by annealing to high temperature or by bombarding the surface with energetic electrons. Hereby, tempering in an O₂ ambience was used to produce subsurface vacancies (V_{sub}) that appeared as trifoliate depression in empty-state STM images (Fig. 2.11b) [135, 136]. The image contrast arises from changes in the empty state-density of nearby Ce ions due to the missing O ion in the third layer. In corresponding AFM images, three maxima with a mutual distance of two lattice parameters (7.6 Å) were detected instead, a contrast that originates from a slight outward relaxation of the surface oxygen ions above the O vacancy [124]. Surface defects (V_{surf}), on the other hand, were produced via vacuum annealing to 900–1,000 K, or alternatively via nonthermal routes such as electron bombardment [135]. The V_{surf} defects show up as



Fig. 2.11 a STM topographic image of a crystalline CeO₂ film grown on Ru(0001) (3.1 V, 12×12 nm²). **b**-e Zoom-in STM images showing a subsurface O vacancy (**b**), a surface O vacancy imaged at negative sample bias (-2.2 V, filled states, **c**) and two surface vacancies at positive bias (+1.2 V, empty states, **d**, **e**) (3 × 3 nm²). The subsurface defect appears as tri-foliated depression at positive bias, but is invisible in negative-bias STM images. The surface defect shows up as a plain depression at negative bias and as a double or triple protrusion at positive bias, respectively. All images were taken with 0.01 nA setpoint current

simple holes in negative-bias STM or AFM images, reflecting the missing surface atom (Fig. 2.11c). In empty-state STM images that are more sensitive to the Ce 4*f* states, paired or tripled protrusions with ~0.4 Å apparent height were found (Fig. 2.11b, c). This rather surprising contrast was explained with the spill-out of the 4*f* orbitals of Ce⁴⁺ ions next to the vacancy, and will be explained in detail later in this chapter [135].

As long as the CeO₂ films are stoichiometric, only the CeO₂ band gap, extending from the valence band onset at -2.3 V to the conduction band at +3.3 V (Fig. 2.12) appears in the STM conductance spectra. The measured gap size closely matches the ceria bulk value of 6.0 eV. An extra dI/dV peak at \sim 2.3 eV marks the unoccupied Ce 4f band inside the gap region. The width of this band was found to rise from 0.2 to 0.6 V with increasing film thickness (Fig. 2.12b) [136]. These different values reflect the structural inhomogeneity experienced by the 4f orbitals in the ceria films. Whereas in thin films, essentially all Ce^{4+} ions are close to the surface, the cationic species may be localized at the metal-oxide interface, in the interior or in the surface region of thicker films. In oxygen-deficient CeO₂, additional peaks could be detected in the occupied region of the oxide band gap (Fig. 2.12a) [135]. These extra states emerged at about -1.5 V and were always detected in the vicinity to O defects or other structural in-homogeneities (e.g. step edges) in the surface [136]. Moreover, the signal intensity and shape varied with the nature of the defect and the precise positioning of the tip. While surface O defects that appeared as triple-protrusions in the topographic images always showed a single peak at -1.3 V (Fig. 2.12a, Spec. 2), the paired protrusions were characterized by a double peak with maxima at -1.1 and -1.5 V (Fig. 2.12a, Spec. 1). In both cases, the empty-state spectrum of the defect was found to be identical to the one of the stoichiometric oxide regions.



Fig. 2.12 a Filled-state STM conductance spectra (setpoint +1.0 V, 0.005 nA) taken on a stoichiometric CeO₂(111) region (*bottom*) and above different O defects, as displayed in the *inset* (*top curves*). **b** Corresponding empty-state spectra taken on films of different thickness (setpoint +3.5 V, 0.005 nA). While only the valence and conduction band onsets as well as the empty Ce 4*f* band are detectable on defect-free oxide regions, occupied defect states are seen in the vicinity of O vacancy sites

The high spatial localization and the energy position of the gap states suggest a correlation to the filled 4f orbitals that develop in the Ce^{3+} ions upon ceria reduction. This assignment is supported by earlier EELS and PES measurements that found occupied states of similar energy (-1.5 V) in reduced ceria [109, 110, 116, 117]. Further verification came from DFT+U calculations performed in the Sauer group at the Humboldt University in Berlin [135]. In favorable binding geometries of surface O defect and associated Ce^{3+} ion-pair, a defect state emerged below the Fermi energy, indicating electron transfer from the defect position to a split-off state of the 4f band of the respective Ce ion (Fig. 2.13). Interestingly, mainly those configurations in which the two Ce³⁺ ions are somewhat displaced from the vacancy site turned out to be energetically preferred [123]. The lowest defect formation energy $(2.26 \text{ eV} \text{ as calculated with respect to } \frac{1}{2} O_2)$ was revealed when both Ce³⁺ ions sit in the 2nd coordination shell of the defect and are 7.6 Å apart [9]. When moving one Ce^{3+} to the 1st coordination shell, the formation energy rises by 160 meV if both Ce^{3+} ⁺ ions are opposite to each other and by 230 meV if they locate on neighboring sites (Fig. 2.13). All other configurations have even higher formation energies, in particular if the Ce^{3+} ion pair occupies nearest neighbor sites to the V_{sub}. Apparently, the Ce^{3+} repel each other and prefer configurations, in which both ions sit in the 2nd coordination shell of the defect and are spaced by two lattice constants. We note that this energetic preference also explains the development of (2×2) superstructures of oxygen vacancies in heavily reduced CeO₂ films [125].

The DFT calculations also helped rationalizing the splitting of the filled 4*f* orbitals for certain vacancy configurations (Fig. 2.13) [135]. The detection of two peaks is explained with the fact that the two Ce^{3+} ions produced by the O defect experience different chemical environments and have a different number of O ligands in their vicinity. The coordination number of a Ce^{3+} ion may vary between eight, when it sits in a regular bulk position, seven on a regular surface site and finally six for surface positions next to an O vacancy. If both ions of the Ce^{3+} pair



Fig. 2.13 Calculated LDOS for a single O-vacancy in two different spatial configurations with respect to the associated Ce^{3+} defect-pair. Only a single, occupied Ce 4*f* state is observed when both Ce^{3+} ions experience the same chemical environment (**a**), while a splitting of the state is revealed for two reduced Ce^{3+} species with different coordination number (**b**) [135]

experience the same coordination number, their filled f orbitals have exactly the same energy and only one defect state appears in dI/dV spectra taken in the band gap (Fig. 2.12a, Spec. 2). Conversely, for Ce³⁺ ions with different coordination numbers, the filled f orbitals have different energies in accordance with their deviating chemical environment (Spec. 1). The splitting is of the order of 0.1 eV if the coordination number differs by one, but increases to 0.5 V for a coordination mismatch of two (Fig. 2.13). The latter case corresponds to the situation of Fig. 2.13b, where the Ce³⁺ ion-pair is apparently formed by one six-fold and one eight-fold coordinated species and the 4f orbital is consequently split into two subpeaks. The two Ce³⁺ ions in Fig. 2.13a, on the other hand, occupy comparable lattice sites and only one 4f state is detected [135, 136].

The spatial correlation between the Ce^{3+} ion-pair and the associated O vacancy can be deduced also directly from empty-state STM images, as visualized in the STM simulations shown in Fig. 2.14. In all three cases, the Ce^{3+} ions (large blue dots) appear with reduced contrast, as their empty 4f states have moved out of the bias window for tunneling due to a better screening of the Ce core potential by one extra electron (Fig. 2.13). The Ce^{4+} ions, on the other hand, appear bright, in particular if they are adjacent to the O vacancy (large green dots). The enhanced Ce⁴⁺ contrast in presence of the O defect is explained with a substantial spill-out of the Ce 4f orbitals into the vacancy, enabling better overlap with the tip electronic states (Fig. 2.14d) [135]. This interpretation allows us to draw conclusions on the position of the excess electrons with respect to the surface O defect. If the vacancy is exclusively surrounded by Ce⁴⁺ ions and the Ce³⁺ occupy more distant coordination shells, a symmetric triple protrusion is detected in empty state images (Fig. 2.14a). The most frequently observed defect type is however the paired protrusion, which occurs if two bright Ce⁴⁺ ions reside next to an O vacancy, while the third neighbor is a Ce³⁺ of reduced contrast (Fig. 2.14b). Note that a last possible configuration, comprising two Ce³⁺ and one Ce⁴⁺ ion surrounding the O defect, has not been observed experimentally. This is in agreement with the large formation energy of defect complexes, in which both members of the Ce³⁺ ion-pair are localized in the first coordination shell of the defect [9].

2.2.2.2 Adsorption at Ceria Point Defects

The adsorption characteristic of ceria point defects has been extensively studied in the past, both with theoretical and experimental approaches, in particular IRAS, TDS and electron spectroscopy [111, 112]. Main purpose of this effort was a rationalization of the high oxygen-storage capacity of ceria as compared to other reducible oxides, and of the associated high reactivity of this material in various oxidation reactions [114].

In the framework of molecular adsorbates, mainly simple probe molecules such as CO, CO₂ and H₂O have been investigated. According to DFT calculations, CO chemisorbs in the form of a surface carbonate on the regular surface [137, 138]. On the reduced oxide, the Ce³⁺ ions offer more favorable adsorption sites, suggesting

Fig. 2.14 a-c Comparison between measured and simulated STM images for a single O_{surf} defect (*red circle*) with the associated Ce3+ ionpair (dark blue) localized in three different positions. The Ce⁴⁺ ions next to a vacancy site (green) always appear with enhanced contrast. The mechanism behind this contrast enhancement is visualized in panel (d). Note that configuration (c) has not been found in the experiment [135]



that CO can be used as a probe molecule to identify the reduced Ce species even on powder samples [139]. Similar results have been obtained for SO₂ and N₂O that were found to bind as sulfate, sulfite or thionite species and often poison the surface due to their strong binding energy [137, 138]. Water was found to adsorb in an associative as well as a dissociative form on ceria supports, whereby the latter pathway becomes increasingly ineffective at higher coverage [140]. The H₂O binding strength is controlled by the coordination of the involved cerium atom, while the hydrogenbonding network dictates the orientation of the molecules. With increasing oxide reduction, the adsorption energy increases, as O-vacancies become available as active sites for water dissociation. In turn, the presence of water promotes further reduction of the ceria surface and is therefore crucial to its redox chemistry. Oxygen adsorption on reduced ceria surfaces often comes along with the formation of superoxo-species (O_2^{-}) due to a charge transfer from near-surface Ce³⁺ ions [141]. In general, the interplay between molecular adsorbates and the ceria surface is expected to respond sensitively to the presence of dopants in the oxide lattice that promote charge transfer reactions into or out of the ad-species [142–144]. Whereas dopantmediated binding scenarios have been analyzed in detail by theoretical means, clearcut experimental verification of such effects still needs to be given.

Particularly interesting is the deposition of different precious metals, such as Pt and Au, onto the ceria surface, as this material combination shows outstanding performance in a variety of catalytic processes, e.g. in the water-gas-shift reaction and the low-temperature CO oxidation [115, 116, 145]. The high reactivity has been interpreted as a cooperative effect of charge donation from the metal, resulting in Ce^{3+} formation, and oxygen spillover from the ceria lattice [146]. In this context, also the interaction between metallic adsorbates and the regular/defective oxide surface has moved into the focus of research. From a theoretical point of view, there is agreement that Au atoms preferentially bind to the surface O vacancies, where they take up one extra electron from a Ce^{3+} next to the defect [111, 112]. On ideal surfaces, on the other hand, formation of both neutral and positively charged gold is proposed, and no consensus has been reached on the preferred Au binding site, being either a surface O^{2-} or an oxygen bridge site [128, 147–150]. Moreover, a possible adsorption on the Ce^{3+} sites of a reduced oxide has not been considered by theory so far.

The experimental situation is even more ambiguous. In photoelectron experiments, formation of Ce^{3+} species is observed upon Au exposure onto the ceria surface, however the charge state of gold could not be determined [151]. Other studies reported the formation of positively charged gold, but did not identify the role of surface defects in the underlying charge-transfer reaction [152, 153]. The elucidation of the binding mechanism between metal adatoms and defects in the ceria surface requires atomic scale information, as provided by highly resolved STM measurements for example [154–156]. From the results obtained on ceria, the direction and amount of charge transfer between gold atoms and the oxide surface has been reconstructed and the role of surface defects was analyzed in the different adsorption scenarios [8, 9].

In the experiments, small quantities of gold were dosed onto the sample at 10 K in order to produce individual adatoms and to suppress formation of larger deposits (Fig. 2.15a). The Au monomers were imaged as round protrusions of approximately 1.5 Å height and 10 Å diameter at positive sample bias. The STM image in Fig. 2.15b displays the atomically resolved Ce sublattice with three Au atoms bound atop. From such images, the preferred Au adsorption site on the ideal $CeO_2(111)$ was identified as surface O-top position, although O-O bridge sites have been detected as well [9].

Additional binding geometries emerge in the presence of oxygen defects. As expected, surface vacancies appeared to be effective traps for Au atoms and serve as nucleation centers for the incoming Au atoms. Figure 2.15c [111, 128, 147, 148, 157]. However, also subsurface defects, more precisely the Ce³⁺ ions associated to them, were found to influence the adsorption behavior, as concluded from the unusual arrangement of Au atoms on films with a high density of subsurface vacancies [9]. At low gold exposure, up to 40 % of the Au species appeared in the form of characteristic atom-pairs with a mean separation of 7.6 Å (two CeO₂ lattice parameters). Note that this distance corresponds to the favorable separation of two Ce³⁺ ions generated by a single O defect, but is clearly too long to allow for direct Au-Au coupling (Fig. 2.15a). The atom-pairs are metastable, as they could be merged into a single upright Au₂



Fig. 2.15 a $CeO_2(111)$ after dosing 0.05 ML of gold at 10 K (2.5 V, $26 \times 20 \text{ nm}^2$). Note the abundance of atom pairs on the surface. The atom pair in the *inset* shows a *shallow sombrero ring*, indicating its charged nature. **b** STM image with enhanced contrast showing the Ce sub-lattice and three Au atoms bound to regular O-top sites (1.2 V, $3.8 \times 3.0 \text{ nm}^2$). **c** Au atoms sitting in a V_{surf} defect (*left*) and a regular lattice site (*right*). **d** Transformation of an Au pair into an upright standing dimer via a tip-voltage pulse ($5.5 \times 3.0 \text{ nm}^2$). **e** Single Au atom bound to a subsurface defect (*top*). The binding site was identified from the atomically resolved image taken after atom removal with the tip (*bottom*) ($4.2 \times 3.0 \text{ nm}^2$). All images have been taken with 0.025 nA current. Data from [9]

dimer with a bias pulse at the tip (Fig. 2.15d). Further manipulation experiments enabled the determination of the binding sites for the Au pairs, for instance by desorbing them with the tip (Fig. 2.15e). After atom removal, a subsurface O defect could be identified in the vicinity to the former Au pair in many cases. Finally, all atoms in a paired arrangement but also a couple of isolated monomers featured a specific contrast in low bias images, characterized by a dark ring around the maximum (Fig. 2.15a, inset). In earlier experiments on alumina [154] and magnesia films [98], such sombrero shapes were associated with a non-zero charge of the adatom, inducing a local bending of the oxide bands. The Au adsorption experiments on reduced ceria therefore suggested a titration of the Ce³⁺ ions generated by oxygen removal from the ceria lattice, accompanied by a charge transfer from the Ce³⁺ ions to the ad-gold.

This binding scenario was indeed confirmed by DFT calculations, in which the Ce^{3+} ions and not the O-top or O-O bridge positions were identified as the preferred Au binding sites [9]. The energetic preference was determined to be 70–110 meV, depending on the computational approach and the alignment of the two Ce^{3+} spins. In the preferred binding position, the 4*f* electron of the Ce^{3+} ion gets transferred to

the Au 6*s* orbital, generating a Ce⁴⁺ and an Au⁻ species on the surface. The charge transfer is feasible, as the half-filled Au 6*s* orbital is energetically close to the occupied 4*f* state of Ce³⁺ (Fig. 2.16). The finding is in line with the titration scenario of Ce³⁺ ions and explains the formation of Au ion-pairs on the ceria surface.

A detailed analysis of the Au-Ce³⁺ binding preference indicates a crucial role of the lattice strain in the partly reduced ceria lattice [123]. The Ce³⁺ titration effect only emerges in the calculations when a highly strained (2 × 2) cell is used to simulate a single V_{sub} defect, but disappears in a more relaxed (4 × 4) unit. In the latter case, the energetic ordering for Au adsorption is reversed and binding to O-top sites becomes favorable again by 70 meV with respect to the Ce³⁺ sites. Moreover, only a partial electron transfer occurs when fixing the Au on top of the Ce³⁺ ion, pushing the resulting electron configuration closer to Ce³⁺(4f⁴) plus Au⁰(6s¹). Apparently, the build-up of lattice strain, arising from a gradual replacement of the regular Ce⁴⁺ with Ce³⁺ ions (ion radii 0.87 vs. 1.01 Å) governs the Au adsorption behavior on reduced ceria. The surface tension gets reduced again upon electron transfer out of the Ce³⁺ into the ad-gold, leading to a substantial stabilization of the Au-Ce bond [9]. As a consequence, the Ce³⁺ titration effect mainly occurs in regions with a high density of Ce³⁺ species, explaining why the Au atom-pairs are not homogenously distributed on the reduced oxide surface.

As shown for the gold example, ceria defects are able to initiate charge-transfer reactions with adsorbates bound to the oxide surface. In this context, regular Ce⁴⁺ ions typically act as charge acceptors, while Ce³⁺ ions have pronounced donor properties [114]. The facile generation and annihilation of O vacancies is therefore closely related to the unique redox properties of ceria. Thanks to their ability to switch oxidation states, covalently bound oxides play a tremendous role in catalytically relevant processes in general. In fact, various transition-metal oxides are widely used as support materials and as active components in heterogeneous catalysis, in particular the vanadium and manganese oxides, the oxides of ceria and ruthenium and different mixed oxides with sometimes complex stoichiometries.



Fig. 2.16 Projected local density of states for an Au atom bound to (*left*) a Ce³⁺ and (*right*) an O²⁻ top site in a (2×2) cell [9]

2.3 Line Defects

As discussed in the preceding chapters, defects in the crystal structure of wide-gap oxides govern the electronic, optical and chemical properties to a large extent [158, 159]. At first glance, they perturb mainly the local stoichiometry of the oxide lattice, as individual ions or small ion-clusters are absent. The oxide lattice responds to these perturbations with more or less pronounced structural relaxations. In addition, defects may induce a set of discrete electronic states into the gap region of the oxide that are filled with electrons according to the local Fermi level. Apart from the point defects that have been comprehensively discussed before, line defects are archetypical defects in oxide materials. In thin oxide films grown on metal and semi-conducting supports, they may even represent the dominant defect type and are more abundant than the various point defects [160-163]. Line defects develop for two primary reasons [164]. First, they help releasing the lattice strain that originates from the unavoidable mismatch of lattice parameters in the oxide overlayer and the substrate beneath. In this respect, they are of fundamental importance for the gradual transition from strained oxide films to a fully relaxed material characterized by its bulk lattice constant. The second reason is the coalescence of different oxide grains that nucleate independently on the substrate surface and cannot merge into a single domain due to an antiphase crystallographic relation. Given their specific role in the oxide lattice, various kinds of line defects can be distinguished, such as screw- and edge dislocations that help overcoming the lattice mismatch as well as domain boundaries that develop between different rotational and antiphase domains in the oxide [164]. Line defects have been observed in almost every oxide thin film, in particular in Al₂O₃ [165, 166], MgO [49], V₂O₃ [103], SiO₂ [167], CoO [168] and MnO [169]. First, we discuss the structural and electronic properties of line defects in alumina thin films grown on a NiAl(110) single crystal. This system is of interest because an atomistic model for strain relaxation in the oxide lattice could be developed in that case [170, 171].

2.3.1 Dislocation Network in Alumina Thin Films

The alumina thin film on NiAl(110) is probably the best characterized oxide film in surface science, as it can be prepared in a simple and robust way by oxidizing and annealing a NiAl(110) surface [172]. The film is Ni free due to the high Al oxidation enthalpy. Its thickness is limited to 5 Å; a value that is governed by the high diffusion barrier to remove Ni from the reaction zone and to replenish Al from the bulk metal. Alumina on NiAl(110) does not adopt a bulk corundum structure, as its atom arrangement is largely governed by the metal support. Still, certain structural elements of bulk Al₂O₃ reoccur in the film, such as tetrahedrally and octahedrally coordinated Al ions [172]. The following atomic structure has been deduced from STM measurements in combination with DFT calculations [173]. The surface plane

is made of an oxygen layer (O_s) with O^{2^-} ions forming a network of squares and triangles. It is followed by a hexagonal aluminum layer (AI_s) with AI^{3+} ions in pyramidal (according to the O_s squares) and tetrahedral coordination (according to the O_s triangles). The third layer is an O^{2^-} plane again that reproduces the structure of the AI_s layer above. Finally, the interface to the NiAl metal is formed by AI_i ions arranged in pentagonal and heptagonal rings, a configuration that enables maximum overlap between the oxide AI_i ions and the Ni rows in the support. The unusual atomic structure of alumina/NiAl(110) is reflected in an exceptionally large unit cell of 17.9×10.6 Å² that contains as many as 40 aluminum and 52 oxygen ions [165]. The corresponding stoichiometry is $AI_{10}O_{13}$ and therefore oxygen deficient with respect to bulk AI_2O_3 . This difference is owed to the presence of the metal-oxide interface, which stabilizes one electron per interface Al ion that cannot interact with oxygen anymore.

The oxide film exposes a regular network of reflection and antiphase domain boundaries (APDBs) [171]. While the first type separates the two reflection domains A and B, being tilted by 48° against each other, the second type develops between identical domains in the film (A–A or B–B) (Fig. 2.17a). Especially the APDBs are inserted into the oxide lattice to release compressive stress that arises from the lattice mismatch with the NiAl support. As the film growth is commensurate only along the NiAl[110] but not along the NiAl[001] direction, the dislocation lines are relatively homogenous and follow distinct crystallographic directions. Two kinds of APDBs can be distinguished; a straight and a zig-zag type (Fig. 2.17a). Straight APDBs form along the short unit vectors of the two reflection domains (A, B), while the zig-zag lines run along the diagonals of the A and B cells [171].

In well prepared alumina films, the APDBs are inserted every 8–10 nm into the regular film (Fig. 2.17b). Over these distances, the interfacial lattice strain has accumulated to a level that renders the oxide lattice instable and enforces the introduction of a dislocation line. For straight APDBs, the following atomic structure has been revealed with the help of atomically-resolved STM images and DFT calculations [170, 171, 174]. Directly at the defect line, the rectangular unit cell of the oxide is enlarged by 3 Å to allocate space for releasing the compressive strain induced by the NiAl(110) support (Fig. 2.18a). To fill this extra space, additional atoms are introduced along the line defect. In the interfacial Al plane, the five and seven-membered Al_i rings of the unperturbed unit cell are replaced by Al₇ and Al₉ rings at the line defect, which requires the insertion of three extra Al atoms. Four additional Al_s atoms are placed into the surface Al_s layer directly at the boundary (Fig. 2.18b, c) [170]. In accordance to the building principle of the alumina film discussed above, the oxygen sub-lattice is replenished with four O_i ions at the interface and another four Os ions in the surface plane. As a result, the atomic structure along the line defect becomes even more oxygen deficient, as the local O to Al ratio decreases from $Al_{40}O_{52}$ (or $AlO_{1,3}$) in unperturbed alumina to Al₄₇O₆₀ (AlO_{1 27}) in the defect cells. A similar structural change has been identified for the zig-zag APDB, where essentially one extra Al or O row is inserted into each atomic plane [171].



Fig. 2.17 a Structural model of the alumina film on NiAl(110) showing the unit cells of the two reflection domains and the NiAl support, as well as the direction of antiphase domain boundaries (APDB). **b** STM topographic image of the film (4.5 V, 0.5 nA, 38 x 38 nm²). The four different APDB (*I–IV*) and the two reflection domain boundaries (*A–B*) are marked in the image



Fig. 2.18 a Alumina film on NiAl(110) with antiphase and reflection domain boundaries (3.5 V, 0.1 nA, 40 x 40 nm²). Whereas the former type separates two equally-oriented oxide domains and runs along defined crystallographic directions, the latter one forms between domains of different orientation and has no defined atomic structure. b Domain boundary between two A-domains with atomically resolved Al *top* layer (0.2 V, 1 nA, 4.6 x 4.9 nm²). The inserted Al row along the defect line is marked by *blue spheres* in the *right* image. c Domain boundary between two *B* domains showing the Al interface layer. Along the line defect, five and seven-membered Al rings are replaced by Al₇ and Al₉ configurations (-2.0 V, 0.5 nA, 4.6 x 4.6 nm²). The modified regions in the oxide lattice are marked by *dashed lines* in (b) and (c)

The oxygen deficient composition of the alumina film along the line defects is responsible for local modifications in the oxide electronic structure. Along the domain boundaries, new unoccupied states appear in the oxide band gap that give rise to a strong bias-dependent contrast of the line defects in empty-state STM images (Fig. 2.19) [175].

At low sample bias, the defect lines are almost invisible, as they exhibit nearly the same topographic corrugation as the unperturbed oxide lattice. However, they feature a pronounced contrast enhancement and become the most dominant element in the STM images at higher positive bias. Particularly bright contrast of the domain boundaries with respect to the unperturbed oxide is revealed at +2.5, +3.5 and +4.5 V sample bias. Apparently, defect states are available in the oxide band gap at these bias positions, enabling an efficient electron transport through the oxide film. The presence of localized gap states in the alumina film has been verified by STM conductance spectroscopy (Fig. 2.19) [175]. On the stoichiometric oxide, only the



Fig. 2.19 Bias series showing several antiphase-domain boundaries in alumina/NiAl(110) (0.1 nA, $30 \times 30 \text{ nm}^2$). The defect lines are nearly invisible at small imaging bias, but appear bright when the bias value matches a defect state in the oxide band gap (apparent for +2.5, +3.5 and +4.5 V). The *right panel* at the *bottom* depicts dI/dV spectra taken on two defect lines and a stoichiometric oxide region. The first defect-induced gap state shows up as pronounced maximum at +2.5 V [175]

onsets of valence and conduction band at -4.5 and +3.0 V are detected, while the gap region in between is characterized by zero conductivity. Conversely, a pronounced dI/dV peak at +2.5 V, hence inside the oxide band gap, shows up along the line defects. This maximum corresponds to the lowest defect state of the APDBs as identified in bias-dependent maps, while the higher resonances at 3.5 and 4.5 V are not resolved due to the dominant conductance rise at the onset of the alumina bulk bands. The high resolution of the conductance measurements provides even information on the spatial extension of the perturbed electronic structure around the line defects, or more precisely on the localization and symmetry of the underlying defect levels [175]. Whereas the first defect state at +2.5 V is imaged as single line running on top of the inserted atoms, a double strand with a ladder-like pattern appears for the second level at +3.5 V (Fig. 2.19).

The origin of the unoccupied defect states could be clarified in a subsequent DFT study [170]. The missing O atom in the enlarged unit cell containing an APDB is expected to leave behind two extra electrons that are located in the vacancy site. In bulk alumina, the defect electrons fill Al-3s like states in the oxide band gap [176], forming a neutral F^0 color center as discussed for MgO before [84]. In the thin alumina film, however, these electrons are transferred to the NiAl(110) support, as even the lowest defect state lies above the Fermi energy of the metal support [170]. This charge transfer out of the oxide layer is counterbalanced by an electric field across the metal-oxide interface that induces a downward bending of the alumina bands. The observed increase of unoccupied state density around the line defects has therefore two origins: It results from the presence of unfilled defect levels related to the oxygen vacancies and reflects the down-shift of the alumina conduction band in response to the charge transfer into the metal. The localization of positive charges along the line defects has been verified with Kelvin probe spectroscopy measurements performed in a low-temperature tuning fork AFM [177]. In those measurements, the dislocation lines show up as a network of dark lines, indicating a reduced surface potential. Interestingly, the same potential drop is revealed for the straight and zig-zag type APDBs as well as for the reflection domain boundaries. Although the latter do not follow a regular building principle and are partly amorphous, they apparently contain the same oxide units and express a similar oxygen deficiency as the ordered APDBs.

Not surprisingly, the oxygen-poor character of APDB boundaries in alumina thin films makes them attractive for metals with high oxidation potential [163]. Deposition of rhodium, vanadium, chromium and even palladium results in a pronounced decoration effect of the dislocation lines, reflecting the preferred adsorption of those metals at the defect lines [178]. The adsorption might be accompanied by a charge transfer out of the metal, increasing the local metal-oxide adhesion. Noble metals, such as gold and platinum, on the other hand, avoid the APDBs and preferentially bind to regular oxide terraces [154, 179]. The underlying adsorption mechanism is governed by a charge transfer from the oxide into the metals, a process that is energetically unfavorable on top of the positively charged domain boundaries of the alumina film.

2.3.2 Line Defects in MgO Thin Films

Line defects have not only been identified in alumina films, but are commonly found in more or less all thin dielectric layers grown on single crystalline supports [162, 180]. A system were the various kinds of line defects, their morphology and electronic properties have been studied in great detail are MgO thin films grown on a Mo(001) support [49]. Substrate and MgO overlayer experience a 5.3 % lattice mismatch, with the Mo lattice being slightly larger [181]. The magnitude of the mismatch marks the limit, at which pseudomorphic growth between dielectric overlayer and support can still be maintained [164]. The system therefore shows a variety of line defects that even self-assemble into an ordered network [50]. We note that similar dislocation networks have been detected for other oxide thin films, e.g. CoO on Ag(001) and NiO on Pd(100) [86, 168, 182].

Because of the large MgO-Mo lattice mismatch, the dislocation network develops right at the interface in the first oxide plane (Fig. 2.20) [50]. The line defects have been identified by STM in real space and by grazing incidence X-ray diffraction (GIXD) in reciprocal space. The interfacial network has a periodicity of 55–60 Å and the dislocation lines run parallel to the two orthogonal MgO[110] directions (that correspond to the Mo[100] orientation). Along these directions, one additional Mg-O row that has no correspondence in the Mo support, is introduced for every eighteen regular rows of the MgO lattice. The result is a (19 × 19) MgO on (18 × 18) Mo coincidence lattice with square symmetry [49]. The calculated lattice parameter of the superstructure (56.7 Å when using bulk values) perfectly matches the periodicity seen in STM and deduced from the GIXD data (Fig. 2.20b).



Fig. 2.20 Growth morphology of MgO thin films on a Mo(001) support (4.0 V, 0.1 nA, 100 x 100 nm²). **a** Submonolayer coverage resulting in uniform MgO islands of *square shape*. Their size is controlled by the interfacial lattice strain. **b** 3 ML thick film displaying an interfacial coincidence lattice. **c** 7 ML thick film characterized by wide, atomically flat terraces, separated by edge and screw dislocations. **d** 18 ML film featuring an almost relaxed MgO lattice parameter, as deduced from GIXD [50]. The image quality in the latter example is already deteriorated due to the vanishing conductivity of the sample

On the atomic scale, the dislocation network is associated to periodic changes in the interface registry that switches from O ions bound on top of Mo atoms to Mg ions sitting on Mo top sites. From the two configurations, the O-Mo registry is energetically preferred [183]. This becomes evident at sub-monolayer coverage, where only square MgO islands with O-Mo registry can be found in the STM images, while the regions of potential Mg-Mo registry are left open (Fig. 2.20a) [184].

The different interaction strength is also reflected in different interfacial binding lengths for the two registries of the compact film. As expected, the O-Mo configuration features a much smaller binding distance (2.3 Å) than the Mg-Mo registry (3.5 Å), as the O-Mo coupling is highly attractive while a weak repulsion governs the Mg-Mo interaction [183]. As a result, the MgO film is subject to a considerable rumpling, in which the Mg-Mo and O-Mo domains lie on different height levels but are intrinsically flat, while the intermediate regions show a considerable titling. The presence of tilted domains can be immediately deduced from LEED, where a pronounced splitting of the fundamental MgO spots into four sub-spots is found [49]. From the spacing of the satellite spots, the tilt angle is determined to 5° for the interfacial plane. Interestingly, the central spot arising from flat oxide regions is only detectable at certain energy conditions, demonstrating the impact of constructive and destructive interference of the electron beam between the two primary MgO/Mo registries. The MgO/Mo lattice mismatch therefore results in well-ordered domains with fixed tilt angles against the substrate plane, a phenomenon that is known as mosaicity [185, 186]. The energetically favorable O-Mo domain is hereby interpreted as regular stacking; the smaller Mg-Mo region may be considered as 2D defect zone. This concept is validated by the fact that the Mg-Mo regions display a high concentration of point defects even at ideal preparation conditions, while O-Mo regions are essentially defect free [184]. Moreover, the O-Mo regions are slightly strained in a tensile fashion in order to maximize interfacial contact with the larger Mo lattice; in contrast to the Mg-Mo domains that are compressively strained.

The different interfacial geometries are also reflected in spatial modulation of the adsorption behavior of MgO thin films [183]. In fact, the MgO/Mo coincidence lattice can be used as template to produce well-ordered ensembles of metal particles, as demonstrated for Fe and Cr (Fig. 2.21). Preferential binding of the adparticles occurs in the Mg-Mo regions that experience compressive strain, while the O-Mo regions are unsuitable for metal attachment. The possibility to prepare well-shaped metal particles with narrow size distribution on oxide templates has an enormous impact on applications in catalysis and magnetism.

With increasing oxide thickness, the rumpling of the MgO film decreases and the four satellite spots converge to a single spot in LEED, being indicative for flat MgO. At 15 ML thickness, the mosaicity of the film essentially reduces to zero and local variations in the lattice parameter homogenize towards the bulk value of MgO [50]. The relaxation process can be accelerated by annealing the films to 1,000 K. However, a new relaxation phenomenon emerges for films thicker than 15 ML, when the tilting direction rotates by 45° to align with the MgO[110] orientation. The rotation appears simultaneously with a new pattern of edge dislocations that



Fig. 2.21 a Overview ($80 \times 80 \text{ nm}^2$, 3.5 V) and **b** close-up image ($30 \times 30 \text{ nm}^2$, 3.5 V) of 0.1 ML Cr dosed on 5 ML thick MgO/Mo(001). The Cr deposits prefer the Mg-Mo domains of the MgO/Mo coincidence lattice for nucleation. **c** STM topographic images of 3 ML Fe deposited onto 5 ML MgO/Mo(001) ($100 \times 100 \text{ nm}^2$). The spatial ordering of the Fe particles becomes evident in the Fourier transform shown in the *inset*

align with the non-polar MgO[100] direction and enclose relatively wide domains of up to $1,000 \text{ nm}^2$ size (Fig. 2.20c).

Most of the edge dislocations have their origin in screw dislocations that reach down to the MgO-Mo interface [49, 50]. Oxide domains that are enclosed in a loop of edge dislocations typically exhibit 3° tilting against the surface normal, as revealed from LEED and STM. The origin of this new mosaicity is not entirely clear. It seems to be not essential for strain relief, as the interfacial coincidence lattice already removes more than 90 % of the original strain. A likely reason is the warping between neighboring oxide grains that feature an out-of-phase crystallographic relation and cannot merge into a single domain [187, 188]. Upon relaxation of the MgO lattice, the associated in-plane strain increases, which eventually leads to a cracking of the film and the insertion of new line defects. Consequently, this defect pattern does not heal with film thickness, in contrast to the interfacial dislocation network that fades away with thickness (Fig. 2.20d). We finally note that the mismatch-induced strain at the interface still influences the density of line defects in thick films, as seen from comparing the morphology of MgO films grown on Ag(001) [52] and Mo(001) [49]. While dislocation lines in MgO/Mo(001) films form a rather dense network given the 5 % lattice mismatch, hardly any line defects are found in MgO/Ag(001) that features only 3 % mismatch between oxide and metal lattice parameter.

2.3.3 Electron Trapping in MgO Line Defects

In the following, we will demonstrate that line defects are not only important morphological perturbations of the MgO lattice, but influence the electronic structure and surface chemistry of the oxide material as well. As discussed for point defects in Sect. 2.1.4, oxide defects, especially if accompanied by a local nonstoichiometry, introduce new electronic states in the band gap [84, 175]. Those gap states are potentially able to trap electrons, which might then be released to suitable adsorbates bound to the oxide surface. These defect-mediated charge-transfer processes often constitute the first step in a chemical reaction on oxide surfaces. The concept of electron trapping has been explained above for oxygen vacancies that may hold either two (F^0 center) or one extra electrons (F^+ center) [42, 81, 83, 87]. Not surprisingly, the trapping capacity of defects depends on the dimensionality. their position in the crystal and on modalities of their formation. Consequently, a much higher trapping ability is anticipated for line defects as compared to zerodimensional point defects [189, 190]. Also in the 1D case, the extra charges are hold in place by the attractive Coulomb potential produced by the oxide ions surrounding the defect [15, 27]. In the following, we provide experimental evidence for electron trapping in misfit dislocations of MgO/Mo(001) thin films.

A first indication for the presence of trapped electrons comes from the deviating electronic structure of the dislocation lines, as revealed from STM images taken at bias values higher than the sample workfunction (Fig. 2.22a) [191]. In this regime, the line defects appear with negative contrast as compared to the regular film, although the purely geometric corrugation, measured at low bias, is negligible. The dark



Fig. 2.22 a STM image of 12 ML MgO/Mo(001) (0.5 nA, $100 \times 100 \text{ nm}^2$) taken as a function of bias voltage. The line defects appear as deep grooves in the oxide surface as the bias increases. **b** Topographic image and photon maps (1 nA, $75 \times 75 \text{ nm}^2$) taken at the bias position of the 2nd FER on the MgO terraces (*middle*) and the line defects (*right*). The contrast reversal between both images reflects work-function modulations in the film

appearance indicates low electron transmissibility through the line defects, forcing the tip to approach the surface in order to maintain a preset tunneling current. Electron transport at elevated bias is governed by field-emission resonances (FERs) that can be considered as vacuum states above the sample surface, altered by the electric field of the STM tip [192]. Their energy position is defined by the condition that multiples of half the free-electron wavelength fit into a triangular potential formed by the tunnel barrier on one side, and the sample surface on the other side (Fig. 2.23c). Quantum mechanically, the FERs are described as the eigenstates E_n of a triangular box potential, the bottom and slope of which are given by the sample work function ϕ

and the tip-electric field *F*, respectively: $E_n = \phi + \left(\frac{3\pi\hbar e \cdot F}{2\sqrt{2m}}\right)^{2/3} n^{2/3}$ [193].

As FERs carry most of the tunnel current at high bias, their availability determines the image contrast in the STM [194]. Apparently, the MgO line defects offer no or fewer FERs than the regular surface and therefore appear with negative contrast (Fig. 2.22a). According to the equation above, this can be translated into a local workfunction increase around the defects, which shifts the FERs out of the accessible bias window and makes them inaccessible for the tip electrons. The workfunction shift can be quantified with the help of dz/dV spectra taken at the dislocation lines (Fig. 2.23a). Here, the FERs show up as characteristic minima produced by a sudden tip-retraction when the next resonance becomes available for electron transport. On defect-free oxide patches (Fig. 2.23a, position A–J), the 1st and 2nd FER typically appear at 3.7 and 5.4 V, respectively, but experience a systematic up-shift to 4.4 and 6.0 V above the line defects (position K-M), reflecting the anticipated workfunction increase.



Fig. 2.23 a Series of dz/dV spectra measured with enabled feedback loop on terrace (A-J) and defect sites (K-M) of 12 ML MgO/Mo. The tip positions for spectroscopy are marked in the *inset* of **b** (0.05 nA, 50 × 50 nm²). **b** Energy of the lowest FER on MgO terraces and defects sites. **c** Visualization of the electron transport through an STM junction in the FER regime

Similar information can be obtained from STM luminescence data measured on the MgO/Mo films (Fig. 2.22b) [195, 196]. Also the optical response of the oxide film is governed by the FERs, more precisely by radiative electron transitions from the 2nd to the 1st resonance being accompanied by the emission of a 700 nmphoton. Workfunction modulations on the oxide film are therefore evident in the luminescence maps as well. On regular MgO, the emission channel opens up at 4.8–5.0 V excitation bias, coinciding with the position of the 2nd FER on the defect-free oxide surface (Fig. 2.22b, middle). In contrast, the luminescence starts only at 5.8 V on the defect lines, reflecting the up-shift of the FERs on these positions (Fig. 2.22b, right). Local workfunction modulations on the MgO surface can thus be visualized by luminescence maps taken with the STM. Note that the photon energy remains unchanged across the surface, as the FERs undergo a rigid energy shift as a function of ϕ [195, 196].

Both, STM conductance and luminescence spectroscopy, reveal a consistent workfunction increase of ~ 0.7 eV along MgO/Mo line defects with respect to the regular film [191]. This effect is explained with the presence of excess charges localized in the dislocation network. While electron-poor defects, such as F^{2+} centers or cationic edge and corner sites would induce a positive surface dipole that lowers ϕ , electron-rich defects lead to electron accumulation at the surface, hence a higher workfunction [85]. The higher ϕ value measured for MgO line defects is therefore indicative for electron trapping in the dislocation lines. This conclusion is in agreement with DFT calculations that have identified electrostatic pockets in the Madelung potential of MgO grain boundaries that can be filled with electrons [190, 197]. The associated gap states are localized close to the conduction band onset. Due to their high energy, they can only be filled when the oxide film is sufficiently thick to inhibit electron tunneling into the metal support below. Alternatively, 'chemical trapping' of electrons is conceivable. In that case, the excess electrons are captured in the form of reduced Mg⁰/Mg⁺ ions or interstitial oxygen, as produced by a non-stoichiometric oxide composition at the line defect [198]. Such chemical traps are readily filled with electrons from the metal support and thus dominate the charging of defect states in thin films. The observed workfunction rise along MgO line defects is partly attributed to chemically trapped electrons, as the phenomenon becomes evident already in ultra-thin films [195, 196].

In thicker films, also high lying defects states at the dislocation lines can be filled with electrons, for instance by saturating the surface with atomic hydrogen as an electron donor. The trapped electrons are readily identified with electron paramagnetic resonance (EPR) spectroscopy, where a pronounced bulk-like resonance at g = 2.003 shows up [191]. Its position near the free-electron g-value and the lack of the hyperfine signature of hydrogen indicates that the electrons are abstracted from H atoms bound to the line defects. The EPR signal is not observed for films below 7 ML thickness, most likely because the electrons are able to tunnel into the Mo support in that case. It also vanishes when thicker films are annealed to 500 K, suggesting thermal activation of the trapped carriers into the MgO conduction band.

From this threshold temperature, the energy gap between the trap states and the band onset is estimated to be 1.0 eV by assuming an Arrhenius like behavior with 1×10^{13} s⁻¹ attempt frequency. This activation energy is in line with the DFT results obtained for MgO grain boundaries [197]. The intensity of the EPR line is compatible with 5×10^{13} electrons, which is however only a lower bound of the total number, as EPR is sensitive to unpaired electrons only. By projecting this number onto the length of all line defects as deduced from the STM data, a number of three extra electrons per nm line defect can be estimated. This quantity is at least a factor of ten larger than the maximum amount of electrons that can be stored in paramagnetic point defects in the MgO surface [83, 87].

Finally, the high-lying trap states in thick films can be filled via electron injection from the STM tip [191]. Electron accumulation in the line defects is monitored in this case through the optical response (Fig. 2.24). Whereas an untreated defect emits photons at 6.0 V excitation bias as shown in Fig. 2.22b, this photon signal disappears after ramping the bias to 13 V. Upon reversing the polarity, the photon signal recovers at the line defect (Fig. 2.24). Apparently, electrons from the tip occupy the high-lying trap states of the line defect, which further increases the workfunction and renders the FERs unavailable for optical transitions. The electrons immediately leave the trap states at negative polarity, which restores the initial photon response. No comparable hysteresis in the optical signal is revealed on defect-free oxide terraces, reflecting the crucial role of the dislocation lines for the phenomenon of electron trapping [191].

In summary, not only point but also line defects play a crucial role as electron traps in the oxide lattice. The often weakly bound excess charges are prone to be transferred to adsorbates, making defects indispensable for the redox chemistry taking place on oxide surfaces [96, 199, 200]. This interrelation has been verified in

Fig. 2.24 Light emission spectra taken on a pristine line defect (*top*), after a bias ramp to +13 V (*center*) and after reversing the polarity (*bottom*). All spectra are acquired at +6 V sample bias and 1 nA current. The suppressed emission after the ramp is ascribed to electron trapping in the line defect, being reversed at negative polarity (see *insets*)



a number of adsorption and reaction experiments on oxide surfaces, for instance for the low temperature CO-oxidation over defective MgO/Mo(001) films [40, 75]. Engineering the defect landscape of oxides might thus be a promising route to influence their surface chemistry. By exploiting defect-mediated charge-transfer, certain redox properties can be installed even on non-reducible oxides, improving the performance of these materials in catalytic processes.

2.4 Summary

Atomic scale characterization techniques as well as a strong interplay between theory and experiment are required to obtain fundamental understanding of the properties of defects on oxide surfaces. As concerns the experimental side, the examples presented in this chapter have shown that such understanding can be obtained by applying both, ensemble averaging spectroscopic techniques and tools that generate local microscopic and spectroscopic information, to single-crystalline oxide thin films as model substrates.

Magnesia and ceria as archetypical examples for non-reducible and reducible oxides, respectively, were addressed in this article. Oxygen vacancies, as the primary defect type, occur in rather different manifestations in the two systems. Whereas MgO develops color centers, i.e. oxygen vacancies that may trap zero, one or two electrons, the reduction of two Ce cations next to the O defect is observed in ceria. On the basis of atomically resolved experiments combined with density functional calculations, the preferred lattice position of O defects, their charge state and electronic structure, as well as the effect of electron localization could be determined. Moreover, the interaction of defects with different adsorbates, with particular focus on charge-transfer processes, could be revealed in detail. The experiments were performed with CO, a prototype inorganic molecule, and gold and palladium atoms, as metallic species. Our discussion included also line defects in the oxide lattice, such as step edges, dislocation lines and grain boundaries. The formation of line defects is directly connected to phenomena occurring during oxide growth, such as strain relaxation and competing growth regimes. We have shown that certain properties of point defects, e.g. the formation of localized gap states and the propensity to trap electrons, is revealed for line defects as well. The results obtained on our model systems allow the general impact of defects on the nucleation behavior and chemistry of oxide surfaces to be addressed.

Our article demonstrates how fundamental properties of oxide defects can be tackled with modern surface science techniques. The results provide insight into the manifold of phenomena introduced by oxide defects and depict routes, how a controlled manipulation of the defect landscape can be used to engineer oxide properties. 2 Atomic Scale Characterization of Defects on Oxide Surfaces

References

- M. Chen, D.W. Goodman, Catalytically active gold on ordered titania supports. Chem. Soc. Rev. 37, 1860–1870 (2008)
- 2. G. Ertl, H.-J. Freund, Catalysis and surface science. Phys. Today 52, 32-38 (1999)
- H.-J. Freund, M. Heyde, N. Nilius, S. Schauermann, S. Shaikhutdinov, M. Sterrer, Model studies on heterogeneous catalysts at the atomic scale: from supported metal particles to twodimensional zeolites. J. Catal. 308, 154–167 (2013)
- 4. M. Arenz, U. Landman, U. Heiz, CO combustion on supported gold clusters. ChemPhysChem 7, 1871–1879 (2006)
- H.-J. Freund, G. Pacchioni, Oxide ultra-thin films on metals: new materials for the design of supported metal catalysts. Chem. Soc. Rev. 37, 2224–2242 (2008)
- H.-J. Freund, D.W. Goodman, Ultrathin Oxide Films, in *Handbook of Heterogeneous Catalysis*, vol. 3, 2nd edn., ed. by G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp (Wiley-VCH Verlagsgesellschaft mbH, Weinheim, 2008), pp. 1309–1338
- 7. G. Pacchioni, H. Freund, Electron transfer at oxide surfaces. The MgO paradigm: from defects to ultrathin films. Chem. Rev. **113**, 4035–4072 (2012)
- Y. Pan, Y. Cui, C. Stiehler, N. Nilius, H.-J. Freund, Gold adsorption on CeO₂ thin films grown on Ru(0001). J. Phys. Chem. C 117, 21879–21885 (2013)
- 9. Y. Pan, N. Nilius, H.-J. Freund, J. Paier, C. Penschke, J. Sauer, Titration of Ce^{3+} ions in the $CeO_2(111)$ surface by Au adatoms. Phys. Rev. Lett. **111**, 206101 (2013)
- M. Haruta, Catalysis of gold nanoparticles deposited on metal oxides. CatTech 6, 102–115 (2002)
- S. Coluccia, A.J. Tench, in *Spectroscopic Studies of Hydrogen Adsorption on Highly Dispersed MgO*, ed. by T. Seiyama, K. Tanabe. Studies in Surface Science and Catalysis, vol. 7, Part B (Elsevier, Amsterdam, 1981), pp. 1154–1169
- E. Garrone, A. Zecchina, F.S. Stone, An experimental and theoretical evaluation of surfacestates in MgO and other alkaline-earth oxides. Phil. Mag. B 42, 683–703 (1980)
- J.D. Levine, P. Mark, Theory and observation of intrinsic surface states on ionic crystals. Phys. Rev. 144, 751–763 (1966)
- H.F. Ivey, Spectral location of the absorption due to color centers in alkali halide crystals. Phys. Rev. 72, 341–343 (1947)
- A.L. Shluger, P.V. Sushko, L.N. Kantorovich, Spectroscopy of low-coordinated surface sites: theoretical study of MgO. Phys. Rev. B 59, 2417–2430 (1999)
- A.J. Tench, G.T. Pott, Surface states in some alkaline-earth oxides. Chem. Phys. Lett. 26, 590–592 (1974)
- S. Coluccia, A.M. Deane, A.J. Tench, Photo-luminescent spectra of surface states in alkalineearth oxides. J. Chem. Soc. Faraday Trans. I 74, 2913–2922 (1978)
- V.A. Shvets, A.V. Kuznetsov, V.A. Fenin, V.B. Kazansky, On the nature of the luminescence centers on MgO surface. J. Chem. Soc. Faraday Trans. I 81, 2913–2919 (1985)
- M. Anpo, Y. Yamada, Y. Kubokawa, S. Coluccia, A. Zecchina, M. Che, Photoluminescence properties of MgO powders with coordinatively unsaturated surface ions. J. Chem. Soc. Faraday Trans. I 84, 751–764 (1988)
- M.L. Bailly, G.N. Costentin, J.M. Krafft, M. Che, Discrimination of MgO ions by means of an improved in situ photoluminescence cell and of propyne as probe molecule. Catal. Lett. 92, 101–105 (2004)
- C. Chizallet, G. Costentin, H. Lauron-Pernot, J.M. Krafft, M. Che, F. Delbecq, P. Sautet, Assignment of photoluminescence spectra of MgO powders: TD-DFT cluster calculations combined to experiments. Part II. Hydroxylation effects. J. Phys. Chem. C 112, 19710–19717 (2008)
- C. Chizallet, G. Costentin, H. Lauron-Pernott, J.M. Krafft, M. Che, F. Delbecq, P. Sautet, Assignment of photoluminescence spectra of MgO powders: TD-DFT cluster calculations

combined to experiments. Part I: structure effects on dehydroxylated surfaces. J. Phys. Chem. C **112**, 16629–16637 (2008)

- A. Sternig, D. Koller, N. Siedl, O. Diwald, K. McKenna, Exciton formation at solid-solid interfaces: a systematic experimental and ab initio study on compressed MgO nanopowders. J. Phys. Chem. C 116, 10103–10112 (2012)
- P.V. Sushko, K.P. McKenna, D.M. Ramo, A.L. Shluger, A. Sternig, S. Stankic, M. Müller, O. Diwald, in *Photoluminescence Properties of Alkaline-Earth Oxide Nanoparticles*, ed. by D.J. Lockwood, P. Mascher. Nanoscale Luminescent Materials, vol 28. ECS Transactions, vol 3. pp. 67–80 (2010)
- A. Sternig, S. Stankic, M. Müller, N. Siedl, O. Diwald, Surface exciton separation in photoexcited MgO nanocube powders. Nanoscale 4, 7494–7500 (2012)
- P.V. Sushko, A.L. Shluger, C.R.A. Catlow, Relative energies of surface and defect states: ab initio calculations for the MgO(001) surface. Surf. Sci. 450, 153–170 (2000)
- P.V. Sushko, J.L. Gavartin, A.L. Shluger, Electronic properties of structural defects at the MgO (001) surface. J. Phys. Chem. B 106, 2269–2276 (2002)
- Y. Chen, R.T. Williams, W.A. Sibley, Defect cluster centers in MgO. Phys. Rev. 182, 960–964 (1969)
- R.L. Nelson, A.J. Tench, B.J. Harmswor, Chemisorption on some alkaline earth oxides. 1. Surface centers and fast irreversible oxygen adsorption on irradiated MgO CaO and SrO. Trans. Faraday Soc. 63, 1427–1446 (1967)
- A.M. Ferrari, G. Pacchioni, Electronic structure of F and V centers on the MgO surface. J. Phys. Chem. 99, 17010–17018 (1995)
- E. Scorza, U. Birkenheuer, C. Pisani, The oxygen vacancy at the surface and in bulk MgO: an embedded-cluster study. J. Chem. Phys. 107, 9645–9658 (1997)
- 32. A.J. Tench, R.L. Nelson, Paramagnetic defects associated with hydrogen adsorbed on surface of magnesium and calcium oxides. J. Colloid Interface Sci. **26**, 364–373 (1968)
- 33. G. Pacchioni, P. Pescarmona, Structure and stability of oxygen vacancies on sub-surface, terraces, and low-coordinated surface sites of MgO: an ab initio study. Surf. Sci. 412–413, 657–671 (1998)
- M.C. Paganini, M. Chiesa, E. Giamello, S. Coluccia, G. Martra, D.M. Murphy, G. Pacchioni, Colour centres at the surface of alkali-earth oxides. A new hypothesis on the location of surface electron traps. Surf. Sci. 421, 246–262 (1999)
- 35. J.H. Lunsford, J.P. Jayne, An electron paramagnetic resonance study of surface defects on magnesium oxide. J. Phys. Chem. **70**, 3464–3469 (1966)
- L. Ojamäe, C. Pisani, Theoretical characterization of divacancies at the surface and in bulk MgO. J. Chem. Phys. 109, 10984–10995 (1998)
- D. Ricci, G. Pacchioni, P.V. Sushko, A.L. Shluger, Electron trapping at neutral divacancy sites on the MgO surface. J. Chem. Phys. 117, 2844–2851 (2002)
- D. Ricci, C. Di Valentin, G. Pacchioni, P.V. Sushko, A.L. Shluger, E. Giamello, Paramagnetic defect centers at the MgO surface. An alternative model to oxygen vacancies. J. Am. Chem. Soc. 125, 738–747 (2003)
- M. Chiesa, M.C. Paganini, E. Giamello, C. Di Valentin, G. Pacchioni, First evidence of a single-ion electron trap at the surface of an ionic oxide. Angew. Chem. Int. Ed. 42, 1759– 1761 (2003)
- B. Yoon, H. Hakkinen, U. Landman, A.S. Wörz, J.M. Antonietti, S. Abbet, K. Judai, U. Heiz, Charging effects on bonding and catalyzed oxidation of CO on Au-8 clusters on MgO. Science 307, 403–407 (2005)
- C. Sousa, G. Pacchioni, F. Illas, Ab initio study of the optical transitions of F centers at lowcoordinated sites of the MgO surface. Surf. Sci. 429, 217–228 (1999)
- 42. J. Kramer, C. Tegenkamp, H. Pfnür, Formation of surface color centers at differently coordinated sites: MgO/Ag(1,1,19). Phys. Rev. B 67, 235401 (2003)
- L. Marchese, S. Coluccia, G. Martra, A. Zecchina, Dynamic and static interactions in CO layers adsorbed on MgO smoke (100) facelets—a FTIR and HRTEM study. Surf. Sci. 269, 135–140 (1992)

- 44. E. Knözinger, O. Diwald, M. Sterrer, Chemical vapour deposition—a new approach to reactive surface defects of uniform geometry on high surface area magnesium oxide. J. Mol. Catal. A 162, 83–95 (2000)
- T. Berger, M. Sterrer, S. Stankic, J. Bernardi, O. Diwald, E. Knözinger, Trapping of photogenerated charges in oxide nanoparticles. Mat. Sci. Eng. 25, 664–668 (2005)
- 46. C. Barth, C.R. Henry, Atomic resolution imaging of the (001) surface of UHV cleaved MgO by dynamic scanning force microscopy. Phys. Rev. Lett. **91**, 196102 (2003)
- T.V. Ashworth, C.L. Pang, P.L. Wincott, D.J. Vaughan, G. Thornton, Imaging in situ cleaved MgO(100) with non-contact atomic force microscopy. Appl. Surf. Sci. 210, 2–5 (2003)
- M.C. Wu, J.S. Corneille, C.A. Estrada, J.W. He, D.W. Goodman, Synthesis and characterization of ultra-thin MgO films on Mo(100). Chem. Phys. Lett. 182, 472–478 (1991)
- 49. S. Benedetti, H.M. Benia, N. Nilius, S. Valeri, H.-J. Freund, Morphology and optical properties of MgO thin films on Mo(001). Chem. Phys. Lett. **430**, 330–335 (2006)
- 50. S. Benedetti, P. Torelli, S. Valeri, H.M. Benia, N. Nilius, G. Renaud, Structure and morphology of thin MgO films on Mo(001). Phys. Rev. B 78, 195411 (2008)
- J. Wollschläger, D. Erdös, K.M. Schröder, The formation of mosaics during the reactive growth of MgO films on Ag(100). Surf. Sci. 402, 272–276 (1998)
- S. Schintke, S. Messerli, M. Pivetta, F. Patthey, L. Libioulle, M. Stengel, A. De Vita, W.D. Schneider, Insulator at the ultrathin limit: MgO on Ag(001). Phys. Rev. Lett. 87, 276801 (2001)
- 53. M. Sterrer, unpublished results
- J. Pal, M. Smerieri, E. Celasco, L. Savio, L. Vattuone, M. Rocca, Morphology of monolayer MgO films on Ag(100): switching from corrugated islands to extended flat terrace. Phys. Rev. Lett. 112, 126102 (2014)
- A. Zecchina, S. Coluccia, G. Spoto, D. Scarano, L. Marchese, Revisiting MgO-CO surface chemistry—an IR investigation. J. Chem. Soc. Faraday Trans. 86, 703–709 (1990)
- S. Coluccia, M. Baricco, L. Marchese, G. Martra, A. Zecchina, Surface morphology and reactivity towards CO of MgO particles - FTIR and HRTEM studies. Spectrochim. Acta A 49, 1289–1298 (1993)
- 57. G. Spoto, E.N. Gribov, G. Ricchiardi, A. Damin, D. Scarano, S. Bordiga, C. Lamberti, A. Zecchina, Carbon monoxide MgO from dispersed solids to single crystals: a review and new advances. Prog. Surf. Sci. 76, 71–146 (2004)
- J. Heidberg, M. Kandel, D. Meine, U. Wildt, The monolayer CO adsorbed on MgO(100) detected by polarization infrared-spectroscopy. Surf. Sci. 331, 1467–1472 (1995)
- G. Spoto, E. Gribov, A. Damin, G. Ricchiardi, A. Zecchina, The IR spectra of Mg-5C(2+) (CO) complexes on the (001) surfaces of polycrystalline and single crystal MgO. Surf. Sci. 540, L605–L610 (2003)
- P. Audibert, M. Sidoumou, J. Suzanne, CO adsorbed on MgO(100)—a high-resolution LEED study. Surf. Sci. 273, L467–L471 (1992)
- R. Gerlach, A. Glebov, G. Lange, J.P. Toennies, H. Weiss, Structure and dynamics of CO/ MgO(001)—a helium atom scattering study. Surf. Sci. 331, 1490–1495 (1995)
- M. Sterrer, T. Risse, H.-J. Freund, Low temperature infrared spectra of CO adsorbed on the surface of MgO(001) thin films. Surf. Sci. 596, 222–228 (2005)
- L. Marchese, S. Coluccia, G. Martra, A. Zecchina, Dynamic and static interactions in CO layers adsorbed on MgO smoke (100) facelets: a FTIR and HRTEM study. Surf. Sci. 269–270, 135–140 (1992)
- 64. R. Wichtendahl, M. Rodriguez-Rodrigo, U. Härtel, H. Kuhlenbeck, H.-J. Freund, Thermodesorption of CO and NO from vacuum-cleaved NiO(100) and MgO(100). Phys. Stat. Sol. A 173, 93–100 (1999)
- 65. Z. Dohnalek, G.A. Kimmel, S.A. Joyce, P. Ayotte, R.S. Smith, B.D. Kay, Physisorption of CO on the MgO(100) surface. J. Phys. Chem. B 105, 3747–3751 (2001)

- 66. M. Sterrer, T. Risse, H.-J. Freund, CO adsorption on the surface of MgO(001) thin films. Appl. Catal. A **307**, 58–61 (2006)
- 67. J.W. He, J.S. Corneille, C.A. Estrada, M.C. Wu, D.W. Goodman, CO interaction with ultrathin MgO films on a Mo(100) surface studied by infrared reflection absorption spectroscopy, temperature programmed desorption, and X-ray photoelectron spectroscopy. J. Vac. Sci. Technol. A 10, 2248–2252 (1992)
- G. Pacchioni, Quantum chemistry of oxide surfaces: from CO chemisorption to the identification of the structure and nature of point defects on MgO. Surf. Rev. Lett. 7, 277–306 (2000)
- R. Valero, R. Costa, I. Moreira, D.G. Truhlar, F. Illas, Performance of the M06 family of exchange-correlation functionals for predicting magnetic coupling in organic and inorganic molecules. J. Chem. Phys. **128**, 114103 (2008)
- A.D. Boese, J. Sauer, Accurate adsorption energies of small molecules on oxide surfaces: CO-MgO(001). Phys. Chem. Phys. 15, 16481–16493 (2013)
- S. Ehrlich, J. Moellmann, W. Reckien, T. Bredow, S. Grimme, System-dependent dispersion coefficients for the DFT-D3 treatment of adsorption processes on ionic surfaces. ChemPhysChem 12, 3414–3420 (2011)
- 72. C.R. Henry, C. Chapon, C. Duriez, S. Giorgio, Growth and morphology of palladium particles epitaxially deposited on a MgO(110) surface. Surf. Sci. **253**, 177–189 (1991)
- 73. G. Haas, A. Menck, H. Brune, J.V. Barth, J.A. Venables, K. Kern, Nucleation and growth of supported clusters at defect sites: Pd/MgO(001). Phys. Rev. B 61, 11105–11108 (2000)
- 74. C. Barth, C.R. Henry, Kelvin probe force microscopy on MgO(001) surfaces and supported Pd nanoclusters. J. Phys. Chem. C **113**, 247–253 (2009)
- 75. S. Abbet, E. Riedo, H. Brune, U. Heiz, A.M. Ferrari, L. Giordano, G. Pacchioni, Identification of defect sites on MgO(100) thin films by decoration with Pd atoms and studying CO adsorption properties. J. Am. Chem. Soc. **123**, 6172–6178 (2001)
- 76. M. Sterrer, T. Risse, L. Giordano, M. Heyde, N. Nilius, H.P. Rust, G. Pacchioni, H.-J. Freund, Palladium monomers, dimers, and trimers on the MgO(001) surface viewed individually. Angew. Chem. Int. Ed. 46, 8703–8706 (2007)
- 77. M. Sterrer, unpublished results
- V.E. Henrich, G. Dresselhaus, H.J. Zeiger, Energy-dependent electron-energy-loss spectroscopy—application to the surface and bulk electronic-structure of MgO. Phys. Rev. B 22, 4764–4775 (1980)
- M.C. Wu, C.M. Truong, D.W. Goodman, Electron-energy-loss-spectroscopy studies of thermally generated defects in pure and lithium-doped MgO(100) films on Mo(100). Phys. Rev. B 46, 12688–12694 (1992)
- A. Kolmakov, J. Stultz, D.W. Goodman, Characterization of surface defects on MgO thin films by ultraviolet photoelectron and metastable impact electron spectroscopies. J. Chem. Phys. 113, 7564–7570 (2000)
- J. Kramer, W. Ernst, C. Tegenkamp, H. Pfnür, Mechanism and kinetics of color center formation on epitaxial thin films of MgO. Surf. Sci. 517, 87–97 (2002)
- F. Illas, G. Pacchioni, Optical properties of surface and bulk F centers in MgO from ab initio cluster model calculations. J. Chem. Phys. 108, 7835–7841 (1998)
- M. Sterrer, E. Fischbach, T. Risse, H.-J. Freund, Geometric characterization of a singly charged oxygen vacancy on a single-crystalline MgO(001) film by electron paramagnetic resonance spectroscopy. Phys. Rev. Lett. 94, 186101 (2005)
- M. Sterrer, M. Heyde, M. Novicki, N. Nilius, T. Risse, H.P. Rust, G. Pacchioni, H.-J. Freund, Identification of color centers on MgO(001) thin films with scanning tunneling microscopy. J. Phys. Chem. B **110**, 46–49 (2006)
- T. König, G.H. Simon, H.P. Rust, G. Pacchioni, M. Heyde, H.-J. Freund, Measuring the charge state of point defects on MgO/Ag(001). J. Am. Chem. Soc. 131, 17544–17545 (2009)
- M. Klaua, D. Ullmann, J. Barthel, W. Wulfhekel, J. Kirschner, R. Urban, T.L. Monchesky, A. Enders, J.F. Cochran, B. Heinrich, Growth, structure, electronic, and magnetic properties of MgO/Fe(001) bilayers and Fe/MgO/Fe(001) trilayers. Phys. Rev. B 64, 134411 (2001)

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 - M. Sterrer, E. Fischbach, M. Heyde, N. Nilius, H.P. Rust, T. Risse, H.-J. Freund, Electron paramagnetic resonance and scanning tunneling microscopy investigations on the formation of F+ and F-0 color centers on the surface of thin MgO(001) films. J. Phys. Chem. B 110, 8665–8669 (2006)
 - S.L. Ling, M.B. Watkins, A.L. Shluger, Effects of oxide roughness at metal oxide interface: MgO on Ag(001). J. Phys. Chem. C 117, 5075–5083 (2013)
 - L. Giordano, U. Martinez, G. Pacchioni, M. Watkins, A.L. Shluger, F and F+ centers on MgO/Ag(100) or MgO/Mo(100) ultrathin films: are they stable? J. Phys. Chem. C 112, 3857–3865 (2008)
 - K.M. Neyman, C. Inntam, A.V. Matveev, V.A. Nasluzov, N. Rösch, Single d-metal atoms on F-s and F-s(+) defects of MgO(001): a theoretical study across the periodic table. J. Am. Chem. Soc. 127, 11652–11660 (2005)
 - L. Giordano, C. Di Valentin, J. Goniakowski, G. Pacchioni, Nucleation of Pd dimers at defect sites of the MgO(100) surface. Phys. Rev. Lett. 92, 096105 (2004)
 - A. Del Vitto, G. Pacchioni, F.O. Delbecq, P. Sautet, Au atoms and dimers on the MgO(100) surface: a DFT study of nucleation at defects. J. Phys. Chem. B 109, 8040–8048 (2005)
 - A. Bogicevic, D.R. Jennison, Effect of oxide vacancies on metal island nucleation. Surf. Sci. 515, L481–L486 (2002)
 - H. Häkkinen, W. Abbet, A. Sanchez, U. Heiz, U. Landman, Structural, electronic, and impurity-doping effects in nanoscale chemistry: supported gold nanoclusters. Angew. Chem. Int. Ed. 42, 1297–1300 (2003)
 - 95. T. König, G.H. Simon, U. Martinez, L. Giordano, G. Pacchioni, M. Heyde, H.-J. Freund, Direct measurement of the attractive interaction forces on F-0 color centers on MgO(001) by dynamic force microscopy. ACS Nano. 4, 2510–2514 (2010)
 - M. Sterrer, M. Yulikov, E. Fischbach, M. Heyde, H.-P. Rust, G. Pacchioni, T. Risse, H.-J. Freund, Interaction of gold clusters with color centers on MgO(001) films. Angew. Chem. Int. Ed. 45, 2630–2632 (2006)
 - M. Walter, P. Frondelius, K. Honkala, H. Hakkinen, Electronic structure of MgO-supported Au clusters: quantum dots probed by scanning tunneling microscopy. Phys. Rev. Lett. 99, 096102 (2007)
 - M. Sterrer, T. Risse, U.M. Pozzoni, L. Giordano, M. Heyde, H.P. Rust, G. Pacchioni, H.-J. Freund, Control of the charge state of metal atoms on thin MgO films. Phys. Rev. Lett. 98, 096107 (2007)
- M. Yulikov, M. Sterrer, M. Heyde, H.P. Rust, T. Risse, H.-J. Freund, G. Pacchioni, A. Scagnelli, Binding of single gold atoms on thin MgO(001) films. Phys. Rev. Lett. 96, 146804 (2006)
- M. Mihaylov, H. Knözinger, K. Hadjiivanov, B.C. Gates, Characterization of the oxidation states of supported gold species by IR spectroscopy of adsorbed CO. Chem. Ing. Tech. 79, 795–806 (2007)
- 101. M. Sterrer, M. Yulikov, T. Risse, H.-J. Freund, J. Carrasco, F. Illas, C. Di Valentin, L. Giordano, G. Pacchioni, When the reporter induces the effect: unusual IR spectra of CO on Au-1/MgO(001)/Mo(001). Angew. Chem. Int. Ed. 45, 2633–2635 (2006)
- 102. P.A. Cox, Transition metal oxides (An introduction to their electronic structure and properties. Clarendon, Oxford, 1992)
- 103. S. Surnev, M.G. Ramsey, F.P. Netzer, Vanadium oxide surface studies. Prog. Surf. Sci. 73, 117–165 (2003)
- 104. N.V. Skorodumova, S.I. Simak, B.I. Lundqvist, I.A. Abrikosov, B. Johansson, Quantum origin of the oxygen storage capability of ceria. Phys. Rev. Lett. **89**, 166601 (2002)
- 105. A. Hamnet, G.B. Goodenough, Binary Transition Metal Oxides (Springer, Berlin, 1984)
- 106. C. Hagendorf, S. Sachert, B. Bochmann, K. Kostov, W. Widdra, Growth, atomic structure, and vibrational properties of MnO ultrathin films on Pt(111). Phys. Rev. B 77, 075406 (2008)

- 107. B. Tepper, B. Richter, A.-C. Dupuis, H. Kuhlenbeck, C. Hucho, P. Schilbe, M.A. bin Yarmo, H.-J. Freund, Adsorption of molecular and atomic hydrogen on vacuum-cleaved V2O5(001). Surf. Sci. 496, 64–72 (2002)
- 108. A.C. Dupuis, M. Abu Haija, B. Richter, H. Kuhlenbeck, H.-J. Freund, V2O3(0001) on Au (111) and W(110): growth, termination and electronic structure. Surf. Sci. 539, 99–112 (2003)
- 109. D.R. Mullins, P.V. Radulovic, S.H. Overbury, Ordered cerium oxide thin films grown on Ru (0001) and Ni(111). Surf. Sci. 429, 186–198 (1999)
- 110. D.R. Mullins, L. Kundakovic, S.H. Overbury, The interaction between NO and CO on Rh-loaded CeOx(111). J. Catal. **195**, 169–179 (2000)
- 111. C.J. Zhang, A. Michaelides, S.J. Jenkins, Theory of gold on ceria. Phys. Chem. Chem. Phys. 13, 22–33 (2011)
- 112. J. Paier, C. Penschke, J. Sauer, Oxygen defects and surface chemistry of ceria: quantum chemical studies compared to experiment. Chem. Rev. **113**, 3949–3985 (2013)
- 113. C.J. Zhang, A. Michaelides, D.A. King, S.J. Jenkins, Oxygen vacancy clusters on ceria: decisive role of cerium f electrons. Phys. Rev. B **79**, 075433 (2009)
- 114. A. Trovarelli, *Catalysis by Ceria and Related Materials* (World Scientific Publishing, London, 2002)
- 115. Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, Active nonmetallic Au and Pt species on ceria-based water-gas shift catalysts. Science **301**, 935–938 (2003)
- 116. J.A. Rodriguez, Gold-based catalysts for the water-gas shift reaction: active sites and reaction mechanism. Catal. Today **160**, 3–10 (2011)
- 117. A. Pfau, K.D. Schierbaum, The electronic structure of stoichiometric and reduced CeO₂ surfaces—an XPS, UPS and HREELS study. Surf. Sci. **321**, 71–80 (1994)
- 118. P.S. Bagus, C.J. Nelin, E.S. Ilton, M. Baron, H. Abbott, E. Primorac, H. Kuhlenbeck, S. Shaikhutdinov, H.-J. Freund, The complex core level spectra of CeO₂: an analysis in terms of atomic and charge transfer effects. Chem. Phys. Lett. **487**, 237–240 (2010)
- E. Wuilloud, B. Delley, W.D. Schneider, Y. Baer, Spectroscopic evidence for localized and extended F-symmetry states in CeO₂. Phys. Rev. Lett. 53, 202–205 (1984)
- 120. H. Nörenberg, G.A.D. Briggs, Defect structure of nonstoichiometric CeO₂(111) surfaces studied by scanning tunneling microscopy. Phys. Rev. Lett. **79**, 4222–4225 (1997)
- 121. H. Nörenberg, G.A.D. Briggs, Surface structure of CeO₂(111) studied by low current STM and electron diffraction. Surf. Sci. **402**, 734–737 (1998)
- 122. F. Esch, S. Fabris, L. Zhou, T. Montini, C. Africh, P. Fornasiero, G. Comelli, R. Rosei, Electron localization determines defect formation on ceria substrates. Science **309**, 752–755 (2005)
- 123. M.V. Ganduglia-Pirovano, J.L.F. Da Silva, J. Sauer, Density-functional calculations of the structure of near-surface oxygen vacancies and electron localization on CeO₂(111). Phys. Rev. Lett. **102**, 026101 (2009)
- 124. S. Torbrügge, M. Reichling, A. Ishiyama, S. Morita, O. Custance, Evidence of subsurface oxygen vacancy ordering on reduced CeO₂(111). Phys. Rev. Lett. **99**, 056101 (2007)
- 125. G.E. Murgida, M.V. Ganduglia-Pirovano, Evidence for subsurface ordering of oxygen vacancies on the reduced CeO₂(111) surface using density-functional and statistical calculations. Phys. Rev. Lett. **110**, 246101 (2013)
- 126. D.C. Grinter, R. Ithnin, C.L. Pang, G. Thornton, Defect structure of ultrathin ceria films on Pt (111): atomic views from scanning tunnelling microscopy. J. Phys. Chem. C 114, 17036– 17041 (2010)
- 127. S. Eck, C. Castellarin-Cudia, S. Surnev, K.C. Prince, M.G. Ramsey, F.P. Netzer, Adsorption and reaction of CO on a ceria-Rh(111) "inverse model catalyst" surface. Surf. Sci. 536, 166–176 (2003)
- 128. M. Nolan, S.C. Parker, G.W. Watson, The electronic structure of oxygen vacancy defects at the low index surfaces of ceria. Surf. Sci. **595**, 223–232 (2005)
- 129. S. Fabris, G. Vicario, G. Balducci, S. de Gironcoli, S. Baroni, Electronic and atomistic structures of clean and reduced ceria surfaces. J. Phys. Chem. B 109, 22860–22867 (2005)

- 130. H.Y. Li, H.F. Wang, X.Q. Gong, Y.L. Guo, Y. Guo, G.Z. Lu, P. Hu, Multiple configurations of the two excess 4f electrons on defective CeO₂(111): origin and implications. Phys. Rev. B 79, 193401 (2009)
- 131. C. Loschen, S.T. Bromley, K.M. Neyman, F. Illas, Understanding ceria nanoparticles from first-principles calculations. J. Phys. Chem. C 111, 10142–10145 (2007)
- A. Migani, K.M. Neyman, F. Illas, S.T. Bromley, Exploring Ce³⁺/Ce⁴⁺ cation ordering in reduced ceria nanoparticles using interionic-potential and density-functional calculations. J. Chem. Phys. **131**, 064701 (2009)
- J.L. Lu, H.J. Gao, S. Shaikhutdinov, H.-J. Freund, Morphology and defect structure of the CeO₂(111) films grown on Ru(0001) as studied by scanning tunneling microscopy. Surf. Sci. 600, 5004–5010 (2006)
- 134. J.L. Lu, H.J. Gao, S. Shaikhutdinov, H.-J. Freund, Gold supported on well-ordered ceria films: nucleation, growth and morphology in CO oxidation reaction. Catal. Lett. 114, 8–16 (2007)
- 135. J.F. Jerratsch, X. Shao, N. Nilius, H.-J. Freund, C. Popa, M.V. Ganduglia-Pirovano, A.M. Burow, J. Sauer, Electron localization in defective ceria films: a study with scanning-tunneling microscopy and density-functional theory. Phys. Rev. Lett. **106**, 246801 (2011)
- 136. X. Shao, J.F. Jerratsch, N. Nilius, H.-J. Freund, Probing the 4f states of ceria by tunneling spectroscopy. Phys. Chem. Chem. Phys. 13, 12646–12651 (2011)
- 137. C. Müller, B. Herschend, K. Hermansson, B. Paulus, Application of the method of increments to the adsorption of CO on the CeO(2)(110) surface. J. Chem. Phys. 128, 214701 (2008)
- 138. Z. Lu, C. Müller, Z. Yang, K. Hermansson, SO_x on ceria from adsorbed SO₂. J. Chem. Phys. 134, 184703 (2011)
- 139. K. Mudiyanselage, H.Y. Kim, S.D. Senanayake, A.E. Baber, P. Liu, D. Stacchiola, Probing adsorption sites for CO on ceria. Phys. Chem. Chem. Phys. 15, 15856–15862 (2013)
- 140. M. Molinari, S.C. Parker, D.C. Sayle, M.S. Islam, Water adsorption and its effect on the stability of low index stoichiometric and reduced surfaces of ceria. J. Phys. Chem. C 116, 7073–7082 (2012)
- 141. M. Huang, S. Fabris, Role of surface peroxo and superoxo species in the low-temperature oxygen buffering of ceria: density functional theory calculations. Phys. Rev. B 75, 081404 (2007)
- I. Yeriskin, M. Nolan, Effect of La doping on CO adsorption at ceria surfaces. J. Chem. Phys. 131, 244702 (2009)
- 143. B. Li, H. Metiu, DFT studies of oxygen vacancies on undoped and doped La_2O_3 surfaces. J. Phys. Chem. C **114**, 12234–12244 (2010)
- 144. Z.P. Hu, B. Li, X.Y. Sun, H. Metiu, Chemistry of doped oxides: the activation of surface oxygen and the chemical compensation effect. J. Phys. Chem. C **115**, 3065–3074 (2011)
- 145. T. Bunluesin, R.J. Gorte, G.W. Graham, Studies of the water-gas-shift reaction on ceriasupported Pt, Pd, and Rh: implications for oxygen-storage properties. Appl. Catal. B 15, 107–114 (1998)
- 146. G.N. Vayssilov, Y. Lykhach, A. Migani, T. Staudt, G.P. Petrova, N. Tsud, T. Skala, A. Bruix, F. Illas, K.C. Prince, V. Matolin, K.M. Neyman, J. Libuda, Support nanostructure boosts oxygen transfer to catalytically active platinum nanoparticles. Nat. Mater. 10, 310–315 (2011)
- 147. C. Loschen, A. Migani, S.T. Bromley, F. Illas, K.M. Neyman, Density functional studies of model cerium oxide nanoparticles. Phys. Chem. Chem. Phys. 10, 5730–5738 (2008)
- 148. M.M. Branda, N.J. Castellani, R. Grau-Crespo, N.H. de Leeuw, N.C. Hernandez, J.F. Sanz, K.M. Neyman, F. Illas, On the difficulties of present theoretical models to predict the oxidation state of atomic Au adsorbed on regular sites of CeO₂(111). J. Chem. Phys. **131**, 094702 (2009)
- 149. C. Zhang, A. Michaelides, D.A. King, S.J. Jenkins, Structure of gold atoms on stoichiometric and defective ceria surfaces. J. Chem. Phys. 129, 194708 (2008)
- 150. G. Pacchioni, Electronic interactions and charge transfers of metal atoms and clusters on oxide surfaces. Phys. Chem. Chem. Phys. **15**, 1737–1757 (2013)

- 151. M. Skoda, M. Cabala, I. Matolinova, K.C. Prince, T. Skala, F. Sutara, K. Veltruska, V. Matolin, Interaction of Au with CeO₂(111): a photoemission study. J. Chem. Phys. 130, 034703 (2009)
- Q. Fu, W.L. Deng, H. Saltsburg, M. Flytzani-Stephanopoulos, Activity and stability of lowcontent gold-cerium oxide catalysts for the water-gas shift reaction. Appl. Catal. B 56, 57–68 (2005)
- 153. R. Si, J. Tao, J. Evans, J.B. Park, L. Barrio, J.C. Hanson, Y.M. Zhu, J. Hrbek, J.A. Rodriguez, Effect of ceria on gold-titania catalysts for the water-gas shift reaction: fundamental studies for Au/CeOx/TiO₂(110) and Au/CeOx/TiO₂ powders. J. Phys. Chem. C 116, 23547–23555 (2012)
- 154. N. Nilius, M.V. Ganduglia-Pirovano, V. Brazdova, M. Kulawik, J. Sauer, H.-J. Freund, Counting electrons transferred through a thin alumina film into Au chains. Phys. Rev. Lett. 100, 096802 (2008)
- 155. X. Lin, N. Nilius, H.-J. Freund, M. Walter, P. Frondelius, K. Honkala, H. Hakkinen, Quantum well states in two-dimensional gold clusters on MgO thin films. Phys. Rev. Lett. 102, 206801 (2009)
- 156. N. Nilius, V. Brazdova, M.V. Ganduglia-Pirovano, V. Simic-Milosevic, J. Sauer, H.-J. Freund, Nucleation of gold atoms on vanadyl-terminated V₂O₃(0001). New J. Phys. 11, 093007 (2009)
- 157. P. Ghosh, M.F. Camellone, S. Fabris, Fluxionality of Au clusters at ceria surfaces during CO oxidation: relationships among reactivity, size, cohesion, and surface defects from DFT simulations. J. Phys. Chem. Lett. 4, 2256–2263 (2013)
- 158. H.-J. Freund, Introductory lecture: oxide surfaces. Faraday Discuss. 114, 1-31 (1999)
- 159. G. Pacchioni, Ab initio theory of point defects in oxide materials: structure, properties, chemical reactivity. Solid State Sci. 2, 161–179 (2000)
- 160. C.T. Campbell, Ultrathin metal films and particles on oxide surfaces: structural, electronic and chemisorptive properties. Surf. Sci. Rep. 27, 1–111 (1997)
- W. Weiss, W. Ranke, Surface chemistry and catalysis on well-defined epitaxial iron-oxide layers. Prog. Surf. Sci. 70, 1–151 (2002)
- 162. N. Nilius, Properties of oxide thin films and their adsorption behavior studied by scanning tunneling microscopy and conductance spectroscopy. Surf. Sci. Rep. 64, 595–659 (2009)
- M. Bäumer, H.-J. Freund, Metal deposits on well-ordered oxide films. Prog. Surf. Sci. 61, 127–198 (1999)
- 164. I.V. Markov, Crystal Growth for Beginners (World Scientific, Singapore, 2003)
- 165. J. Libuda, F. Winkelmann, M. Bäumer, H.-J. Freund, T. Bertrams, H. Neddermeyer, K. Müller, Structure and defects of an ordered alumina film on NiAl(110). Surf. Sci. 318, 61–73 (1994)
- 166. A. Rosenhahn, J. Schneider, C. Becker, K. Wandelt, The formation of Al₂O₃-layers on Ni₃Al (111). Appl. Surf. Sci. **142**, 169–173 (1999)
- 167. T.K. Todorova, M. Sierka, J. Sauer, S. Kaya, J. Weissenrieder, J.L. Lu, H.J. Gao, S. Shaikhutdinov, H.-J. Freund, Atomic structure of a thin silica film on a Mo(112) substrate: a combined experimental and theoretical study. Phys. Rev. B 73, 165414 (2006)
- 168. P. Torelli, E.A. Soares, G. Renaud, S. Valeri, X.X. Guo, P. Luches, Nano-structuration of CoO film by misfit dislocations. Surf. Sci. 601, 2651–2655 (2007)
- 169. C. Hagendorf, R. Shantyr, H. Neddermeyer, W. Widdra, Pressure-dependent Ni-O phase transitions and Ni oxide formation on Pt(111): an in situ STM study at elevated temperatures. Phys. Chem. Chem. Phys. 8, 1575–1583 (2006)
- 170. M. Schmid, M. Shishkin, G. Kresse, E. Napetschnig, P. Varga, M. Kulawik, N. Nilius, H. P. Rust, H.-J. Freund, Oxygen-deficient line defects in an ultrathin aluminum oxide film. Phys. Rev. Lett. 97, 046101 (2006)
- 171. M. Kulawik, N. Nilius, H.P. Rust, H.-J. Freund, Atomic structure of antiphase domain boundaries of a thin Al_2O_3 film on NiAl(110). Phys. Rev. Lett. **91**, 256101 (2003)

- 172. R.M. Jaeger, H. Kuhlenbeck, H.-J. Freund, M. Wuttig, W. Hoffmann, R. Franchy, H. Ibach, Formation of a well-ordered aluminium-oxide overlayer by oxidation of NiAl(110). Surf. Sci. 259, 235–252 (1991)
- 173. G. Kresse, M. Schmid, E. Napetschnig, M. Shishkin, L. Köhler, P. Varga, Structure of the ultrathin aluminum oxide film on NiAl(110). Science 308, 1440–1442 (2005)
- 174. G.H. Simon, T. König, L. Heinke, L. Lichtenstein, M. Heyde, H.-J. Freund, Atomic structure of surface defects in alumina studied by dynamic force microscopy: strain-relief-, translationand reflection-related boundaries, including their junctions. New J. Phys. 13, 123028 (2011)
- 175. N. Nilius, M. Kulawik, H.P. Rust, H.-J. Freund, Defect-induced gap states in Al₂O₃ thin films on NiAl(110). Phys. Rev. B **69**, 121401 (2004)
- 176. A. Stashans, E. Kotomin, J.L. Calais, Calculations of the ground and excited states of F-type centers in corundum crystals. Phys. Rev. B 49, 14854–14858 (1994)
- 177. L. Heinke, L. Lichtenstein, G.H. Simon, T. König, M. Heyde, H.-J. Freund, Structure and electronic properties of step edges in the aluminum oxide film on NiAl(110). Phys. Rev. B 82, 075430 (2010)
- 178. S. Stempel, M. Bäumer, H.-J. Freund, STM studies of rhodium deposits on an ordered alumina film-resolution and tip effects. Surf. Sci. **402**, 424–427 (1998)
- 179. N. Nilius, M.V. Ganduglia-Pirovano, V. Brazdova, M. Kulawik, J. Sauer, H.-J. Freund, Electronic properties and charge state of gold monomers and chains adsorbed on alumina thin films on NiAl(110). Phys. Rev. B **81**, 045422 (2010)
- S.C. Street, C. Xu, D.W. Goodman, The physical and chemical properties of ultrathin oxide films. Annu. Rev. Phys. Chem. 48, 43–68 (1997)
- Y.D. Kim, J. Stultz, D.W. Goodman, Characterization of MgO(100) thin film growth on Mo (100). Surf. Sci. 506, 228–234 (2002)
- J. Schoiswohl, W. Zheng, S. Surnev, M.G. Ramsey, G. Granozzi, S. Agnoli, F.P. Netzer, Strain relaxation and surface morphology of nickel oxide nanolayers. Surf. Sci. 600, 1099– 1106 (2006)
- 183. S. Benedetti, F. Stavale, S. Valeri, C. Noguera, H.J. Freund, J. Goniakowski, N. Nilius, Steering the growth of metal Ad-particles via interface interactions between a MgO thin film and a Mo support. Adv. Funct. Mater. 23, 75–80 (2013)
- H.M. Benia, P. Myrach, N. Nilius, H.-J. Freund, Structural and electronic characterization of the MgO/Mo(001) interface using STM. Surf. Sci. 604, 435–441 (2010)
- 185. M. Bäumer, D. Cappus, H. Kuhlenbeck, H.-J. Freund, G. Wilhelmi, A. Brodde, H. Neddermeyer, The structure of thin NiO(100) films grown on Ni(100) as determined by low-energy-electron-diffraction and scanning tunneling microscopy. Surf. Sci. 253, 116–128 (1991)
- 186. G. Renaud, A. Barbier, O. Robach, Growth, structure, and morphology of the Pd/MgO(001) interface: epitaxial site and interfacial distance. Phys. Rev. B 60, 5872–5882 (1999)
- 187. C. Tegenkamp, H. Pfnür, W. Ernst, U. Malaske, J. Wollschläger, D. Peterka, K.M. Schröder, V. Zielasek, M. Henzler, Defects in epitaxial insulating thin films. J. Phys.: Condens. Matter 11, 9943–9954 (1999)
- 188. J. Wollschläger, D. Erdös, H. Goldbach, R. Hopken, K.M. Schröder, Growth of NiO and MgO films on ag(100). Thin Solid Films 400, 1–8 (2001)
- T. Berger, M. Sterrer, O. Diwald, E. Knözinger, The color of the MgO surface—a UV/Vis diffuse reflectance investigation of electron traps. J. Phys. Chem. B 108, 7280–7285 (2004)
- K.P. McKenna, A.L. Shluger, Electron-trapping polycrystalline materials with negative electron affinity. Nat. Mater. 7, 859–862 (2008)
- 191. H.M. Benia, P. Myrach, A. Gonchar, T. Risse, N. Nilius, H.-J. Freund, Electron trapping in misfit dislocations of MgO thin films. Phys. Rev. B 81, 241415 (2010)
- 192. G. Binnig, K.H. Frank, H. Fuchs, N. Garcia, B. Reihl, H. Rohrer, F. Salvan, A.R. Williams, Tunneling spectroscopy and inverse photoemission—image and field states. Phys. Rev. Lett. 55, 991–994 (1985)

- 193. O.Y. Kolesnychenko, Y.A. Kolesnichenko, O. Shklyarevskii, H. van Kempen, Fieldemission resonance measurements with mechanically controlled break junctions. Phys. B 291, 246–255 (2000)
- 194. E.D.L. Rienks, N. Nilius, H.P. Rust, H.-J. Freund, Surface potential of a polar oxide film: FeO on Pt(111). Phys. Rev. B **71**, 241404 (2005)
- H.M. Benia, N. Nilius, H.-J. Freund, Photon mapping of MgO thin films with an STM. Surf. Sci. 601, L55–L58 (2007)
- 196. H.M. Benia, P. Myrach, N. Nilius, Photon emission spectroscopy of thin MgO films with the STM: from a tip-mediated to an intrinsic emission characteristic. New J. Phys. **10**, 013010 (2008)
- 197. K.P. McKenna, A.L. Shluger, First-principles calculations of defects near a grain boundary in MgO. Phys. Rev. B **79**, 224116 (2009)
- 198. S. Benedetti, N. Nilius, P. Myrach, I. Valenti, H.-J. Freund, S. Valeri, Spontaneous oxidation of Mg atoms at defect sites in an MgO surface. J. Phys. Chem. C 115, 3684–3687 (2011)
- 199. Y. Cui, X. Shao, M. Baldofski, J. Sauer, N. Nilius, H.-J. Freund, Adsorption, activation, and dissociation of oxygen on doped oxides. Angew. Chem. Int. Ed. 52, 11385–11387 (2013)
- 200. L.M. Molina, B. Hammer, Some recent theoretical advances in the understanding of the catalytic activity of Au. Appl. Catal. A **291**, 21–31 (2005)