

TDPAC study of Cd-doped SnO

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Abstract The combination of hyperfine techniques and ab initio calculations has been shown to be a powerful tool to unravel structural and electronic characterizations of impurities in solids. A recent example has been the study of Cd-doped SnO, where ab initio calculations questioned previous TDPAC assignments of the electric-field gradient (EFG) in ^{111}In -implanted Sn-O thin films. Here we present new TDPAC experiments at ^{111}In -difused polycrystalline SnO. A reversible temperature dependence of the EFG was observed in the range 295–900 K. The TDPAC results were compared with theoretical calculations performed with the full-potential linearized augmented plane wave (FP-LAPW) method, in the framework of the density functional theory. Through the comparison with the theoretical results,

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we infer that different electronic surroundings around Cd impurities can coexist in the SnO sample.

Keywords SnO · Cd · TDPAC · Electric-field gradient

1 Introduction

The study of the interaction of the atomic nucleus with extra nuclear fields has proven to be quite useful in many contexts [1, 2]. Nuclear resonance and spectroscopic techniques, such as nuclear quadrupole resonance (NQR), nuclear magnetic resonance (NMR), Mössbauer spectroscopy (MS), and time-differential perturbed-angular correlations (TDPAC), have been extensively applied to study materials from the point of view of solid state physics, chemistry, and biology, in order to elucidate the microscopic environment of constituent or impurity atoms in solids [3–5]. The experimental information can be compared very often with theoretical calculations where the electric quadrupole interactions can be characterized by two hyperfine interaction parameters describing the electric-field gradient (EFG) tensor at a given nuclear site: the asymmetry parameter $\eta = |V_{11} - V_{22}|/V_{33}$, with $|V_{11}| < |V_{22}| < |V_{33}|$, where V_{ii} are the components of the EFG tensor in the axis system where the tensor is diagonal, and V_{33} that is the largest component of the EFG tensor and is usually named EFG.

In 1991, Rentería et al. [6] performed a series of TDPAC and MS experiments in Sn-O thin films that underwent different disproportionate thermal treatments in air before each measurement. In these experiments, the authors found that two oxidation states of Sn coexisted in these films. Furthermore, the initially disordered SnO and SnO₂ phases were transformed into the crystalline SnO₂ phase by appropriate annealing treatments. However, the hyperfine interaction parameters of ¹¹¹Cd located at an undisturbed SnO environment could not be definitely characterized. Since different phases coexisted in the sample, multiple interactions were necessary to reproduce the whole set of experimental results. One interaction (that appeared in these films within a very small window of annealing treatments) was characterized by an asymmetry parameter $\eta = 0.0$ and was attributed to Cd replacing a Sn atom at the unique axially symmetric cationic site of SnO. But this interaction showed a very large EFG distribution and represented only 10% of the probes implanted in these films. Also, the TDPAC spectra, obtained always at room temperature, were strongly dampened along all the series of annealing treatments (probably due to the presence of electron-capture after-effects). Under these circumstances, it is very difficult to guarantee the site assignment reported for that interaction. In these complex cases theory can be of great help since reliable calculations assuming different structural and electronic scenarios can be compared with the experimental results. Very recently three of us [7] have studied the EFG tensor at substitutional Cd impurities in SnO through state-of-the-art all-electron methods. Since the reported experiments were not conclusive about the hyperfine interaction assigned to substitutional Cd localized at free of defects cationic sites in crystalline SnO, we suggested that new and accurate experiments were necessary.

In this work we present a series of TDPAC experiments to study the Cd-doped SnO semiconductor. These new TDPAC results are compared with previous TDPAC experiments and ab initio calculations, performed with the Full-Potential Linearized

Augmented Plane Wave (FP-LAPW) method, reported in the literature [7]. Through this analysis we are lead to the interesting fact that different electronic surroundings around Cd impurities can coexist in the SnO sample.

2 Sample preparation and measurements

SnO is tetragonal ($a = b = 3.79982(9)$ Å, $c = 4.816(1)$ Å [8]). The unit cell contains two formula units with the oxygen atoms placed at (0; 0; 0) and (1/2; 1/2; 0) and the tin atoms at (0; 1/2; v) and (1/2; 0; $-v$), with $v = 0.2374(8)$ [8]. The structure of SnO is made of layers in which each Sn atom is at the apex of a square pyramid whose base is formed by four oxygen atoms. All Sn-nearest oxygen neighbors (ONN) distances are equal to 2.22 Å.

In order to obtain the Cd-doped SnO samples, $^{111}\text{InCl}_3$ was dropped onto a SnO (99% purity) powder pellet and thermally diffused undergoing a thermal annealing in Ar atmosphere (10^{-3} Torr) in seven steps from 423 to 1,000 K. The temperature dependence of the EFG was measured afterwards in the range 295–1,000 K using a conventional slow-fast coincidence TDPAC spectrometer with four conical BaF_2 detectors. The previous diffusion process was also monitored by TDPAC. The experimental $R(t)$ perturbation functions were derived from eight (of 12 possible) concurrently measured coincidence spectra, four taken between detectors positioned with 180° symmetry and four with 90° symmetry. To analyze the measured perturbation functions we used a multiple-site model for nuclear–electric–quadrupole interactions, polycrystalline samples, spin $I = 5/2$ intermediate level and considering the Båverstam and Othaz *after-effects* model for dynamic hyperfine interactions [9, 10]. Both the starting powder and the doped pellet after the whole set of TDPAC measurements were subjected to x-ray diffraction (XRD) characterizations. XRD results show that the sample, before and after the thermal treatments, consist of pure and crystalline SnO. In effect, only the lines of SnO were present in the diffractograms. Principal lines corresponding to SnO_2 , to the intermediate tin oxides (Sn_3O_4 , Sn_2O_3), or to metallic tin were not observed.

3 Results and discussion

Figure 1 shows the $R(t)$ spectra and their corresponding Fourier transforms taken at the indicated selected temperatures after the whole diffusion process. The dampening of the $R(t)$ signal at low temperatures, very well described in the whole temperature range of measurement by a dynamic perturbation factor [9, 10], is correlated with the presence of the well-known $^{111}\text{In} \rightarrow ^{111}\text{Cd}$ electron-capture decay after-effects, already observed and studied in detail in ^{111}In -doped polycrystalline SnO₂ [11, 12]. Two well-defined hyperfine interactions (HFI) were found to be necessary in order to reproduce the experimental $R(t)$ spectra in the whole temperature range of measurements. These interactions are well defined (low EFG distributions of 1% were fitted in the 900 K $R(t)$ spectrum, value kept fixed at lower temperatures), their populations are constant in the temperature range studied, and both interactions are characterized by small asymmetry parameters that goes to zero (as predicted by the crystal symmetry of SnO) at high temperatures (see Fig. 2). At 295 K, the values

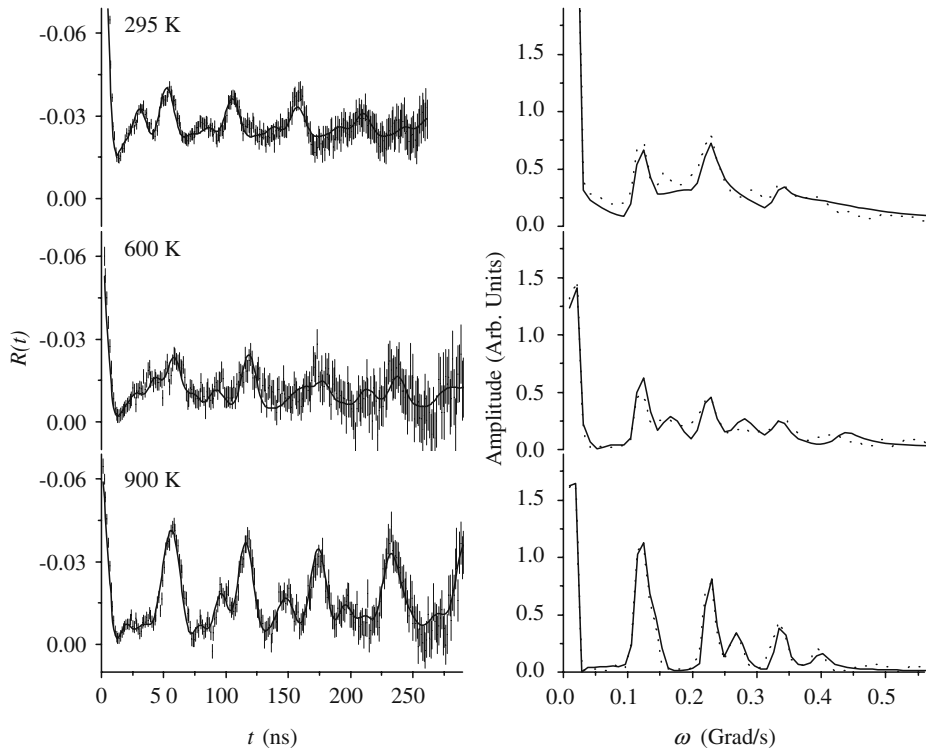


Fig. 1 $R(t)$ spectra (left) and their corresponding Fourier transforms (right) of ^{111}Cd probes in SnO at the indicated measuring temperature after the diffusion thermal annealing series. Solid lines in the $R(t)$ spectra are the best least-squares fits of dynamic perturbation factors [9, 10] to the experimental data. Solid lines in the Fourier spectra come from the Fourier transform of the $R(t)$ fits

of V_{33} (HFI1) and V_{33} (HFI2) are $5.7(9) \times 10^{21}$ and $8(1) \times 10^{21}$ V/m², respectively. The behavior of the observed hyperfine interactions is the typical one for probes located at substitutional sites, and then we can tentatively assign HFI1 and HFI2 to Cd located at cationic sites of SnO. But we must explain why two interactions are present, considering that there is only one cationic site in the structure. In order to elucidate this point, we will compare our experimental results with ab initio calculations.

Before making the comparison of our TDPAC results with the ab initio calculations, there is an important point we want to comment related with the charge state of the Cd impurity in the host system. As it was reported in [7], it is initially assumed that when a neutral Cd substitutes Sn in SnO, it takes the same oxidation state as Sn in this compound. We will name this charge state “neutral charge state” ($q = 0$). But it is known that the presence of defects like vacancies, interstitial Cd or Sn atoms, other impurities, etc., can modify the impurity charge state. For this reason in [7] additional ab initio calculations were performed, removing ($q = +1$) or adding ($q = -1$) one electron to the whole super cell.

Accordingly to the ab initio calculations, the substitution of a Sn atom by a Cd impurity in the super cell produces structural distortions in the SnO host, especially in

Fig. 2 Evolution of the hyperfine parameters of interactions HFI1 and HFI2 (see text) found in ¹¹¹Cd-doped polycrystalline SnO as a function of the measuring temperature *T*. *Q* = 0.83(14) b [13] was used to obtain *V*₃₃ from the experimental nuclear-quadrupole frequency ω_Q

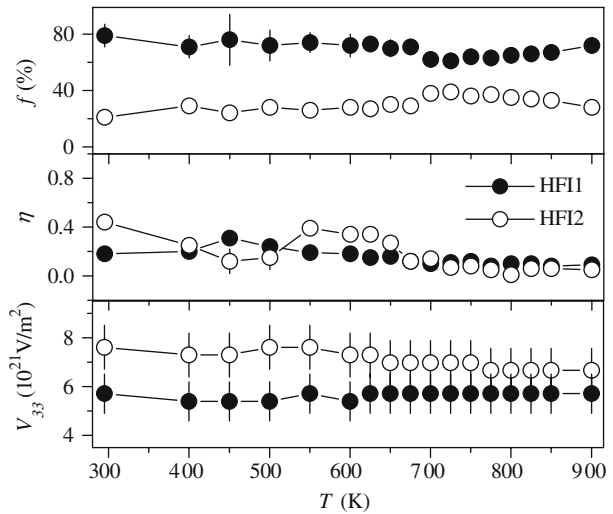


Table 1 Distances from Cd to its nearest oxygen neighbors, *d* [Cd-ONN], EFG (*V*₃₃) and asymmetry parameter η at the Cd site obtained in the FP-LAPW calculations [7] for three different charge states (see text), compared with experimental TDPAC results at 295 K obtained in this work

	<i>d</i> [Cd-ONN] (Å)	<i>V</i> ₃₃ (10 ²¹ V/m ²)	η
32-atoms supercell [7]			
<i>q</i> = −1	2.38	−4.3	0.0
<i>q</i> = 0	2.26	+6.2	0.0
<i>q</i> = +1	2.24	+10.4	0.0
Experiment (295 K)			
HFI 1	–	5.7 (9)	0.18 (1)
HFI 2	–	8 (1)	0.44 (2)

Q = 0.83(14) b [13] was used to obtain *V*₃₃ from the experimental nuclear-quadrupole frequency ω_Q . The sign of the experimental *V*₃₃ is unknown. Large uncertainties in *V*₃₃ are essentially due to the error of *Q*

the Cd-ONN bond-lengths. For easy reference we repeat here some relevant results obtained in [7] and the relaxed Cd-ONN distances are shown in Table 1 (we note that, as mentioned before, the nearest neighbors distance in undoped SnO is 2.22 Å). The largest component of the EFG tensor, *V*₃₃, and the asymmetry parameter η are also shown. As can be seen in Table 1, the Cd-ONN distance and the EFG depend on the charge state of the impurity. The effect of the extra-electron is to change the Coulomb repulsion: when one electron is added to the system (*q* = −1), the Coulomb repulsion increases and, as a consequence, the Cd-ONN distances are enlarged causing a decrease in the magnitude of the EFG (this can cause also, as in the present case, a change in the EFG sign); on the other hand, when one electron is removed (*q* = +1), the bond-length is reduced and the EFG becomes larger than in the case of the neutral cell. It is important to mention that, for the same atomic positions, the EFG is nearly independent of the charge state of the impurity [7]. Preliminary calculations performed during the writing of the present work with a larger super cell of 108 atoms show that size effects in the 32-atoms

super cell reported in [7] are small, and no significant variations in the structural relaxations and the EFG should be expected if calculations in even larger super cells are considered. The most important modification between the results obtained in the two calculations is that the EFG corresponding to $q = +1$ changes by the order of 20% towards smaller values.

If we compare the experimental results with the ab initio predictions, we can see that HF11, the interaction with the higher population, presents hyperfine parameters very similar to those predicted for Cd impurities located at cationic sites in SnO in a neutral charge state ($q = 0$). HF12 (the interaction with 20% of population) can also be assigned to Cd impurities located in cationic sites, but in a different charge state, most probably in this case, $q = +1$. From these results we can infer that all probes are located at substitutional sites in the SnO structure, but with different electronic environments. These different environments could be associated with the presence of defects in the sample (other impurities, vacancies, interstitials atoms), which produce a different charge state in a sub-ensemble of Cd probes. The charge state ($q = +1$) is not completely unexpected to be present in 20% of the Cd probes. In effect, the charge state $q = +1$ (a Cd atom with an electron hole) exists for 80% of the ^{111}Cd probes at least during a certain period of time before the Cd^{+n} probe (which has several electron holes) achieves the final neutral charge state $q = 0$ after the “switch-off” of the dynamic interactions. These dynamic interactions are originated in the relaxation of the several electronic holes produced in the ^{111}Cd shells after the electron-capture decay of ^{111}In . It is possible that a certain amount of probes (20%) can not reach this $q = 0$ state, due to the presence of acceptor defects in the neighborhood of these probes.

4 Conclusions

In this work we presented new TDPAC experiments in tin monoxide (SnO) using ($^{111}\text{In} \rightarrow$) ^{111}Cd as probe. The accuracy of the present experiments enables us to successfully characterize the EFG at Cd probes substitutionally located at cation sites in crystalline and single-phase SnO samples. Two well-defined hyperfine interactions were found in the temperature range 295–900 K. Ab initio calculations enable us to assign the most populated interaction to Cd probes located at Sn sites in a neutral charge state. The second interaction can also be associated to Cd substitutionally located at cation sites in SnO but, in this case, in a charged state. New experiments, performed at lower temperatures and as a function of different concentrations of acceptor and donor impurities are in progress in order to validate our interaction assignments.

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