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Electronic, structural, and hyperfine properties of pure and Cd-doped hexagonal La_2O_3 semiconductor

D. Richard [a,*], L.A. Errico [a,b], M. Rentería [a]

[a] Departamento de Física and Instituto de Física La Plata (IFLP, CONICET), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CC 67, (1900) La Plata, Argentina
[b] Universidad Nacional del Noroeste de la Pcia. de Buenos Aires (UNNOBA), Monteagudo 2772, (2700) Pergamino, Argentina

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ABSTRACT

We present a detailed first-principles study of structural, electronic, and hyperfine properties of pure and Cd-doped lanthanum sesquioxide (La_2O_3) with the hexagonal structure (*A*-phase). We calculated the equilibrium structure, the density of states (DOS), the energy band-gap and, finally, the electric-field-gradient (EFG) tensor at the different atomic sites (La, O, and Cd at substitutional La sites) using different approximations for the exchange and correlation potential. In the case of pure *A*-La_2O_3 our predictions are compared with available experimental data obtained in X-ray Diffraction experiments and Nuclear Quadrupole Resonance and Nuclear Magnetic Resonance spectroscopies. The excellent agreement between theory and experiments gave us a solid base for the study of Cd-doped *A*-La_2O_3. In the case of the doped system, a very good agreement between the predicted and the experimental EFG at the ^{111}Cd sites (obtained in Time-Differential Perturbed γ–γ Angular Correlations experiments) was found. From the comparison of the EFGs obtained at different probe sites we can discuss and elucidate the role played by the electronic structure of the probe atoms, and the structural and electronic modifications induced by the Cd impurity in the La_2O_3 host, on the origin of the EFG.

1. Introduction

Nuclear techniques, such as Mössbauer Spectroscopy (MS), Time-Differential Perturbed γ–γ Angular Correlations (PAC), Nuclear Quadrupole Resonance (NQR), and Nuclear Magnetic Resonance (NMR) are widely used in material science. With these techniques the local environment (at a subnanoscopic scale) around a given probe atom can be elucidated and an accurate knowledge of the structural, electronic, and magnetic properties of a solid is potentially affordable. All these techniques are based on the hyperfine interaction of a probe-nucleus with its surrounding electronic charge distribution [1]. In the case of pure nuclear quadrupole interactions, the electric-field-gradient (EFG) tensor at the probe-nucleus can be determined. Due to the r^{-3} dependence of the EFG from the charge sources, this observable is an extremely sensitive tool for investigating the crystal electronic charge density at a given site.

Recently, we applied electronic structure calculations based on Density Functional Theory (DFT) to the study of the EFG at cationic sites of lanthanide sesquioxides with the cubic bixbyite structure (*C*-Ln_2O_3) [2]. In those systems an accurate description of the electronic structure is a great challenge due to the presence of Ln-4*f* electrons. In that study we showed that the inclusion of an on-site Coulomb repulsion parameter *U* to describe the strong *f*–*f* interactions produce a better description of the crystal structure and the insulating ground state for the entire *C*-Ln_2O_3 series, but this capability of the method does not always guarantee a good prediction of the EFG at Ln sites. The most important discrepancies between the APW+lo prediction and the experimental EFG at the cationic sites of the Ln_2O_3 structures arise in the cases that involve a partially filled Ln-4*f* shell, being the prime example the *C*-Yb_2O_3 case [2].

Lanthanum sesquioxide (La_2O_3) is a semiconductor that has been largely investigated due to its potential application as a high-permittivity material, i.e. as gate insulator in metal–oxide-semiconductor structures [3–5]. It is the only lanthanide oxide with an empty Ln-4*f* shell, and at low temperatures it crystallizes in a simple hexagonal structure (*A*-phase, space group *P*-3*m*1), with a single cationic site. For this reason, a precise (and easy to analyze) experimental characterization of the EFG is potentially reachable.

Over the last years the hyperfine interactions at La and O sites of the *A*-La_2O_3 structure were studied using NQR and NMR techniques [6–9]. *A*-La_2O_3 has also been studied by means of PAC spectroscopy [10,11]. PAC provides a high-resolution determination of the EFG tensor at the site of a probe atom (generally an impurity in the

* Corresponding author. Tel.: +54 221 4246062; fax: +54 221 4252006.
E-mail address: richard@fisica.unlp.edu.ar (D. Richard).

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system under study, in the present case ^{111}Cd). The measured EFG may give structural and electronic information of the system that cannot be obtained by other techniques, but the interpretation of such measurements is not straightforward and involves understanding of chemical differences between the probe atom and the ion replaced by the impurity. Additional difficulties (such as the hygroscopic nature of A-La_2O_3) must be considered during the experiment and, afterwards, in the data analysis. The published PAC studies of ^{111}Cd-doped A-La_2O_3 refer to a unique hyperfine interaction. This interaction was assigned (based in the symmetry of the La sites) to ^{111}Cd substitutionally located at the cation sites of the structure [10,11].

From the first-principles point of view, different *ab initio* studies were performed in order to describe different structural or electronic properties of pure A-La_2O_3 [12–20], but neither of them examined the EFG. Considering the fact that the La atom does not involve 4*f* electrons, the A-La_2O_3 system is a unique candidate to study the EFG at La sites without the strong *f*–*f* correlation. In addition, the availability of EFG measurements at the different atomic sites in pure A-La_2O_3, and at the Cd-impurity site in ^{111}Cd-doped A-La_2O_3 turns this oxide in a very interesting system to be investigated by means of first-principles methods such as the APW+lo method, one of the state-of-the-art and most accurate tool for the calculation of the EFG tensor.

In the present work we present an APW+lo study of the electronic, structural, and hyperfine properties of pure A-La_2O_3, focusing on the EFG. After that, we analyzed the Cd-doped system. The goal is not only to reproduce the experimental results but also to elucidate the structural and electronic modifications induced in the host by the presence of the impurity and to understand the origin of the EFG tensor.

The paper is organized as follows. In Section 2 we outline the way we applied the APW+lo method to the study of pure and Cd-doped A-La_2O_3 and, in Section 3, we present and discuss the obtained results. In all cases the theoretical predictions are compared to the existing experimental data in the literature. Finally, in Section 4, we present our conclusions.

2. Method of calculation

A-La_2O_3 crystallizes in the hexagonal structure of the rare earth sesquioxides (space group *P*-3*m*). The unit cell contains one formula unit with the two equivalent La atoms located at positions 2*d*: ±(1/3,2/3,*u*). Two nonequivalent sites for the oxygen atoms (O1 and O2 in the following) characterize the structure. The O1 are located at positions 1*a* (at the origin) and O2 are at 2*d*: ±(1/3,2/3,*v*,O2) (see Fig. 1(a)). The experimentally determined internal and lattice parameters are $u = 0.245(5)$, $v = 0.645(5)$, $a = 3.9373$ Å, $c = 6.1299$ Å, respectively [21]. Each La atom is coordinated with seven oxygen nearest neighbours (ONN, see Fig. 1(b)).

As mentioned before, the experimental hyperfine techniques whose results will be discussed in this work allow the determination of the EFG tensor, which is a fingerprint of the asymmetry of the electronic charge density near and at the probe nucleus. The EFG is a rank 2 traceless symmetric tensor whose components, denoted by V_{ij}, are defined by the second derivative (with respect to the spatial coordinates) of the Coulomb potential $V(\boldsymbol{r})$ created by the charge density surrounding a given probe-nucleus. In the principal axis system the three diagonal components of the EFG tensor are labeled according to the conventional choice $|V_{xx}| < |V_{yy}| < |V_{zz}|$. Hence, V_{zz} is the largest eigenvalue of the EFG tensor. The measured magnitudes (in the case of the experiments discussed here) are the nuclear quadrupole coupling constant ν_Q, related to V_{zz} by [1]:

$$\nu_Q = \frac{eQV_{zz}}{h} \quad (1)$$

and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. Q is the nuclear quadrupole moment of the sensitive states of ^{111}Cd (PAC probe) and ^{139}La, and ^{17}O (MNR, NQR probes). From the symmetry of the La, O1, and O2 sites, which present axial symmetry, the observed/calculated quadrupole interactions should have $\eta = 0$, and V_{zz} is expected to be oriented along the [0, 0, 1] direction.

The calculations were performed with the WIEN2 k implementation of the APW+lo method [22]. The exchange and correlation effects were treated using both the local density approximation (LDA) [23] and the Wu and Cohen parameterization of the generalized gradient approximation (WC-GGA) [24]. Also, we employed the LDA approximation plus the Hubbard *U* term (LDA+*U* approach), in the self-interaction-corrected scheme [25,26]. To this purpose we took $U = 10.9$ eV (0.8 Ry) for the La-4*f* orbitals [2]. The product of the smallest muffin-tin radius (R_{MT}) and the largest wavenumber of the basis set (K_{max}) was fixed to 7. Integration in the reciprocal space was performed using the tetrahedron method, taking up to 100 k points in the first Brillouin zone. The muffin-tin radii used for cations and O atoms were 1.06 and 1.00 Å, respectively.

For the pure A-La_2O_3 system we used the experimental lattice and internal parameters as starting values. We first calculated the electronic band structure and the density of states (DOS) of the pure compound by using the LDA and the WC-GGA approximations. Due to the well-known deficiency of the LDA and WC-GGA to predict the energy band-gaps of semiconductors [27], we additionally used the modified version of the Becke and Johnson exchange potential proposed by Tran and Blaha (TB–mBJ method), which in general predicts very accurate energy band-gaps in most semiconductors and insulators [19,28–30]. To determine the equilibrium structural properties of the system we fitted the Birch-Murnaghan equation of state (EOS) [31] to the calculated energy vs. volume data. Also, we predicted the equilibrium atomic positions, i.e., we obtained the *u* and *v* parameters predicted by the *ab initio* calcula-

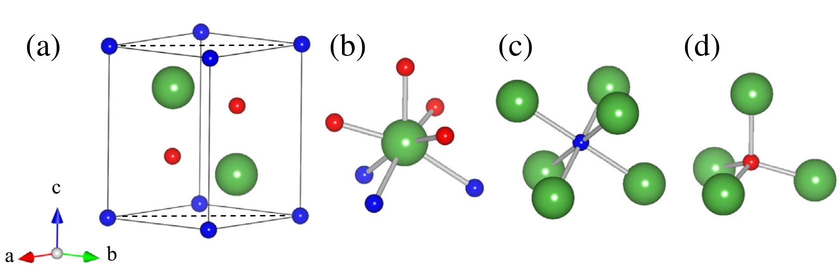

Fig. 1. (a) A-La_2O_3 unit cell, and coordination of the atomic sites of (b) La, (c) O1, and (d) O2 atoms. The big green spheres represent La atoms, the small blue spheres represent O1 atoms, and the small red spheres represent O2 atoms. In the dashed lines are used to indicate the (1 1 0) plane. In the three O1 atoms are the more distant to the La atom, while the three non azimuthal O2 atoms are the nearest. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)