



## FP-LAPW Calculations of the EFG at Cd Impurities in Rutile SnO<sub>2</sub>

L. A. ERRICO, G. FABRICIUS and M. RENTERÍA

*Instituto de Física La Plata (IFLP-CONICET) – Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C. 67, 1900 La Plata, Argentina*

**Abstract.** We report an *ab initio* study of the electric-field gradient (EFG) at Cd impurities located at the cation site in the semiconductor SnO<sub>2</sub> (rutile phase). The study was performed with the WIEN97 implementation of the FP-LAPW method. In order to simulate the diluted Cd-impurity in the SnO<sub>2</sub> host and to calculate the electronic structure of the system we used a 72-atoms super-cell, studying the relaxation introduced by the impurity in the lattice. The free-relaxation process performed shows that the relaxations of the oxygen nearest-neighbors of the impurity are not isotropic. Our prediction for the EFG tensor are compared with experimental results and point-charge model predictions.

**Key words:** impurities, relaxations, tin oxide, *ab initio*, electric field gradient.

### 1. Introduction

The experimental study of nuclear–quadrupole interactions is often used as a powerful tool to obtain information about local symmetry, coordination and valence of defect or structural centers in solids. In the case of pure electric quadrupole interactions, the measured quantities are the quadrupole coupling constant  $\nu_Q = eQV_{ZZ}/h$  (where  $V_{ZZ}$  is the principal component of the diagonalized electric-field gradient (EFG) tensor) and the asymmetry parameter  $\eta$ . The EFG is measured via its interaction with the nuclear–quadrupole moment  $Q$  of a suitable probe-atom (generally an impurity in the system under study) by different techniques, such as Perturbed-Angular Correlations (PAC). The presence of the impurity probe-atom modifies the local electrostatic potential and creates its own characteristic EFG.

As there is not a simple and accurate model to obtain the charge distribution from known experimental values of the EFG  $V_{ii}$  components, conclusions drawn from the experimental data are usually restricted to symmetry considerations and empirically-established trends. Approaches for a quantitative calculation of  $V_{ii}$  are often based on the point-charge model (PCM). Such an interpretation of the EFG measurements depends on the applicability of anti-shielding factors; it could only provide crude information on a possible charge transfer (ionicity) and ignores covalency. Therefore, it is desirable to calculate the EFG in an *ab initio* approach. Since the EFG is very sensitive to the anisotropic charge distribution close to the probe-nucleus, for its accurate calculation the entire electronic configuration of the

host, perturbed by the presence of the impurity, has to be determined. This can be done in the frame of the density-functional theory. Examples of this kind of calculations are the works of Sato *et al.* (Cd in TiO<sub>2</sub>) [1] and Lany *et al.* (group V acceptors in CdTe) [2].

In 1999, we began a systematic study using the Full-Potential Linearized-Augmented-Plane Waves (FP-LAPW) method of the EFG at Cd impurities in binary oxides (<sup>111</sup>Cd is widely used in PAC experiments), starting with TiO<sub>2</sub> using a super-cell consisting of two unit-cells (12 atoms) and a free-relaxation process of the oxygen nearest-neighbour atoms of the impurity [3]. This work was followed by a more detailed study using a 72-atoms super-cell and taking into account the charge-state of the impurity in a self-consistent way [4]. In this work we extend these calculations to Cd in rutile SnO<sub>2</sub>. We showed that in these systems this approach gives very good results in comparison to previously determined experimental data [5–7].

## 2. Method of calculation

Our aim was to calculate from first-principles the EFG tensor at a Cd impurity replacing Sn in rutile SnO<sub>2</sub> taking into account the structural relaxations introduced by the impurity in the host lattice. To deal with this problem we considered a periodically repeated super-cell containing a single Cd-atom and performed first-principles calculations in order to determine the self-consistent potential and the charge density inside the super-cell. We studied the relaxation introduced by the impurity computing the forces on the Cd neighbors and moving them until the forces vanish. The calculations were performed with the WIEN97 implementation [8] of the FP-LAPW method [9] and we worked in the LDA [10] approximation. In this method no shape approximation on either the potential or the electronic charge-density is made, being thus specially suited for EFG calculations. For methodological purposes the unit-cell is divided into non-overlapping spheres with radius  $R_i$  and an interstitial region. The atomic spheres radii used for Cd, Sn and O were 1.11, 1.05 and 0.85 Å, respectively. We took for the parameter  $RK_{MAX}$ , which controls the size of the basis-set in these calculations, the value of 6. The correctness of the choice of this parameters was checked by performing calculations for  $RK_{MAX} = 7$ . We also introduced local orbitals to include Sn-4*d* and 5*p*, O-2*s* and Cd-4*p* and 5*d* orbitals. Integration in reciprocal space were performed using the tetrahedron method taking 26 k-points in the first Brillouin zone. Once self-consistency of the potential was achieved, quantum-mechanical-derived forces were obtained according to Yu *et al.* [11] and the ions were displaced according to a Newton-damped scheme [12] and the new positions for Cd neighbors were obtained. The procedure was repeated until the forces on the ions were below a tolerance value taken as 0.025 eV/Å. At each position the  $V_{ii}$  elements of the EFG tensor are obtained directly from the  $V_{2M}$  components of the lattice harmonic-expansion of the self-consistent potential [13].

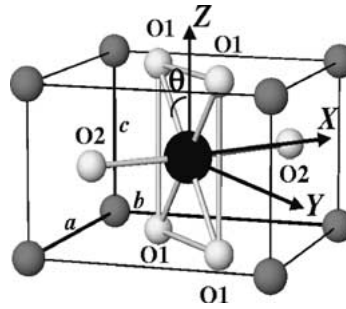


Figure 1. Unit cell of rutile  $\text{SnO}_2$  (Sn gray balls, O white balls). The results discussed in this work are referred to the indicated axes system, assuming that Cd replaces the central Sn atom.

There is still an important point to be taken into account concerning the calculation of the electronic structure: the charge state ( $q_I$ ) of the impurity system, in our case the double acceptor  $\text{Cd}^{2+}$  in  $\text{Sn}^{4+}\text{O}_2^{2-}$ . Pure  $\text{SnO}_2$  is a semiconductor with the oxygen  $p$ -band filled. When a Cd-atom replaces a Sn-atom in the super-cell, the resulting system is metallic because of the lack of two electrons necessary to fill the oxygen  $p$ -band. In the present work we present calculations for the case  $q_I = -2$  adding two electrons to the super-cell that we compensate with an homogeneous positive background in order to have a neutral cell. In ref. [4] we have explored and checked the validity of the charge-state simulation of the Cd-impurity for  $\text{TiO}_2$  replacing two oxygen atoms in the super-cell by fluorine atoms, obtaining similar results. This was also valid for this system.

### 3. Cell and super-cell

Rutile  $\text{SnO}_2$  is tetragonal ( $a = b = 4.7374_1 \text{ \AA}$ ,  $c = 3.1864_1 \text{ \AA}$ ), the unit cell (Figure 1) containing 2 Sn at positions  $2a$  (0, 0, 0) and  $(1/2, 1/2, 1/2)$  and 4 O at positions  $4f \pm(u, u, 0; u + 1/2, 1/2 - u, 1/2)$ , with  $u = 0.3056_1$  [14]. The super-cell considered in the present work consists of twelve unit-cells of  $\text{SnO}_2$  with one body-centered Sn atom replaced by the Cd atom. The resulting 72-atoms super-cell has dimensions  $a' = 2a$ ,  $b' = 2b$ ,  $c' = 3c$  and is also tetragonal with  $c'/a' = 1.009$  giving an almost cubic lattice. Even when the concentration of Cd is unrealistic compared with ppm dilutions of PAC experiments, this super-cell keeps Cd atoms as far as possible from each other ( $9.56 \text{ \AA}$ ) for the given cell volume.

## 4. Results and discussion

### 4.1. STRUCTURAL RELAXATIONS

Let us first consider the relaxation of the 6 oxygen nearest-neighbors (ONN) of the Cd impurity (O1 and O2 in Figure 1). Symmetry restricts O1 and O2 displacements to  $yz$  plane and  $x$  direction, respectively. In Table I, we present the results for this relaxation (2nd row). Looking at the columns 3, 4, and 5 in this table, we see that

Table I. Final distances of the ONN and EFG for Cd in SnO<sub>2</sub> in units of 10<sup>21</sup> V/m<sup>2</sup> for the different relaxations performed.  $d(\text{Cd-O1})$  and  $d(\text{Cd-O2})$  are the distances (in Å) from Cd to O1 and O2 atoms, respectively. In each case, all the coordinates within a radius  $R_C$  (in Å) are relaxed.  $N_A$  is the number of atoms that relax in each case. Sign and direction of the experimental values are unknown. “ $eq$ ” denotes the component of major absolute value.

$R_C$	$N_A$	$d(\text{Cd-O1})$	$d(\text{Cd-O2})$	$\theta$ (deg)	$V_{XX}$	$V_{YY}$	$V_{ZZ}$	$eq$	$\eta$
Unrelaxed	–	2.058	2.047	39.26	–0.89	+4.19	–3.30	+4.19	0.58
2.5	6	2.204	2.158	38.42	–2.94	+5.35	–2.41	+5.35	0.10
4.2	24	2.191	2.143	38.18	–3.46	+5.99	–2.53	+5.99	0.16
4.9	42	2.198	2.159	38.24	–2.79	+5.42	–2.63	+5.42	0.03

the oxygen atoms relax outwards along the Cd–O directions. Our results show that the relaxation is not isotropic. This result is similar to that found in a previous calculation of our group [4] for Cd in TiO<sub>2</sub>. In effect, in both cases the relaxations are not isotropic, and the final distances Cd–ONN are similar. In the case of TiO<sub>2</sub>, O2 atoms are nearer to the impurity at the end of the relaxation than O1 atoms, inverting the initial situation. In SnO<sub>2</sub>, O2 atoms are nearer to Cd in the un-relaxed structure, so the inversion does not exist, but the relaxation is also anisotropic.

To study the effect on the final positions of O1 and O2 of relaxing the coordinates of atoms beyond the nearest neighbours we performed two additional relaxations: first we allow to relax the coordinates of all atoms within a sphere of radius  $R_C = 4.2$  Å centered at Cd (this relaxation involves 24 atoms), and then we extended the radius of the sphere to 4.9 Å (42 atoms involved). For radii larger than 4.9 Å, the farthest atoms that would be relaxed would be nearer to the images of the Cd atom at neighbouring cells than to the Cd itself, so we consider this radius as a limit for the present super-cell. The comparison between the obtained results for both relaxations with the ones corresponding to the NN relaxation is presented in Table I. It is worthy of mention that in the case of Cd in SnO<sub>2</sub> (and TiO<sub>2</sub>), the amount of relaxation per atom decreases rapidly from the NN to other shells, leading to minor changes in the positions of O1 and O2 atoms.

#### 4.2. ELECTRIC FIELD GRADIENT

In Table I we show the results for the EFG  $V_{ii}$  components for Cd in SnO<sub>2</sub> for different relaxations. The different EFGs obtained for the relaxed and un-relaxed structures are very remarkable. In fact, the values obtained for the greatest absolute component of the EFG ( $eq$ ) and the asymmetry parameter  $\eta$  in the case of the ONN relaxation reproduce successfully the experimental values (see Tables I and II). This shows that taking into account the structural relaxations of the nearest-

Table II. Calculated and experimental EFG at Cd sites in rutile SnO<sub>2</sub> and TiO<sub>2</sub>. Atomic positions and lattice parameters used in PCM and LAPW calculations are listed in refs. [14] (SnO<sub>2</sub>) and [15] (TiO<sub>2</sub>).

	SnO <sub>2</sub>			TiO <sub>2</sub>		
	$eq$ ( $10^{21}$ V/m <sup>2</sup> )	$\eta$	Direction	$eq$ ( $10^{21}$ V/m <sup>2</sup> )	$\eta$	Direction
FP-LAPW	+5.35	0.10	Y	+4.52 [4]	0.27 [4]	Y [4]
PCM	+5.21	0.40	Y	-2.21	0.43	X
Experimental	5.83 <sub>4</sub> [7]	0.18 <sub>2</sub>	-	5.23 <sub>5</sub> [5]	0.18 <sub>1</sub>	-
				5.34 <sub>2</sub> [6]	0.18 <sub>1</sub>	-

neighbors oxygen atoms of the impurity is necessary in order to reproduce the experimental results.

In Table I we can observe that there is not any qualitative change in the results already discussed among the relaxations involving other neighbors. This shows that the EFG is mainly determined by the relaxation of the oxygen nearest-neighbours of the impurity atom. There are, however, small variations in the values predicted for the EFG. The differences between results from the 24- and 42-atoms relaxations are in part caused because in the second case the relaxation of O3 atom is allowed (atom O3 is the ONN of O2 atom in the  $x$  direction). The relaxation of O3 of about 0.04 Å allows a further relaxation of about 0.02 Å for the O2 atom. The fact that atom O3 is the one that experiments the larger relaxation (besides O1 and O2) shows that directional bonding plays an important role in this structure.

Finally, in Table II we compare the results of our calculations (for the NN relaxation) with the experimental PAC results and PCM calculations for SnO<sub>2</sub> and TiO<sub>2</sub>. Based on the PCM, one expect that the lattice of each compound gives an EFG that is only amplified by the Cd-Sternheimer anti-shielding factor. This model predicts very different EFG for Cd in TiO<sub>2</sub> and SnO<sub>2</sub>. However, the PAC experiments at Cd sites show similar EFG tensors for both compounds. The FP-LAPW calculations predicts also similar EFGs in the relaxed structures of both oxides, in agreement with the experimental data (see Table II). The *ab initio* approach gives the following explanation for this similarity: at the end of the structural relaxation the neighborhood of Cd is very similar in both compounds, and it is this fact that mainly determines the EFG tensor at Cd site.

## 5. Conclusions

*Ab initio* calculations of the EFG by the FP-LAPW method successfully predicted the experimental EFG at Cd impurity sites in rutile SnO<sub>2</sub> and, at the same time, yielded quantitative information on the lattice relaxation around the impurity. The relaxation is obtained directly by energy minimization and do not rely on the addi-

tional hypothesis often used in simple models. We showed that relaxations of the atoms from their original positions alter the EFG significantly, and for this reason, a free relaxation treatment of the distortion introduced by the impurity in its first shell of neighbors was revealed crucial in order to make EFG predictions. Similar to the case of Cd in rutile TiO<sub>2</sub>, the relaxation of these oxygen atoms is anisotropic, being their final positions very similar for both compounds. Finally, from the study of structural relaxations that involve an increasing number of shells of atoms we conclude that the EFG is mainly determined by the relaxation of the oxygen nearest neighbors to the Cd atom.

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**Note added in proof:** The EFG direction predicted by our FP-LAPW calculations at Cd sites in TiO<sub>2</sub> (see Table II) are in agreement with the EFG orientation determined in a single-crystal PAC experiment, reported after acceptance of this article in L. A. Errico *et al.*, *Phys. Rev. Lett.* **89** (2002), 55503.

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