Computational Materials Science 107 (2015) 15–23

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

# First-principles study of Cd impurities localized at and near the (001) $\alpha$-$Al_2O_3$ surface

Germán N. Darriba [a,*], Ricardo Faccio [b,c], Mario Rentería [a]

[a] Departamento de Física, Instituto de Física La Plata (IFLP, CONICET La Plata), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CC 67, 1900 La Plata, Argentina
[b] Crystallography, Solid State and Materials Laboratory (Cryssmat-Lab), DETEMA, Facultad de Química, Universidad de la República, Gral. Flores 2124, P.O. Box 1157, Montevideo, Uruguay
[c] Centro NanoMat, Polo Tecnológico de Pando, Facultad de Química, Universidad de la República, Cno. Aparicio Saravia s/n, 91000 Pando, Canelones, Uruguay

ARTICLE INFO

*Article history:*
Received 25 February 2015
Received in revised form 7 April 2015
Accepted 12 April 2015
Available online 26 May 2015

*Keywords:*
Impurity
$Al_2O_3$
Surfaces
DFT
EFG
Magnetic moment

ABSTRACT

A combination of two first-principles electronic structure calculation methods in the framework of density-functional theory was applied to investigate the (001) $\alpha$-$Al_2O_3$ surface reconstruction and its structural, electronic, magnetic, and hyperfine properties when doped with Cd impurities at different depths from the surface. The SIESTA approach was used to obtain the equilibrium positions of all atoms and the Full-Potential Augmented Plane Wave plus local orbital (FP-APW+lo) method was employed in order to obtain the electronic structure at these equilibrium positions and all the other physical properties. For the most stable (001) $\alpha$-$Al_2O_3$ surface, we have demonstrated that the inclusion of the Cd atom at substitutional Al sites at and near the surface produces a ground state magnetic behavior. The largest principal component $V_{33}$ of the electric-field-gradient (EFG) tensor at the Cd atom localized just above the $\alpha$-$Al_2O_3$ terrace showed the same [001] orientation and a dominating *p*-character as Cd does when it is localized at bulk $\alpha$-$Al_2O_3$, but exhibits an anomalous $V_{33}$ magnitude four times larger than its value in bulk. Just below the surface, the non symmetric structural relaxation around the Cd impurity is responsible for the strong change in the asymmetry, magnitude, and orientation of the EFG tensor. The changes in the hyperfine properties have been correlated with the modifications observed on the electronic charge density at the different Cd sites and on the *p*-states of the Cd-projected partial density of states. Accordingly, the significant differences on the hyperfine parameters showed for different depths suggest that $^{111}$Cd probe-atoms used in Perturbed $\gamma$–$\gamma$ Angular Correlation experiments could be used for evaluating geometrical and electronic distortions, particularly for positions quite close to the reconstructed surface, as well as contributing to studies of growth, adsorption, and diffusion of atoms in oxide surfaces and interfaces.



## 1. Introduction

The behavior of structural and electromagnetic properties as long as one approaches surfaces and interfaces is fundamental to get insight of the interatomic interactions present at these particular boundary conditions. The surface of $\alpha$-$Al_2O_3$, and in particular its (001) surface, is a major interface because of its extensive use as substrates in microelectronics, spintronics [1,2], ultrathin technology [3,4] and, more recently, as substrate in superconducting qubit devices [5]. Related with the use of $Al_2O_3$ substrates in qubit devices for quantum computation applications, recent important investigations were driven to unravel the origin of the magnetic noise present in real samples, in order to passivate it [5]. In particular, the capability to passivate the magnetic noise in qubits systems based on (001) $\alpha$-$Al_2O_3$ surfaces doped with metallic impurities at different depths should be investigated from first-principles. Therefore, the surface reconstruction and the understanding of the behavior of the alumina surface properties, in pure and as well as in doped systems, are relevant in both basic and applied physics.

One way to obtain physical information at the atomic scale in solids (among other systems) is to study hyperfine properties of suitable probe-atoms in the material under consideration. The magnetic hyperfine interactions at surfaces are important to understand the exchange interactions, whereas the quadrupole-electric hyperfine interactions are very sensitive to local electronic and structural modifications of the probe-atom neighborhood. Particularly, the electric-field-gradient tensor

* Corresponding author. Tel.: +54 221 4246062; fax: +54 221 4252006.
*E-mail address:* darriba@fisica.unlp.edu.ar (G.N. Darriba).

http://dx.doi.org/10.1016/j.commatsci.2015.04.008
0927-0256/

(EFG) at a given atom is a physical quantity strongly dependant on subtle variations of the electronic charge density anisotropy around the atomic nucleus (since the EFG depends on the distance from the source charges as $r^{-3}$). In effect, their components $V_{ij}(\vec{r}) = \frac{\partial^2 V(\vec{r})}{\partial x_i \partial x_j}$ are defined as the second derivate, with respect to the spatial coordinates, of the Coulomb potential $V(\vec{r})$ originated on the electric charges neighboring the nucleus. Since the EFG tensor is traceless in its principal axes system, it can be completely defined by only two quantities: $V_{33}$ (its largest principal component, using the standard convention $|V_{33}| \geqslant |V_{22}| \geqslant |V_{11}|$) and the asymmetry parameter $\eta = (V_{11} - V_{22})/V_{33}$. In single crystalline samples the direction of the EFG tensor, defined as the orientation of the principal axes system with respect to the crystalline axes, can also be measured.

Experimentally, many hyperfine techniques [6,7] have been widely applied to nuclear condensed-matter physics in order to investigate at the atomic level, electronic, magnetic, and structural properties in both pure and doped systems, mainly in bulk [8]. Particularly, the subnanoscopic environment characterization of native or impurity atoms in solids can be obtained employing the Time-Differential Perturbed $\gamma$–$\gamma$ Angular Correlations (TDPAC) spectroscopy [9–12], through the precise determination of the EFG tensor that it provides at diluted (ppm) suitable radioactive probe-atoms.

In the case of surfaces, Körner et al. [13] and Klas et al. [14–16] were the first to perform a detailed experimental TDPAC study of the EFG tensor at $^{111}$Cd atoms located at the surface of metallic indium and copper, respectively, showing the potential of this technique to study surfaces through the characterization of the EFG tensor.

Nowadays, the EFG can provide valuable information about the studied system (structural deformations, localization and charge state of defect centers and impurities, character of impurity levels, etc.) confronting its experimental determination with very accurate EFG theoretical predictions [10,17–19], using all-electron (AE) *ab initio* electronic structure calculations in the framework of the density functional theory (DFT) [20,21].

As previous steps to the present work, we studied the structural, electronic, and hyperfine properties of isolated Cd atoms in bulk $\alpha$-$Al_2O_3$ [18], and the local environment of reconstructed pure (001) $\alpha$-$Al_2O_3$ surface [22]. Here, we present a detailed theoretical *ab initio* study for determining structural, electronic, magnetic, and hyperfine properties of isolated Cd impurities located at and near the (001) $\alpha$-$Al_2O_3$ surface (at substitutional Al cationic sites), i.e., as a function of the Cd's depth with respect to this surface.

In one of the previous works we successfully employed two *ab initio* methods with different basis set (the Full-Potential Augmented Plane Wave plus local orbital (FP-APW+lo) method and a linear combination of numerical localized atomic-orbitals basis set, implemented in WIEN2k and SIESTA packages, respectively) for the understanding of the reconstruction of pure $\alpha$-$Al_2O_3$ (001) surface [22]. In order to determine the electronic, magnetic, and hyperfine properties in the doped surfaces, we calculated the EFG using the FP-APW+lo method at the equilibrium atomic positions predicted by SIESTA since, as we showed in Ref. [22] for the pure surface, this method predicts final equilibrium structures with comparative lower energy than those predicted by the FP-APW+lo method.

Now, understanding the surface reconstruction and obtaining relevant electronic properties in the presence of Cd impurities, allow us to demonstrate the importance of this extremely sensitive local probe. Particularly, for evaluating electromagnetic and structural properties in the proximity of the $Al_2O_3$ surface.

## 2. Methodology

Following an analogous procedure for the study of the pure (001) $\alpha$-$Al_2O_3$ surface [22], we started with the bulk $\alpha$-$Al_2O_3$ unit cell in its hexagonal representation according to the R-3 c H space group using the following cell and internal parameters: $a$ = 4.75999(3) Å and $c$ = 12.99481(7) Å [23], $u$ = 0.35219(1) and $v$ = 0.30633(5) [23]. According to this, each aluminum atom presents six nearest oxygen neighbors (ONN), three of them located at 1.854 Å (O1) and the rest located at 1.972 Å (O2).

The (001) surface was modeled using the slab approximation, utilizing a standard unit cell and introducing vacuum along the [001] direction, see Fig. 1(a). A vacuum region of 14 Å probed to be sufficient in order to avoid interaction between adjacent images. The selected surface termination used as a starting point of all our calculations corresponds to the most stable optimized pure surface as determined in our previous work [22], which is in agreement with X-ray diffraction [24] and ion-scattering experiments [25,26]. In order to simulate an isolated impurity, a Cd atom replaces one of the Al atoms localized at the lattice sites shown in Fig. 1(b)–(g), obtaining a cationic impurity dilution of 1:12. In Ref. [18] we showed that this dilution is sufficient to simulate a Cd isolated impurity in bulk $\alpha$-$Al_2O_3$. Thus, this dilution warrants the absence of undesired Cd–Cd interactions, in bulk as well as in the slab geometry, in order to be closer to the conditions of diluted probe atoms used in hyperfine experimental techniques. The Cd atom was located at the different Al cation sites shown in Fig. 1, varying the Cd depth from the surface. From here on we establish the following notation for the Cd-doped systems in the (001) $\alpha$-$Al_2O_3$ surface: $Al_2O_3$:$Cd_1$ (Fig. 1(b)), when the Cd atom replaces the topmost Al atom, whereas $Al_2O_3$:$Cd_i$ ($i$ = 2–6), when the Cd atom replaces the corresponding Al atoms as we move away from the surface into the bulk (Fig. 1(c)–(g)).

Two different first-principles DFT implementations were selected in order to get the full geometrical reconstructions for the studied systems. The WIEN2k code [27] implements the FP-APW+lo method [28,29]. In this case the wave functions are expanded in spherical harmonics into non-overlapping spheres, and plane waves in the interstitial region. The spheres are delimited by the so-called muffin-tin radii ($R_{MT}$), and we selected for Al, O, and Cd the following values: 0.87, 0.85, and 1.10 Å, respectively. We used 32 $k$-points for the sampling of the irreducible wedge of the Brillouin Zone, using the tetrahedron method. The size of the basis is controlled by the $R_{MT}K_{\max}$ value, set to 7.0 in our case. The $V_{ii}$ elements of the EFG tensor were obtained for each atom in the final optimized geometries. These elements were obtained from the $V_{2M}$ components of the lattice harmonic expansion of the self-consistent potential [30]. The exchange and correlation (Exc) effects were treated using both the local-density approximation (LDA) [31] and the generalized gradient approximation (GGA). In particular for GGA we use the Perdew–Burke–Ernz erhof (PBE) parametrization [32]. The results obtained from both potentials probed to follow similar trends, for that reason we decided to present here just the results from GGA-PBE Exc-potential.

The SIESTA code [33–35] uses a linear combination of numerical localized atomic orbitals for describing the valence electrons, and norm-conserving non-local pseudopotentials for the description of the atomic core. The pseudopotentials were obtained following the Trouiller and Martins scheme [36]. We used a split-valence with double-$\zeta$ basis set, including polarization orbitals in all the atoms. The real-space extension of the numerical orbitals was determined from an energy confinement of 50 meV. We selected PBE-GGA for the description of the Exc-potential [32]. The charge density and wavefunctions is projected in a real-space grid, as