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Journal

The Journal of Physical Chemistry C, 122(22)

ISSN

1932-7447

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Publication Date

2018-06-07

DOI

10.1021/acs.jpcc.8b03118

Peer reviewed

Multicenter Bonding Effects in Oxygen Vacancy in the Bulk and on the Surface of MgO

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Abstract

We have studied the electronic structure of F-centers in the bulk and on the (100) of the MgO crystal. Chemical bonding analysis performed using the Natural Bond Orbital (NBO) analysis with periodic boundary conditions and Solid State Adaptive Natural Density Partitioning (SSAdNDP) method. For the pristine MgO we found that bonding is very ionic with four lone pairs (s -, p_x -, p_y - and p_z -type) on every oxygen atom with the occupation numbers (ONs) in the range of 1.76-1.86 |e|. For **bulk** MgO with **an** O vacancy we found a ~~lone~~-pair of electrons in the place of missing oxygen atom which is revealed by SSAdNDP as a six-center bond delocalized over six Mg atoms (**ON=1.87 |e|**) ~~(is that true and what is the ON number for it? Alex)~~. For the oxygen vacancy on the (100) surface in MgO we found that again we have a ~~lone~~-pair of electrons in the place of the missing oxygen atom, which is a five-center bond with the ON=1.84 |e|. If we

include in the delocalization [the](#) four closest Mg atoms of the second layer, we recovered 9c-2e bond with $ON=1.91$ |e|. We believe that SSAdNDP method ~~showed~~ [has](#) a great potential in analysis of chemical bonding of surface atoms, bulk and surface defects, ad-atoms and chemical bonding at interfaces.

Keywords: Magnesium Oxide; Oxygen Vacancy; Multicenter Bonding; SSAdNDP

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Introduction

Magnesium oxide is known to be an important catalyst,¹⁻¹⁰ and also supporting surface for catalytic nanoparticle and clusters,¹¹⁻¹⁷ for many reactions. Most of the chemistry at the surface of metal oxides is due to the presence of highly reactive defect sites.¹⁸ These sites can be morphological defects such as kinks, steps, terraces, and edges, or they can be anionic or cationic vacancies. Such vacancies are classified as F-centers, when an oxygen atom is missing, or V-centers, when a magnesium atom is removed.¹⁹ Both, F and V centers are naturally present on the surface and in the bulk of MgO crystal. The F-centers are more prevalent. In the case of surface-supported nanoparticle catalysts, F-centers play a major role as nucleophilic binding sites for the particles. The excess electrons present in the O vacancy can be transferred to the particle and then participate in the activation of the bound substrate molecules. Hence, the importance of O vacancies in catalysis can hardly be underestimated. The concentration of vacancies can be increased by γ -ray or neutron irradiation.¹⁹⁻²¹ F-centers also easily heal and reform in reaction conditions in catalysis. The theoretical studies of the electronic structure and chemical reactivity of F-centers are plentiful (see References,²²⁻²⁶ just to name a few). Yet, the electronic structure of vacancies is not completely understood, in the sense of knowing the precise preferred location of electrons left behind upon the formation of an O vacancy, as well we how this picture changes from one oxide to another. Notice that F-centers on different oxides have markedly different reactivities, indicating strong alterations of their electronic structure. In this work we undertook the electronic structure analysis for F centers in magnesia, in the bulk, and on the (100) surface, the most stable surface²⁴ and most often used in catalysis. MgO is perhaps the best understood oxide in catalysis, and its modeling poses the fewest problems, such as poor representation of electron localization in density functional theory (DFT) (e.g. in TiO_2 ^{25,26}), amorphous structure (e.g. in alumina and silica), or relativistic and multireference effects (e.g. in CeO_2). Hence, the studied materials

serve as a convenient show-case for the method for the analysis of the electronic structure and chemical bonding of important defects in solids and surfaces. The method can be applied to other pristine and defected materials, with a potential link to their reactivity.

Computational Details

Geometry optimization of the stoichiometric MgO and MgO with an oxygen vacancy was performed within the context of DFT using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE)³⁰ exchange-correlation functional and the projected augmented wave (PAW)³¹ approach with, as implemented in the Vienna ab-initio simulation package (VASP).³² MgO was modeled with lattice constants $a = b = c = 4.21 \text{ \AA}$ from experimental crystallographic data³³. For bulk MgO with an Ov we used a 3x3x3 supercell and for To-simulate the MgO slab we used a 3x3x3 unit-cell ~~and~~ added a vacuum gap of $14.3 \text{ \AA}$ in the z direction in order to minimize spurious effects between periodic cells. The lattice parameters in this case where $a = b = 12.63$, and $c = 25 \text{ \AA}$. The surface orientation is chosen to be the (001), which is the most stable one. Among the six layers along the z direction, only the bottom 2 layers were fixed. Large kinetic energy cutoffs of 450.0 eV and convergence criteria of 10^{-5} (10^{-6}) eV for geometric (electronic) relaxation were employed. The Brillouin zone was sampled with a $1 \times 1 \times 1$ Γ -centered Monkhorst-Pack³⁶ k -point grid. Because pure DFT functionals are known to overly-delocalize electrons³⁴, we additionally run a single point calculation for stoichiometric and non-stoichiometric MgO surface using the hybrid HSE06 functional³⁵.

The same parameters were used for the periodic natural bond orbital (NBO)³⁷ and Solid State Adaptive Natural Density Partitioning (SSAdNDP)³⁸ calculations as for the VASP calculations. Similar to the standard NBO code,³⁹ periodic NBO allows determination of Lewis elements of localized bonding, such as 1c-2e bonds (lone pairs) and 2c-2e bonds (classical two-center two-electron bonds). SSAdNDP, which is an extension of the molecular Adaptive Natural Density

Partition (AdNDP)⁴⁰ method for systems with periodic boundary conditions, additionally enables the finding of delocalized bonding elements (*nc*-2e bonds, $n > 2$). Details of the method have been published previously.³⁸ The figure of merit of both NBO and SSAdNDP is the occupation number, ON, which is the number of electrons occupying a particular identified localized state. The closer this number is to 2 electrons, the more reliable the localization scheme is. The SSAdNDP projection algorithm was used to obtain a representation of the delocalized plane wave DFT results in a localized atomic orbital basis. Previously, the AdNDP program (parent to SSAdNDP used for finite molecular systems) was shown to produce results that are insensitive to the level of theory or basis set in use.⁴¹ As long as an appropriate atomic orbital basis set is chosen (it is usually trimmed of any functions with angular momentum $l \geq 4$ as well as diffuse functions with exponents < 0.1), projection is found to result in an accurate density matrix. In this work, for the stoichiometric MgO and MgO with oxygen vacancy, the cc-pVDZ basis set⁴² was used to represent the projected PW density using a 3x3x1 k-point grid. This basis set was selected so that on average no more than 1% of the density of each occupied plane wave band would be lost in projecting into the AO basis to guarantee that the density matrix used in the SSAdNDP procedure accurately represents the original plane wave results. The Visualization for Electronic and Structural Analysis software (VESTA, series 3)⁴³ was used for visualization of the SSAdNDP results. Previously, SSAdNDP program was successfully used to analyze the chemical bonding in 1D-chains,⁴⁴ 2D sheets,⁴⁵ as well as high-pressure 3D-materials.⁴⁶

Results and Discussion

Stoichiometric MgO has the rock salt structure with an experimental Mg-O bond length of 2.11 Å.³³ Upon removal of one O atom, some displacements were observed on the (100) surface in the vicinity of the O vacancy. To be precise, four Mg atoms closest to the vacancy (Mg_i) were slightly pulled away from the vacancy center to

shorten the Mg-O bond length with four neighboring O atoms down to 2.06 Å (Figure 1) as opposed to the Mg_I-O value of 2.11 Å in pristine MgO. As a result, the Mg_I-Mg_I distance in the vacancy has increased up to 4.33 Å, compared to the Mg_I-Mg_I value of 4.21 Å in the stoichiometric MgO (100). On the other hand, the four closest Mg_{II}-O interactions stayed the same (2.11 Å) upon the vacancy appearance. In the bulk, the removal of one oxygen atom creates the same atoms displacements but to a much lesser extent (Mg-Mg distance increases by 0.05 Å and Mg-O distance by 0.01 Å).

Figure 1. Top (a) and side (b) views of the MgO slab unit cell with oxygen vacancy (shown in circle). I, II, and III denote first (surface), second, and third layers respectively. Color scheme: O is red, Mg is green.

In order to understand the calculated geometric changes upon the removal of a single O atom from the MgO surface, we have performed chemical bonding analysis for both the stoichiometric and defected systems using the periodic NBO and SSAdNDP methods. For the pristine MgO, there are 108 Mg atoms and 108 O atoms per unit cell that bring 864 valence electrons in total. As expected, both the periodic NBO and SSAdNDP methods confirmed the classical textbook picture, which showed the presence of ionic bonding between Mg and O atoms. Specifically, the analyses found the following Lewis elements of chemical bonding: 432 lone pairs (LPs) with occupation numbers (ONs) in the range of 1.76-1.86 |e|, which represent four

electron LPs (s-, p_x -, p_y -, and p_z -type) on each O atom (Figure 2) (ON=1.76-1.87 |e| for bulk MgO). The found ON values allow us to judge about the degree of the ionic bonding between Mg and O, which is calculated to be 88-93%, thus supporting the common qualitative $\text{Mg}^{2+}\text{O}^{2-}$ representation. Interestingly, MgO with O vacancy showed less classical bonding picture. In this system, there are 108 Mg atoms and 107 O atoms per unit cell thus bringing 858 valence electrons (429 electron pairs) in total. Similarly to the case of stoichiometric MgO, periodic NBO found four LPs on each O atom; 428 lone pairs on all O atoms, with ON = 1.76-1.87 |e|. One electron pair was still missing according to the NBO analysis. Thus, the natural question is: where do these two electrons go? SSAdNDP provided the answer to this question. According to it, the remaining two electrons are delocalized over the six Mg atoms (ON=1.87X.XX |e|) for the vacancy in the bulk MgO and over five Mg atoms for the surface vacancy (Figure 2).

Figure 2. **A** lone pairs (1c-2e bonds) on oxygen, and **B** top and side views of the 5c-2e σ bond formed by the two excess electrons left behind upon the formation of the O-vacancy on the MgO(100) surface (slab model).

To be precise, there is a five-center two-electron (5c-2e) bond with ON=1.84 |e| that is formed upon the oxygen atom removal. It is

composed of four Mg_I atoms of the surface (first) layer and one Mg_{II} atom of the subsurface layer. The contribution of the Mg_{II} atom is assessed to be appreciably high at 20%. Interestingly, upon the inclusion of the four closest Mg atoms of the second layer (considering the possibility of the formation of a 9c-2e bond, instead of a 5c-2e bond), the ON value slightly increases to 1.91 |e|. This means that the 9c-2e bonding is an alternative and also plausible picture of the chemical bonding in this system. Similarly, for bulk MgO, the two electrons left behind upon the removal of one oxygen atom, can be localized over 14 Mg atoms, with ON = 1.93 |e|.

~~According to the population analysis data obtained from the periodic NBO calculations for the pristine MgO, LPs found in the volume of the system are essentially 100% pure s-type or p-type on oxygen. However, hybridization effects were observed for the MgO (100) with O vacancy. While the oxygen LPs located in the volume and away from the vacancy were found to be almost pure s-type or p-type (up to 0.8 % of hybridization), the four O atoms of the surface layer closest to the vacancy were more affected: s-type LPs are composed of 89% of s-, and 11% of p_x -electron density, and the p_x -type LPs are formed by 90% of p-, and 10% of p_x -electron density, while the p_z - and p_y -type LPs stay intact. Apparently, a certain sp-hybridization of LPs occurs for the closest O atoms within the surface layer when the O atom is removed. Likely this goes together with tightening of the Mg_I -O bonds and the onset of partial covalent character in these bonds.~~ (I do not understand this section. LPs cannot be pure s-character in a pristine MgO. They are s-, p_x -, p_y -, and p_z -type as you stated above. I thought we are talking about pure s-type for the lone pair in vacancies. Am I wrong? Could you please clarify that to me. Thanks. Alex).

According to the population analysis data obtained from the periodic NBO calculations for the stoichiometric MgO, oxygen LPs found in the volume of the system are almost pure in their character (either s- or p-type). There is only a slight sp_z-hybridization of the LPs found on the surface, which is symmetry-allowed and likely to be due to the

unsaturation effects. On average, each surface s-LP of O is formed by 97% of s- and 3% of pz-electron density, whereas pz-LPs of the surface atoms are composed of 97% pz- and 3% of s-electron density. More pronounced hybridization effects are observed in the presence of an O vacancy. We found that the MgO structure featuring O vacancy on its surface has almost pure (up to 0.8 % of hybridization) LPs on the O atoms located in its volume and away from the vacancy, whereas the four surface O atoms closest to the vacancy are more hybridized. Precisely, s-LPs are composed of 89% of s- and 11% of px-electron density while the px-LPs are formed by 90% of px-, and 10% of s-electron density. It is likely that the spx-hybridization of the surface LPs closest to the O vacancy goes together with tightening of the Mg-O bonds and the onset of partial covalent character in these bonds. For the bulk MgO with an Ov no hybridization was found.

Finally, for MgO slab containing an Ov, we repeated the periodic NBO and SSAdNDP calculations from the electronic wavefunction obtained with the hybrid HSE06 functional. With both PBE and HSE06 we found essentially the same results: in the presence of an oxygen vacancy all the electrons are localized into lone-pairs on oxygen atoms ($ON = 1.85-1.74 |e|$) and the remaining 2 electrons can be localized either on a 5c-2e bond ($ON = 1.87 |e|$) or on a 9c-2e bonds ($ON = 1.92 |e|$). The only difference between PBE and HSE06 is the occupation numbers, which is slightly smaller for the lone pairs and larger for the more delocalized 5c-2e bond with the hybrid functional, but both functionals lead to the same bonding picture.

Conclusions

In summary, we have studied the electronic structure of F-centers in the bulk and on the (100) surface of the MgO crystal. Chemical bonding analysis performed using NBO and SSAdNDP methods of the bulk MgO confirmed that the bonding in the pristine crystal is ionic (88-93%), thus supporting the common qualitative $Mg^{2+}O^{2-}$ representation. For the bulk and the surface F centers we found an electron pair in the place of missing oxygen atom. It is a six-center

two electron bond with the occupation number ~~1.87~~ |e| for the vacancy in the bulk and it is a five center two electron bond with the occupation number 1.87 |e| for the vacancy on the (100) surface. The atoms that participate in the bonding for the surface vacancy are specifically four $Mg_{\parallel}$ atoms of the surface (first) layer and one subsurface $Mg_{\parallel}$ atom. The contribution of the $Mg_{\parallel}$ atom is assessed to be appreciably high, ca. 20%. Upon the inclusion of the four closest Mg atoms of the second layer, an alternative bonding picture can be proposed, where a 9c-2e bond instead of 5c-2e bond is formed. Thus, the location of the two electrons residing at the F-center includes nine atoms around the vacancy. This multicenter bonding picture is different from the possible electrone-like picture. For less ionic oxides, such as titania or ceria, the bonding picture is likely to change, and exhibit higher degree of localization, as is known from DFT+U calculations. However, multi-center bonding may still be present. We also would like to mention, tools for analyzing the chemical bonding in extended systems are scarce and the periodic NBO and SSAAdNDP are ideal instruments for deciphering chemical bonding in defected solids, both in the bulk, and on the surface.

Acknowledgments

A.I.B. thanks the National Science Foundation of the U.S. (grant CHE-1361413) for financial support. A.N.A. thanks the NSF CAREER Award (CHE-1351968). E.J.I. acknowledges the Postdoctoral Fellowship of the Basque Country (POS 2015 1 0008). Calculations were performed on the UCLA shared cluster Hoffman2.

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Oxygen vacancy on the surface of MgO exhibits multicenter bonding character involving two upper layers.