Single-Ion Electron Traps

First Evidence of a Single-Ion Electron Trap at the Surface of an Ionic Oxide**

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Electron trapping and the stabilization of charge-separated states in solid systems is an exciting area of research in various branches of chemistry including the synthesis of new materials (for example, electrides),[1] surface science and heterogeneous catalysis,[2] and solar energy storage and conversion.[3] Microporous aluminosilicates (zeolites), for example, have been used to stabilize the products of spontaneous ionization (positive ions and electrons) of various atoms[4] and molecules.[5] Moissette et al indicated that for H-ZSM-5 zeolites,[5] the most probable electron-trapping site is an Al^{3+} Lewis acid center that is located close to an OH group. This implicitly advances the concept that a single, nonreducible surface ion of a solid can stabilize and trap an electron.

In the present communication we report experimental evidence, corroborated by ab initio calculations, of a surface electron trap that consists of a single metal ion at a magnesium oxide surface. Trapped electron centers on MgO are intrinsically important for the general problem of charge-carrier stabilization, as mentioned above, but are also of further interest:

1) They are excellent probes of the local environment of defective sites, which act as electron-trapping centers (topological spectroscopy);[6]
2) They are strong reducing agents (stable up to 320–370 K), which results in remarkable chemical reactivity;[7,8]
3) They play a role in the technological applications of MgO, for example, in catalysis[9] or as protecting layer in plasma displays.[10]

Despite their importance, the nature and location of the surface sites capable of trapping electrons are still elusive. While excess localized electrons (color centers) in the bulk of ionic solids are generally well understood, based on the classical model of de Boer (an electron trapped in an anion vacancy),[11,12] a totally different scenario is observed at the surface. The natural extension of de Boer's model[12] to the surface of a face-centered cubic (fcc) oxide, such as MgO, is a five-coordinated vacancy located on the dominant (100) faces. Many years ago, Tench[13] proposed this model to account for the formation of surface paramagnetic centers created by electron transfer from a dopant to a bare oxygen vacancy,

$$F_S^{2+} + e^- \rightarrow F_S^+ \qquad (1)$$

where $F_S{}^{2+}$ is the diamagnetic precursor of the paramagnetic center and formally derives from the removal of a surface O^{2-} ion. This model suffers from several drawbacks, such as the high formation energy of the oxygen vacancy and the need to compensate negative charge to maintain electroneutrality. In recent years several alternative models have been proposed, which range from low-coordinated vacancies at steps and corners,[14] to neutral divacancies,[15] or morphological defects,[16] all of which involve an array of cations that act as an electron trap. However, recent theoretical calculations[17] surprisingly predicted that single low-coordinate cations on MgO can act as potential electron-trapping sites.

Herein we report the first experimental evidence of the interaction of a trapped electron with a single Mg ion using continuous-wave electron paramagnetic resonance (CW-EPR) spectroscopy, and we present a detailed structural model for this site derived from density functional theory (DFT) calculations.

High-surface-area MgO ($300\,m^2g^{-1}$) was obtained from samples prepared by chemical vapor deposition (CVD). The sample was placed into a vacuum manifold that contained the EPR cell and then activated "in situ" at 1173 K. Excess surface electrons were generated by irradiation with a laser beam ($\lambda = 244$ nm) under an H_2 atmosphere. The same EPR signal, although less sharp, has been obtained with a polychromatic UV lamp. In both cases, the sample changes color from white to deep blue. H_2 is believed to dissociate heterolytically at specific sites to form an H^+/H^- pair.[18] Under UV irradiation, neutral H atoms are desorbed leaving a trapped electron at the surface, close to an adsorbed proton (H^+/e^-). Under these circumstances, a proton is always present near the trapped electron, as shown by a small hyperfine coupling with the ^1H nucleus; the term $F_S{}^+(H)$ has been coined to indicate this small but important feature.[13] The new centers are formed in small amounts along with the above-mentioned $F_S{}^+(H)$ centers (7–8 % of the paramagnetic color centers). The EPR spectrum obtained upon irradiation is shown in Figure 1 a. The signal results from excess electrons localized at the surface; in fact, the blue color is bleached instantaneously by adsorption of a reactive gas, such as O_2. The g values, as well as the ^1H and ^{25}Mg hyperfine coupling constants (see Figure 1 a) are the same as those previously reported.[14] Some line broadening is observed in the present study, which results from a higher concentration of defects. These results allow an observation of new features which can be discussed in terms of the ^{25}Mg hyperfine interaction. The dominant ^{25}Mg hyperfine sextet has a relatively small separation (11 G, Figure 1 a). This value indicates a small interaction of the unpaired electron with the array of Mg^{2+} ions at the surface, and its preferential localization within the electron trap. By recording the spectrum in conditions of overamplification and overmodulation, two

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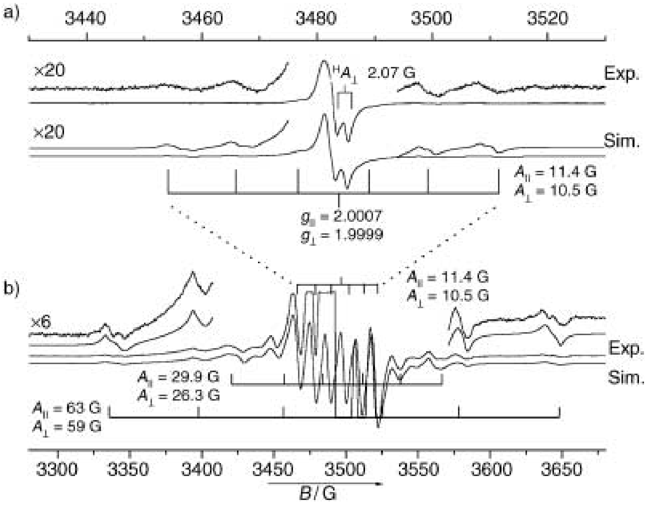

Figure 1. Experimental (upper trace) and simulated CW-EPR spectra of F_s^+(H) centers on MgO. a) 100 G scan-range spectrum recorded with a modulation amplitude of 0.5 G. The ^{1}H hf coupling (2.07 G) and the main ^{25}Mg sextet (average value: 11 G) are both highlighted with the lines shown below the traces. b) 400 G scan-range spectrum (lower scale) of the same sample recorded with a modulation amplitude of 3.5 G. The spectrum is the result of 20 accumulated scans; two new hyperfine structures are observed. Both spectra were recorded at room temperature with a microwave power of 1 mW.

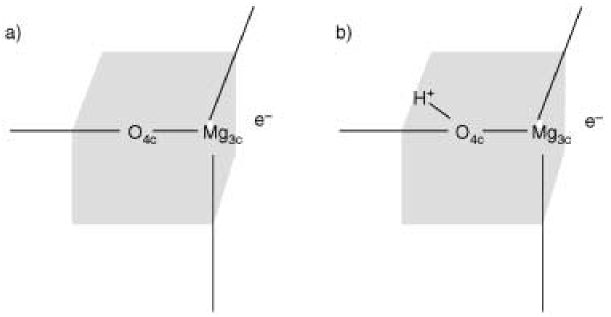

Figure 2. Schematic representation of electron-trapping sites. a) $MgO_{corner}(e^-)$; b) $MgO_{corner}(H^+/e^-)$.

new additional and less intense hyperfine features are observed (Figure 1 b). The two new hyperfine structures have axial symmetry ($A_\perp \neq A_\parallel$) and much higher coupling constants than the main sextet. The first structure has $A_\perp =$ 27.6 and $A_\parallel = 30.4$ G ($a_{iso} = 28.5$, $B = 0.9$ G). For the second structure, $A_\perp = 59$ and $A_\parallel = 63$ G ($a_{iso} = 60.3$, $B = 1.5$ G). The A values were obtained by computer simulation of the spectral profile (Figure 1 b). The first hyperfine structure ($a_{iso} = 28.5$ G) can be ascribed to a "classical" center of the F_s^+(H) family, with an electron trapped by a group of Mg^{2+} ions. In fact, theoretical calculations have shown that the presence of a proton near an F_S^+ center polarizes the trapped electron towards one particular Mg^{2+} ion, which results in a_{iso} values of 20–30 G.[14] In contrast, hyperfine constants as high as 60 G have never been found in theoretical calculations for a model of F_S^+, F_S^+(H), or any other surface paramagnetic centers. Thus, the second sextet must be attributed to an unprecedented trapping site, the high hyperfine constant of which is not compatible with a site that contains several Mg^{2+} ions.

The theoretical study by Shluger and co-workers,[17] shows that a low-coordinate Mg^{2+} ion at the corner site of the MgO surface (Mg_{3c}^{2+}, Figure 2 a), is a shallow trap that binds one electron by 0.6 eV. Mg_{3c}^{2+} sites are present, in low concentrations, on the surface of polycrystalline MgO, as shown by the vibrational shifts of adsorbed CO molecules.[19] In principle, these sites are candidates for the new features described above, but it can be shown that this is not the case. In fact, by means of embedded-cluster DFT calculations[20,21] we can confirm that an Mg_{3c}^{2+} ion is a shallow trap with an electron affinity of 0.65 eV, but the calculated hyperfine coupling constant of this center ($a_{iso} = -35.3$ G) is inconsistent with the experiment, being about one half of the measured constant. Thus, a bare Mg_{3c}^{2+} ion can be ruled out as a possible candidate for the observed features.

Paramagnetic centers on MgO are, as has been already mentioned, created by the reaction of the oxide surface with H_2 under UV irradiation. This process has been considered here for the special case of a Mg_{3c}^{2+} corner site (Figure 2 b) using the same theoretical approach described above.[21] The reaction proceeds in two steps: First, the H_2 molecule is adsorbed with concomitant dissociation to form a proton and an hydride, O_{4c}^{2-}/H^+ and Mg_{3c}^{2+}/H^-, as shown by the Mulliken populations, $H^+ = 0.5$, $H^- = 1.8$. The reaction is exothermic, and the computed value for ΔE (-0.66 eV) is close to that measured using microcalorimetry (-0.5 eV).[16] The Mg–H stretching frequency is found at $\tilde{\nu} = 1446$ cm^{-1} and a bending motion at $\tilde{\nu} = 852$ cm^{-1}; both values are typical for hydride species.[18] The O–H group vibrates at $\tilde{\nu} = 3624$ cm^{-1}. If a H atom is removed from the hydride site (the energy cost, 3.34 eV, is consistent with the use of UV light) one electron is left with the Mg_{3c}^{2+} ion while the proton is still bound to the O_{4c} nearest neighbor. In the resulting $MgO_{corner}(H^+/e^-)$ system (Figure 2 b), the electron density is localized on the corner cation, which can be schematically classified as Mg_{3c}^+ (see Figure 3). It is noteworthy that the same result is obtained by adding a neutral H atom to the corner site. The

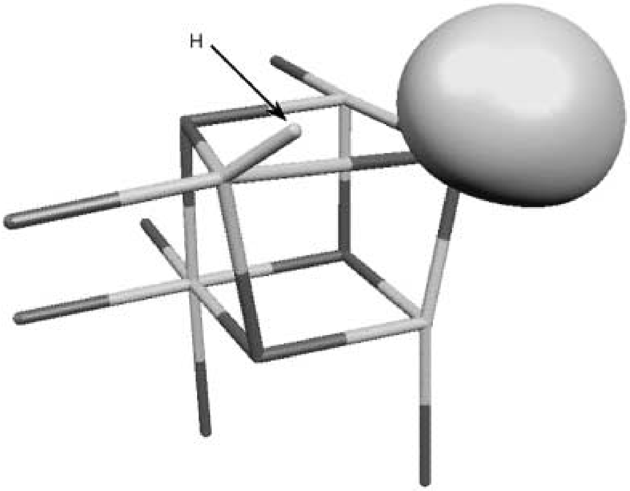

Figure 3. Spin-density plot representing the unpaired electron trapped at the $MgO_{corner}(H^+/e^-)$ site.

hyperfine splitting in $MgO_{corner}(H^+/e^-)$, $a_{iso}(^{25}Mg) = -61.3$ G, is in quantitative agreement with the observed experimental value ($a_{iso} = 60.3$ G; the sign cannot be determined in the experiment). Moreover, the calculations show that the $MgO_{corner}(H^+/e^-)$ center is a deep trap for the electron, which is bound by 3.71 eV, and gives rise to two intense electronic transitions in the visible range at 2.07 ($f = 0.16$) and 2.39 eV ($f = 0.03$).[21] On the basis of these results, the new centers are therefore predicted to be "true" color centers. This is also in agreement with the thermal stability of the new centers. In fact, the hyperfine sextet disappears upon annealing between 320 and 370 K, as do the majority of the $F_s^+(H)$ centers. Because of the absence of experimental data for ^{25}Mg A_0 (the Fermi contact term for an electron in a Mg 3s orbital) and B_0 (the dipolar term for a 3p electron) values, the spin density on the Mg ion has been evaluated on the basis of Mulliken population analysis. The result shows that the unpaired electron is located mainly on the Mg 3s (56%) and Mg 3p orbitals (29%), with the remainder delocalized over a neighboring Mg center.

In conclusion, we have presented experimental and theoretical evidence for a new type of surface paramagnetic defect on MgO. These defects consist of electrons and protons bound at morphological sites, such as at a corner position. The main characteristic of these new centers is the large interaction of the unpaired electron with a Mg ion, a feature which can be schematically related to the formation of Mg^+ ions. Moreover, these findings provide a new scenario in the concept of electron trapping, which shows that morphological features that are naturally present on surfaces can act as potential wells that go beyond the classical de Boer model of an electron trapped in an oxygen vacancy. These findings may also be an interesting aid to understanding the case where electrons are trapped at the Lewis acid sites of H-ZSM-5 zeolites.[5]

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[21] DFT calculations were carried out using the B3LYP exchange-correlation functional (A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785). The MgO surface is represented as a large cluster, divided into regions I and II. Region I is centered on a corner site and includes an Mg_4O_4 quantum-mechanical unit that is surrounded by six interface ions and 932 polarizable classical shell-model ions. Region II is represented by 7054 point charges. All centers in region I are allowed to relax during the geometry optimization. A 6-311+G** basis set has been used on all atoms. Excitation energies have been determined using the time-dependent DFT approach (TD-DFT).