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Ab initio FP-LAPW study of the semiconductors SnO and SnO_2

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Abstract

Structural and electronic properties of tin oxides, SnO and SnO_2, were studied using the full-potential linearized-augmented-plane-waves method within the local density and the generalized gradient approximations. Internal positional parameters, density of states and the electric-field gradient tensor at Sn sites were calculated. The results for the electronic and structural properties are compared to experimental measurements and with results obtained in different band-structure calculations.

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1. Introduction

Two tin oxide compounds, SnO and SnO_2, are known to crystallize under ambient conditions. Tin oxide films are of particular importance due to its applications in solar cells, gas-sensing element sensors, and electronic components. For these reasons, several theoretical and experimental studies have intensively developed (see e.g., Refs. [1–5] and references therein). Very recently, the interest in SnO_2 was renewed due to the discovery of high-temperature ferromagnetism in $Sn_{1-x}Co_xO_{2-\delta}$ films [6]. But, in order to separate the effects induced by the impurities or by the film surfaces on the properties of the oxides, it is necessary to study first the un-doped bulk materials. It is also important to know the accuracy and the failures of the methods of calculation employed.

In the present work we study the electronic structure of pure bulk SnO and SnO_2 based on first-principles solid-state calculations, using the full-potential linearized-augmented-plane-waves (FP-LAPW) method. In particular, we focused our attention on the determination of the internal atomic coordinates and the dependence of the electronic properties on them. The internal coordinates were determined by force minimization. The obtained results are in excellent agreement with those obtained by X-ray diffraction [7–10] and full-potential linear-muffin-tin-orbital (FP-LMTO) [4,5] and first-principles discrete-variational method (DVM) calculations reported in the literature [3]. Using these parameters we determined the electric-field gradient (EFG) tensor. The results for the EFG tensor are compared with those obtained in Mössbauer experiments [2] and in first-principles calculations [3,5].

2. The system under study and method of calculation

SnO is tetragonal ($a = b = 3.8029_5$ Å, $c = 4.8382_8$ Å, $c/a = 1.27$ [7]) in its most common variety (black SnO). The unit cell contains two formula units with the oxygen atoms placed at (0;0;0) and $(\frac{1}{2};\frac{1}{2};0)$ and tin atoms at $(0;\frac{1}{2};v)$ and $(\frac{1}{2};0;-v)$, with $v = 0.2369$ [7]. Other authors reported $v = 0.2384_{11}$ [8]. All Sn and O atoms are equivalent. In Fig. 1(a) we represent a portion of this oxide. The structure of SnO is made of layers and each Sn atom is at the apex of a square pyramid whose based is formed by four oxygen atoms. All Sn–nearest oxygen neighbors (ONN) distances are equal to 2.22 Å. Each oxygen ion is surrounded by four Sn ions.

Stannic oxide, SnO_2, has a rutile structure. Its symmetry is tetragonal ($a = b = 4.7374_1$ Å, $c = 3.1864_1$ Å, $c/a = 0.672$ [9,10]), with a flat unit containing two molecules,

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with the Sn atoms at positions 2*a*: (0;0;0) and ($\frac{1}{2};\frac{1}{2};\frac{1}{2}$) and the six O atoms at positions 4*f*: $\pm(u, u, 0; \frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2})$ with $u = 0.3056_1$ [9] or 0.3064_4 [10]. In this structure, the Sn atoms are surrounded by a slightly distorted oxygen octahedron with a rectangular basal plane of four oxygen atoms with distances to Sn (2.06 Å) slightly larger than those at the vertex (2.05 Å), see Fig. 1(b).

The electronic-structure calculations were performed with the FP-LAPW method [11] as embodied in the WIEN97 code [12], in a scalar relativistic version without spin-orbit coupling. Exchange and correlation effects were treated using both the local density [13] and the generalized gradient [14] approximations (LDA, GGA). 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 nonoverlapping spheres with radius R_i and an interstitial region. The atomic spheres radii used for Sn and O were 1.06 and 0.85 Å, respectively. The parameter RK_{MAX}, which controls the size of the basis-set in these calculations, was chosen as 9, which gave more than 4000 LAPW functions in the basis-set (R is the smallest muffin tin radius and K_{MAX} the largest wave number of the basis set). We introduced local orbitals to include Sn-4d and 5p and O-2s orbitals. Integration in reciprocal space was performed using the tetrahedron method taking 500 k points in the first Brillouin zone. The correctness of the choice of these parameters was checked by performing calculations for different RK_{MAX} values and increasing the number of k points. The V_{ii} elements of the EFG tensor were obtained directly from the V_{2M} components of the lattice harmonic expansion of the self-consistent potential [15].

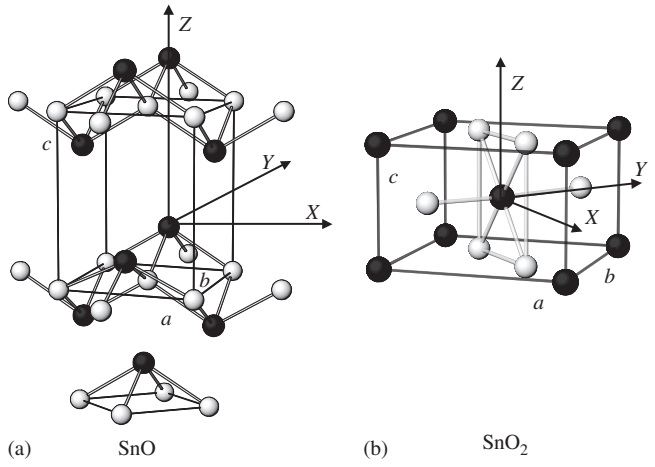

Fig. 1. Simplified ball and stick models of the crystalline structures of (a) black SnO (Sn gray balls, O white balls). Nearest-neighbor (NN) oxygen distribution around the cationic sites is also shown. (b) Crystalline structure of rutile SnO_2. The results discussed in this work are referred to the indicated axes system.

3. Results

3.1. Structural properties

As a first step of our study, we determined the internal positions of the atoms in SnO and SnO_2 by force minimization. To do this we calculated the self-consistent potential and then quantum-mechanical-derived forces were obtained according to Yu et al. [16] and the ions were displaced according to a Newton-damped scheme [17] and the new positions for atoms were obtained. The procedure was repeated until the forces on the ions were below a tolerance value taken as 0.001 eV/Å. We want to mention here that we also calculate the ideal c/a ratio predicted by FP-LAPW. The obtained results for c/a are in excellent agreement with the experimental result, so we decided to fix the lattice parameters at the experimental ones and minimize only the internal coordinates. The results obtained for the parameters u (SnO_2) and v (SnO) with both the LDA and GGA approximations are very similar and are in excellent agreement with the X-ray Diffraction results reported in the literature [7–10] (see

Table 1
FP-LAPW predictions for the internal parameter u and the EFG at Sn sites in pure SnO and SnO_2

	v	V_{33} (10^{21} V/m^2)	η	V_{33} direction	Δ_{eQ} (mm/s)
SnO					
FP-LAPW, LDA	0.2361	−17.29	0.00	*Z*	+1.18
FP-LAPW, GGA	0.2366	−17.75	0.00	*Z*	+1.21
FP-LMTO [5]	—	−16.37	0.00	*Z*	+1.12
DVM [3]	—	−38.3	0.00	*Z*	+2.62
Exp.	0.2369 [7]/0.2384_{11} [8]	—	—	—	1.356 [2]
SnO_2					
FP-LAPW, LDA	0.3060	+5.46	0.73	*Y*	−0.41
FP-LAPW, GGA	0.3054	+5.84	0.57	*Y*	−0.42
DVM [3]	—	+5.55	0.09	*Y*	−0.38
Exp.	0.3056 [9]/0.3064 [10]	—	—	—	0.45 [2]

All the FP-LAPW results for the EFG tensor correspond to the equilibrium positions predicted by FP-LAPW. The obtained results are compared with FP-LMTO and DVM cluster calculations. In order to obtain Δ_{eQ} from V_{ZZ} and η we used $Q = -0.109$ b [21]. Experimental sign of Δ_{eQ} is unknown.