

Ab initio study of Fe-doped SnO: Local structure and hyperfine interactions at the Fe nucleus

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ARTICLE INFO

Article history:

Received 3 February 2009

Received in revised form

11 May 2009

Accepted 6 August 2009

PACS:

71.20.Nr

75.50.dd

71.55.Ht

76.80.+y

71.15.-m

Keywords:

A. Semiconductors

C. *Ab initio* calculations

D. Electronic structure

ABSTRACT

In this work we perform an *ab initio* study of the electric field gradient (EFG) at the nucleus of Fe impurities in crystalline SnO. The Augmented Plane Waves plus Local Orbitals method is used to obtain the electronic structure of the doped system and the atomic relaxations introduced by the impurities in the SnO host in a fully self-consistent way. Most calculations are performed assuming that Fe ions replace the Sn atoms of the structure, in some cases including oxygen vacancies in order to discuss their role in the hyperfine interactions and in determining the local structure around Fe impurities. The case of interstitial Fe sites is also considered. Our predictions are compared with available Mössbauer spectroscopy results and also with theoretical and experimental results obtained for rutile SnO₂ and TiO₂.

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1. Introduction

There are two stoichiometric tin oxides (SnO and SnO₂) that crystallize under ambient conditions in the tetragonal litharge and rutile structures, respectively. These oxides are of considerable technological interest and have different industrial applications. Tin dioxide is used in many devices where transparent semiconductors are needed, such as thin heat-reflecting foils, transparent electrodes, gas sensors, and solar panels, among others. Applications of SnO have been less frequent because this oxide becomes unstable with temperature and undergoes a disproportionation reaction [1]. Three compounds are formed in different concentrations: SnO₂, β-Sn and an intermediate oxide containing tin in both 2+ and 4+ oxidation states [1]. As a consequence of this, in the past the physical properties of SnO have not been studied in the same detail as those of SnO₂. However, SnO powders are used as anode materials in lithium

rechargeable batteries, as coating materials or as catalyst for several acids.

In addition to the mentioned applications, the development of room-temperature ferromagnetism in semiconductor oxides has attracted considerable interest in recent years due to their potential application in spintronics [2]. Experimental results revealed ferromagnetic behaviour in *n*-type semiconductors such as Sn_{1-x}Co_xO₂ [3,4]. In fact, Ogale et al. [3] investigated thin films of Sn_{1-x}Co_xO₂ ($x < 0.3$) produced by pulsed-laser-deposition and found a strong ferromagnetic signal at 300 K with a magnetic moment of 7.5 μ_B/Co. Coey et al. [4] also reported room-temperature ferromagnetism in thin films of Sn_{1-x}Fe_xO₂ ($x = 0.05$) grown by the same method. The magnetic moment measured was 1.8 μ_B/Fe. In 2005, Punnoose et al. [5] reported the development of room-temperature ferromagnetism in chemically synthesized powder samples of Sn_{1-x}Fe_xO₂ ($0.005 < x < 0.05$). In addition, they also reported results for the hyperfine interactions at ⁵⁷Fe, measured by Mössbauer spectroscopy: an IS of 0.37 mm/s and a quadrupole splitting (Δ_{EQ}) of 0.85 mm/s, which agree with previous experimental results [6–8]. However, paramagnetic behaviour was observed in identically synthesized Sn_{1-x}Fe_xO samples. From the experimentally well-defined doublet shown in

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that paper we could derive an IS of about 0.4 mm/s and a Δ_{EQ} of about 0.7–0.8 mm/s. As far as we know, Punnoose's are the only reported Mössbauer experiments for ^{57}Fe in SnO. Little attention is given to the local structure around the dopants in that paper.

In this work we calculate the electronic structure of Fe in SnO in order to interpret the experiment in terms of the local structure around the impurity and the influence of oxygen vacancies. We use the *ab initio* Augmented Plane Waves plus Local Orbitals (APW+LO) method [9] to predict the hyperfine parameters at Fe-impurity sites, as we did previously in anatase TiO_2 , where by comparison with experimental results we could characterize the local structure around the Fe impurities [10]. Calculations were performed assuming that Fe ions replace Sn indigenous atoms of the structure and also with interstitial Fe sites. In all cases, the obtained equilibrium atomic positions, electronic structure of the systems and the hyperfine parameters at the Fe sites were compared with the experimental data and with results for Fe-doped rutile SnO_2 and TiO_2 . We thus consider systems in which the impurity has the same nominal valence as the indigenous Sn atom (SnO) and others in which Fe acts as a double-acceptor impurity.

2. Method of calculation

Two hyperfine parameters are determined in Mössbauer experiments: the isomer shift, which provides information on the local chemical bonds, and the quadrupole splitting, which is a “fingerprint” of the symmetry of the charge distribution around the Mössbauer probe-nucleus [11]. The quadrupole splitting is caused by the interaction of the nuclear quadrupole moment with the nonspherical part of the crystalline potential. For a transition from $l = 3/2$ to $1/2$, as in the case of the ^{57}Fe -Mössbauer experiments that we will discuss in Section 3, the quadrupole splitting is given by

$$\Delta_{EQ} = \frac{eQ}{2} V_{ZZ} \left(1 + \frac{\eta^2}{3} \right)^{1/2}. \quad (1)$$

Here Q stands for the largest component of the nuclear quadrupole moment tensor of the sensitive 14.4 keV excited state of ^{57}Fe and its value is $Q = 0.16b$ [12]. V_{ZZ} is the largest eigenvalue of the diagonalized electric field gradient (EFG) tensor. Its components V_{ii} are calculated as the second derivatives of the Coulomb potential surrounding the nucleus of interest, $V(\mathbf{r})$, with respect to the spatial coordinates [11]. η is the asymmetry parameter defined by

$$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}} \quad (2)$$

with the convention $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|$.

The isomer shift IS is given by [11]

$$\text{IS} = \alpha(\rho_a(0) - \rho_b(0)), \quad (3)$$

where $\rho_a(0)$ and $\rho_b(0)$ are the electron charge densities at the nuclear site for the absorber (a) and the source (b), respectively, and α is a calibration constant. To validate our calculation of the IS we started by calculating it on well-known Fe compounds such as γ -Fe, BCC-Fe, FeO and Fe_2O_3 using the same code and precision as in the rest of this work. We found a linear dependence of the IS with $[\rho_a(0) - \rho_b(0)]$, from which we obtain $\alpha = -0.25a_0^{-3}$ mm/s (a_0 being the Bohr radius), in very good agreement with previous results [13–15].

Black SnO is tetragonal, with space group $P4/nmm$ and unit cell parameters $a = b = 3.8029_5$ Å, $c = 4.8382_8$ Å, $c/a = 1.27$ [16]. The structure is composed of square pyramids containing one Sn atom atop of four oxygen atoms, as shown in Fig. 1. The oxygen nearest

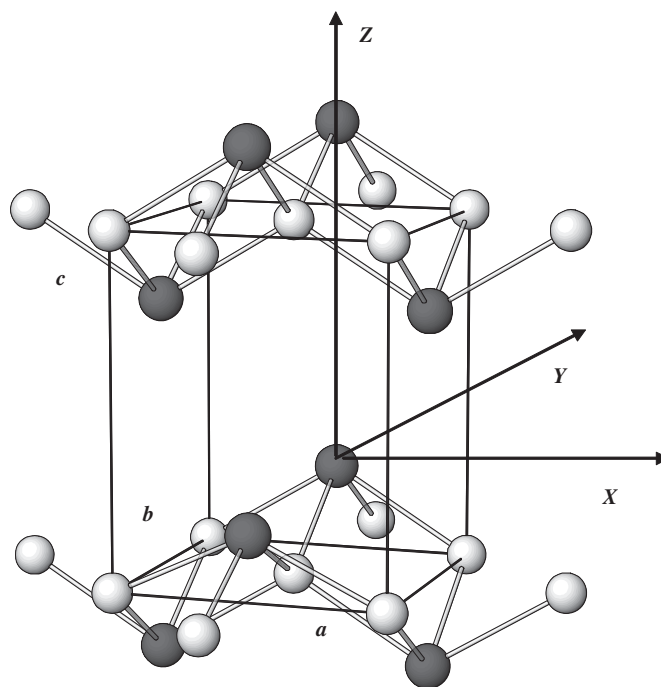


Fig. 1. Simplified ball and stick model of the crystalline structure of SnO. Black balls represent tin atoms and gray balls oxygen atoms.

neighbours to the Sn atom (ONN) are at 2.224_8 Å. The position of all atoms in the unit cell is determined by one internal parameter $u = 0.2374$ [16]: Sn at $(0; .5; -u)$ and $(.5; 0; u)$ and oxygen at $(0; 0; 0)$ and $(.5; .5; 0)$. This gives rise to a plate-like morphology where tin layers are separated by oxygen layers stacked along the c direction with relatively weak van der Waals-type interactions [17] between the Sn–O–Sn layers. The super-cell considered in the present work consists of eight unit cells of SnO with one Sn atom replaced (in the case of substitutional impurities) by Fe. The resulting 32-atom super-cell (SC) has dimensions $a' = 2a = b' = 2b = 7.6059$ Å, $c' = 2c = 9.6764$ Å, which gives a Fe concentration of about 6%.

We have performed the calculations assuming different scenarios. First, we analyse the effect of Fe substitution. Secondly, we consider the effect of both substitutional iron at metal sites and oxygen vacancies (in our calculations, the oxygen vacancy is created simply by taking out one oxygen atom from the super-cell). In the latter, we analyse two situations: (i) removing an oxygen atom located in the first coordination shell of Fe. (ii) Removing an oxygen atom in the second oxygen-coordination sphere of Fe, where the distance Fe–oxygen vacancy is 4.15 Å in the unrelaxed structure. The smallest distance between impurities or vacancies in different unit cells is 7.6 Å, and we consider it large enough to avoid interaction between replicas. However, calculations for selected systems using a unit cell of 108 atoms were also performed and nothing different showed up. We have also considered one case of interstitial Fe atoms, where the Fe atom is located at the centre of the cell shown in Fig. 1 and has four Sn nearest neighbours at 2.29 Å.

The spin-polarized and non-spin-polarized electronic structure calculations were performed with the *ab initio* code Wien2K [18]. Exchange and correlation effects were treated within Density-Functional Theory using the local spin density approximation (LSDA [19]). The muffin tin radii (R_t) used for Sn and Fe were 1.05 Å, while for O we used $R_t = 0.75$ Å. The parameter $R_{mt}K_{max}$, which controls the size of the basis set in these calculations, was chosen as 7 (R_{mt} is the smallest muffin tin radius and K_{max} the largest reciprocal lattice vector of the basis set). Integration in

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