

Electron spin resonance parameters of cation vacancies in tin dioxide doped with fluorine and hydrogen

Viacheslav Golovanov, Viktoria Golovanova, Mikael Kuisma, and Tapio T. Rantala

Citation: *J. Appl. Phys.* **114**, 143907 (2013); doi: 10.1063/1.4824745

View online: <http://dx.doi.org/10.1063/1.4824745>

View Table of Contents: <http://jap.aip.org/resource/1/JAPIAU/v114/i14>

Published by the AIP Publishing LLC.

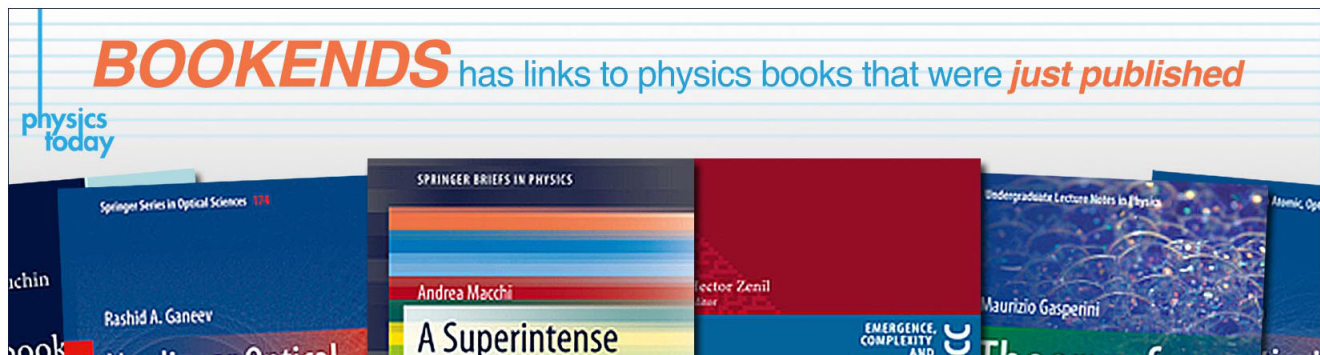
Additional information on J. Appl. Phys.

Journal Homepage: <http://jap.aip.org/>

Journal Information: http://jap.aip.org/about/about_the_journal

Top downloads: http://jap.aip.org/features/most_downloaded

Information for Authors: <http://jap.aip.org/authors>



Electron spin resonance parameters of cation vacancies in tin dioxide doped with fluorine and hydrogen

Viacheslav Golovanov,^{1,2} Viktoria Golovanova,² Mikael Kuisma,¹ and Tapio T. Rantala¹

¹*Department of Physics, Tampere University of Technology, P.O. Box 692, FI-33101 Tampere, Finland*

²*Center of Innovation Technologies, South-Ukrainian University, Staroportofrankovskaya Str., 26, 65008 Odessa, Ukraine*

(Received 18 July 2013; accepted 24 September 2013; published online 11 October 2013)

The spin Hamiltonian parameters of intrinsic defects in tin dioxide (SnO₂) doped with fluorine or hydrogen are examined through the first-principles electronic structure calculations based on density functional theory (DFT). The electron paramagnetic resonance signals with g -tensor value in the range of 1.89–1.94 were found for tin vacancy (V_{Sn}) and its complex with oxygen vacancy ($V_{\text{Sn}}\text{-}V_{\text{O}}$) associated with a donor like interstitial hydrogen or fluorine, substituting oxygen. The calculated parameters are consistent with experimental observations, which indicate that Sn vacancies may be present in SnO₂ at essentially higher concentration than it is predicted by DFT based on the formation energies calculations. Within the second coordination shell of the tin vacancy, the V_{O} may stabilize in the singly ionized charge state, which is otherwise considered to be unstable for isolated oxygen vacancy in the bulk of SnO₂. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4824745>]

I. INTRODUCTION

Tin dioxide (SnO₂) is a wide-band-gap semiconductor which has found a wide variety of practical applications, e.g., as a transparent conducting electrode in solar cells and flat panel displays as well as in gas sensors.^{1–3} One aspect that is recently attracting considerable attention both experimentally and theoretically concerns the nature of n -type conductivity in this material that may originate either from intrinsic defects like oxygen vacancies or extrinsic hydrogen impurities.^{4–6} The charge transfer at these defects is often associated with appearance of paramagnetic species, which can be detected in electron paramagnetic resonance (EPR) experiments.^{7,8} Though electron paramagnetic resonance can provide detailed information about concentrations, chemical identity, and lattice environment of a defect or impurity, the interpretation of the EPR signals requires dedicated expertise, and possibly for that reason, till present there are some discrepancies concerning the structure of paramagnetic centers in SnO₂.

Ivanovskaya *et al.*⁹ and Popescu *et al.*¹⁰ attributed the weak EPR signal with the g factor around 2.00 to a singly ionized oxygen vacancy (V_{O}^+) in the crystal lattice. By contrast, Canevali *et al.*^{11,12} associate V_{O}^+ with a symmetrical resonance line observed at $g = 1.89$. According to numerous calculations,^{4–6} the singly ionized oxygen vacancy is unstable with respect to neutral or doubly ionized state at all conditions, which raises the question of the abundance of isolated V_{O}^+ in a pure SnO₂ bulk crystal. On the other hand, it is plausible to assume that V_{O}^+ defect may stabilize in less symmetrical environment in SnO₂ material, especially as the corresponding EPR signal has been detected experimentally.

The density functional theory (DFT) calculations are important tools providing an independent insight into magnetic properties of materials and, therefore, are indispensable complements to the experimental studies. Recently, we have demonstrated¹³ that under assumption that bulk V_{O}^+ would exist in SnO₂, its isotropic g tensor must be reassigned to a typical

F-center value around 2.00. In contrast, the strong experimental signal at 1.89, reported in a number of preceding papers, is likely to be caused by some other paramagnetic center, which stimulates a quest for defects that can be candidates for stable magnetic centers in tin dioxide. The first-principles calculations¹⁴ showed that neutral cation vacancies in SnO₂ can induce ferromagnetism, provided that concentration of Sn vacancies would be high. It is worth noting, that Sn vacancy has high formation energy and according to DFT calculations, its most stable charge state in n -type material is 4.¹⁵ On the other hand, Varley *et al.*¹⁶ demonstrated that hydrogenated cation vacancy is lower in energy than isolated V_{Sn} and interstitial hydrogen will likely combine with an existing Sn vacancy to form $(V_{\text{Sn}}\text{-H})^{-3}$ complex.

EPR experiments indicate that 1.89 signal increases in the temperature range of 100–300 °C after treatments in dry H₂, CO, and wet argon.^{17,18} Such treatments obviously lead to formation of both oxygen vacancies and hydrogen dopants in SnO₂. Moreover, treatments of SnO₂ films in oxygen atmosphere significantly affect the magnetic ordering.^{19,20} EPR measurements²¹ revealed four symmetrical resonance lines with g -factor values 1.89, 1.91, 1.928, and 1.94, which are developing in gradually reduced SnO₂. Since oxygen deficiency is associated with formation of oxygen vacancies, it can be deduced that oxygen vacancies have obvious impact on the spin polarization of tin dioxide. Therefore, and motivated by the importance to understand the nature of the most abundant magnetic centers in tin dioxide to the function of any SnO₂ based spintronic device, we generate models of the complexes, including hydrogen atoms, tin, and oxygen vacancies in SnO₂ bulk and predict their properties using DFT calculations.

II. METHODS AND MODELS

The computational first-principles density functional (DFT) approaches applied here are based on the plane wave

basis set with pseudopotential concept (CASTEP code),²² and the projector augmented wave method,²³ as implemented in the VASP code.²⁴ Using two different computational codes allows us to exploit the strengths of the both codes and achieve a method-independent understanding of the structure and properties of SnO₂. The CASTEP software uses ultrasoft pseudopotentials²⁵ and enables considerably limit the plane wave basis set²⁶ with cutoff of 380 eV. Electronic exchange and correlation are included there by the Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA) allowing possible spin polarization.²⁷ The VASP software allows efficient use of hybrid PBE0 functional that incorporates 25% of exact Hartree-Fock exchange. The cutoff of the plane wave basis sets was set to 700 eV. In both CASTEP and VASP calculations, the Brillouin zone is sampled with $3 \times 1 \times 3$ mesh of Monkhorst-Pack special k points. In separate test calculations, the number of irreducible k -points was increased up to 6 ($2 \times 2 \times 3$ mesh), which does not alter the obtained results. For charged systems, the negative charge of the unit cell is balanced by using constant background positive charge density.

A unit cell Sn₄O₈ is chosen for convenience of future modeling of the surface of the crystal instead of the conventional primitive cell Sn₂O₄ with different orientations. This choice will, in future, allow us to model the most abundant (110) surface using the same orientation in the slab model. These issues are discussed elsewhere²⁸ in more detail. The computational supercell (Sn₄O₈)₈ is a $1 \times 4 \times 2$ multiple of the chosen unit cell, thus containing 96 atoms. Test calculations were performed with smaller supercell of (Sn₄O₈)₄, which is a $1 \times 4 \times 1$ multiple of the chosen unit cell. All structures considered are relaxed while keeping the lattice parameters fixed at pre-optimized values $a = 4.715$ Å, $c = 3.143$ Å for PBE and $a = 4.754$ Å, $c = 3.185$ Å for PBE0.

The formation energy (E^f) of a vacancy V_X in charge state q in SnO₂ is defined as follows:

$$E^f = [E^{\text{tot}}(V_X, q) - E^{\text{tot}}(\text{SnO}_2)] + \mu_X + q\varepsilon_F, \quad (1)$$

where $E^{\text{tot}}(V_X, q)$ and $E^{\text{tot}}(\text{SnO}_2)$ represent the total energies of the supercell containing a vacancy in the charge state q , and that of a perfect crystal in the same supercell. The atom X removed from the crystal is placed in a reservoir with energy $\mu_X = \mu_X^{\text{el}} + \Delta\mu_X$, where μ_X^{el} is referenced to the energy per Sn atom in the β -phase of bulk tin (for $X = \text{Sn}$) or to the chemical potential of oxygen, which is equal to $1/2 E^{\text{tot}}(\text{O}_2)$ for $X = \text{O}$. The growth conditions are reflected in the chemical potentials μ_X , which can range from O-rich (Sn-poor) to Sn-rich (O-poor) conditions. If compound system is sufficiently large to constitute a particle reservoir for itself, the chemical potentials of the two components are also interrelated by

$$\Delta\mu_{\text{Sn}} + 2\Delta\mu_{\text{O}} = \Delta H_f(\text{SnO}_2), \quad (2)$$

where $\Delta H_f(\text{SnO}_2)$ is the formation enthalpy of SnO₂. In order to change the charge state of the defect, electrons are exchanged with the Fermi level ε_F , which is conventionally referenced to the valence-band maximum (VBM) and ranges

over the band gap from the VBM up to the conduction band minimum.

The prediction of the EPR g -tensor values for paramagnetic defects is done with Kohn-Sham DFT-based implementation of the g -tensor for periodic systems (BAND code).²⁹ The Zeeman g -tensor is represented using two-component approach of Van Lenthe *et al.*³⁰ in which the g -tensor is computed from a pair of spinors related to each other by time-reversal symmetry. We used the TZ2P triple-zeta valence basis set extended by polarization functions and “small” value for frozen core option, i.e., for Sn atom, core has been frozen up to 4p-orbitals, and for oxygen and fluorine atoms up to 1s-orbitals. Hydrogen was included with all electron set. The g -tensor is then computed from the HOMO spinor at the gamma point. Electronic exchange and correlation are included here by the PBE-GGA scheme.

III. RESULTS

SnO₂ crystallizes with the rutile structure, wherein the tin atoms are six coordinated and the oxygen atoms are three coordinated. Herewith, Sn atom occurs in a distorted octahedral coordination and following the notations used in Ref. 16, we denote four oxygen atoms with equal Sn–O bonds as equatorial (O-eq) and two oxygen atoms with longer equal bonds as axial (O-ax), see Figure 1(d). The perfect SnO₂ crystal is regarded as a nonmagnetic and wide band-gap material with all valence bands completely filled with electrons, while the conduction bands are unoccupied. Removing the tin atom caused formation of four holes at O sites of the nearest coordination shell and origin of partially occupied states within the band gap, which can accept up to four electrons depending on the position of Fermi level in the gap.

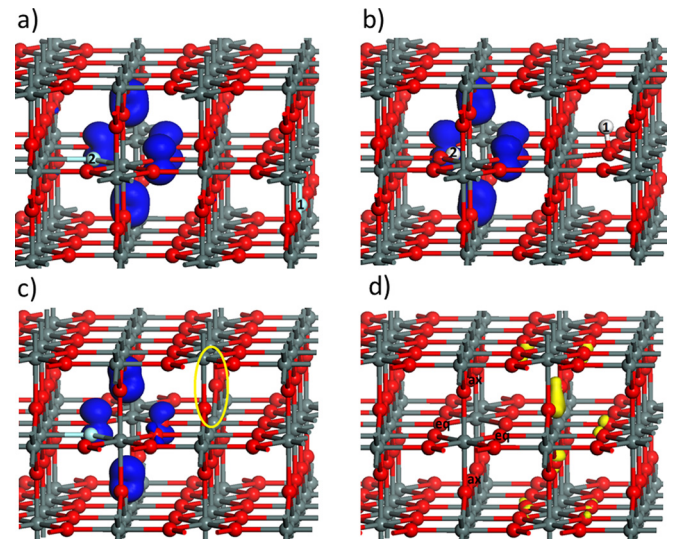


FIG. 1. Isosurfaces of spin density distributions ($0.05 \text{ e } \text{\AA}^{-3}$) of SnO₂ supercell with (a) V_{Sn} and F_{O} located distantly in position (1) or $F_{\text{O-eq}}$ substituting equatorial O atom (2); (b) V_{Sn} and hydrogen interstitial located in position (1) or within the first coordination sphere of V_{Sn} (2); (c) $((V_{\text{Sn-FO-eq}})^{-3}-V_{\text{O}}^{+2})$ and (d) $(V_{\text{Sn}}^{-4}-V_{\text{O}}^{+})$ defect complexes. The gray spheres represent tin atoms and the red spheres oxygen atoms. Fluorine and hydrogen are depicted in cyan and white, respectively. The isovalue surface of the V_{O}^{+} spin density (shown in yellow) is localized in the empty space remaining after removal of the oxygen ion from the bulk (open yellow circle).

Since periodic BAND code does not allow the computation of g tensor within the background charge model, we have used the fluorine or hydrogen dopants in order to introduce the charge into the supercell. The Mulliken population analysis performed with CASTEP code for substitutional fluorine donor (F_O) and interstitial hydrogen (H_i) in pure bulk, their several configurations with tin vacancy (F_O and H_i in positions marked (1) and (2) in Figs. 1(a) and 1(b)), V_{Sn} and V_{Sn}^{-1} (in the presence of negative background charge in the supercell) are presented in Table I. By comparison of the charge values, it can be deduced that F_O dopant provides an extra electron, which is delocalized in the perfect bulk, but trapped at oxygen atoms surrounding the Sn vacancy, when V_{Sn} is presented in the same supercell. Interstitial hydrogen behaves similarly, except slight increasing of the negative charge on the nearest-neighbor oxygen atom observed in position (1), which may be related to quasi-hydroxyl conformation.

The replacement of the one equatorial or distant O atom with fluorine enriches Sn vacancy with one extra electron to compensate one hole among the four holes generated by the Sn deficiency. The corresponding spin distribution is similar for the two cases (1) and (2) as reflected in Fig. 1(a). Accordingly, we find an integrated spin density of 3.00 differ from ~ 4.00 calculated for the neutral V_{Sn} . Therefore, we can conclude that disregard on the position of the substituting fluorine atom (F_O), the main effect of such doping is providing of one extra electron to the supercell.

It must be noted that the calculations based on GGA-PBE scheme are underestimating the band gap and also give defect wavefunctions that are too delocalized. Both effects are due to a lack of self-interaction correction. Accordingly, we found that four holes trapped at the Sn vacancy are delocalized over all six oxygen neighbors. The use hybrid PBE0 functional essentially corrects the band gap and the localization errors. This results in accurate spin distribution picture and band gap of 3.6 eV in good agreement with experiment. Nevertheless, we can conclude that both methods produce qualitatively similar results.

Calculation of the g tensor for V_{Sn} - F_{O-eq} complex gives a value of 1.89 in excellent agreement with experimental observations. This finding may indirectly point out on the V_{Sn}^{-1} defect as a source for such paramagnetic signal in pristine SnO_2 . Although tin vacancy is a deep acceptor, it would be presumptuous to practically exclude existence of V_{Sn} in

the charged states other than -4 , e.g., in defect complexes or in a strong depletion mode, which is in fact typical for polycrystalline films with nanosized grains. It must be mentioned that isolated V_{Sn} has high formation energy and according to DFT calculations, its *equilibrium* concentration should be negligible at the temperatures probed in the EPR experiments.

In principle tin vacancies may be present in SnO_2 in none-equilibrium concentrations because most of the growth techniques operate far from the equilibrium conditions in their final stages. However, the corresponding EPR signals with g -tensor in the range of 1.89–1.94 appear essentially after the treatments associated with formation of both oxygen vacancies and hydrogen dopants in SnO_2 . The estimated amount of the paramagnetic centers responsible for EPR signal with $g = 1.89$ increases up to $5 \times 10^{17} \text{ cm}^{-3}$ after treatment in dry 0.5%-CO atmosphere at 500 °C.¹⁷ Furthermore, EPR experiments indicate that 1.89 signal increases significantly in the temperature range of 100–300 °C after treatments in dry H_2 .^{17,18} The high formation energy suggests that V_{Sn} is unlikely to form significant concentrations at the above mentioned conditions. On the other hand, hydrogen interstitials and oxygen vacancies have much lower formation energies and migration barriers. These facts make it likely that H_i and V_O , which are formed in the temperature range of 100–500 °C, after treatments in H_2 and CO, will combine with V_{Sn} preexisting in the material. The formation energies of the hydrogenated cation complexes are always much lower than the isolated V_{Sn} , suggesting that these complexes are likely to form. According to Ref. 15, hydrogen can either bond to one of the two axial O atoms surrounding the vacancy or one of the four equatorial O atoms, but the latter configuration has lower energy and, therefore, it is more abundant in SnO_2 (Fig. 1(b)). The calculated g -tensor value for such arrangement is 1.9 for smaller $(Sn_4O_8)_4$ supercell and 1.94 for larger $(Sn_4O_8)_8$ supercell, which is in the range of experimentally observed values. Comparison of the total magnetic moments and integrated spin densities for the different supercell sizes points out on the ferromagnetic coupling between the defects provided that their concentration is high, i.e., their separation is less than 6 Å. This finding corroborates the earlier conclusion of Rahman *et al.*¹⁴

In order to clarify the role of oxygen vacancies, we have calculated the g tensor values for the same defects as in Figs. 1(a) and 1(b), but with oxygen vacancy in the second coordination shell (Fig. 1(c)). Note that there are several possible conformations (not shown) that produce qualitatively similar results. We found that oxygen vacancy located close by the V_{Sn} donates its two electrons to the tin vacancy. The Coulomb attraction drives formation of the $(V_{Sn}^{-2}-V_O^{+2})$ defect pair, where two out of the four holes generated by V_{Sn} are compensated by the two electrons of V_O . Doping of this double defect with fluorine or hydrogen leaves behind a single hole at tin vacancy and caused formation of the paramagnetic centers with one unpaired spin remaining at the $((V_{Sn}-H)^{-2}-V_O^{+2})$ defect complex. The calculated g tensor values for these complexes doped with F and H are 1.86 and 1.89, respectively. The latter is in excellent agreement with experiment, which indicates that hydrogen impurities may

TABLE I. Mulliken population-derived charges (|e|) for the various scenarios from Figs. 1(a)–1(d).

Defect	O-eq	O-ax	F_O	H_i	O-bulk (Ref)
V_{Sn}	−0.64	−0.69	...	...	−0.95
V_{Sn}^{-1}	−0.72	−0.69	...	...	−"
F_O	...	...	−0.57	...	−"
$F_{O1}-V_{Sn}$	−0.71	−0.68	−0.57	...	−"
$F_{O2}-V_{Sn}$	−0.72	−0.69	−0.56	...	−"
H_i	...	...	...	+0.37	−"
$H_{i1}-V_{Sn}$	−0.70	−0.69	...	+0.38	−"
$H_{i2}-V_{Sn}$	−0.71	−0.71	...	+0.42	−"

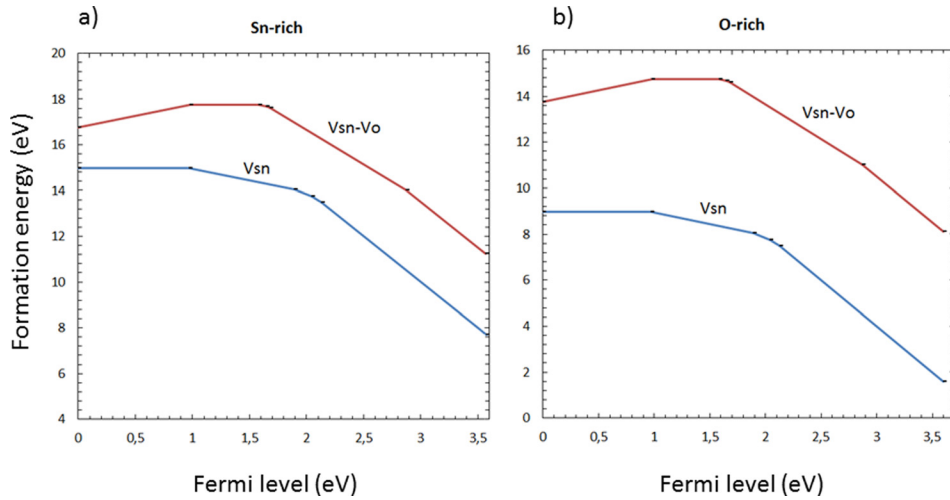


FIG. 2. Formation energies for tin vacancies and their complexes with oxygen vacancies in SnO_2 , shown in the limit of (a) O-rich and (b) Sn-rich conditions.

indeed stimulate the observed EPR signals in SnO_2 material. On the other hand, our results indirectly point out on the $(V_{\text{Sn}}^{-3}-V_{\text{O}}^{+2})$ defect as a source for such paramagnetic signal in pristine SnO_2 .

The adding of the three electrons to the supercell with $(V_{\text{Sn}}-V_{\text{O}})$ defect pair results in the compensation of three holes at tin vacancy. The remaining hole is balanced with one electron donated by the oxygen vacancy, which results in formation of $(V_{\text{Sn}}^{-4}-V_{\text{O}}^{+})$ complex. Thus, the oxygen vacancy may stabilize in singly ionized charge state in the proximity of Sn vacancy as opposed to the isolated bulk calculations (Fig. 1(d)). This fact is intriguing since it is widely believed that V_{O}^{+} are not expected to be stable and present in tin dioxide in any sizable concentrations.

The feasibility of the $(V_{\text{Sn}}-V_{\text{O}})$ configurations has been estimated through the calculation of their defect transition energies. To reproduce the experimental band gap, which is essential for the estimation of the defect formation energies, we have performed these computations with hybrid PBE0 functional. The potential alignment and finite-size correction were included according to scheme proposed in Ref. 31. The corresponding results are presented in Figure 2. The highest transition level of the $(V_{\text{Sn}}^{-4}-V_{\text{O}}^{+})$ complex in bulk is calculated at 0.68 eV below the conduction band minimum, which indicates that such conformations with singly ionized oxygen vacancy can be abundant even in the high conductivity mode. On the other hand $(V_{\text{Sn}}^{-3}-V_{\text{O}}^{+2})$, complexes or isolated V_{Sn}^{-1} vacancies, which can be associated with paramagnetic signals in the range of 1.89–1.94, are stabilized only when the system undergoes a strong electron deficiency. Such a strong depletion mode can be reached in polycrystalline films with nanosized grains and is actually a favorable operation regime for the SnO_2 -based chemical sensors.

The spin polarized DOS for V_{Sn}^{-1} and $(V_{\text{Sn}}^{-3}-V_{\text{O}}^{+2})$ defect complexes are presented in Figs. 3(a) and 3(b). The doping of V_{Sn} and $(V_{\text{Sn}}-V_{\text{O}})$ with hydrogen or fluorine (not shown) leads to qualitatively similar results. The most intriguing charges are seen around the Fermi level. The DOS for V_{Sn}^{-1} defects are spin split and the holes at the neighboring O ligands are localized for spin up, while they are partially localized for spin down electrons. The s-orbitals of Sn atoms surrounding the V_{Sn} couple antiferromagnetically with

the nearest O atoms and contribute to the peak at 0.5 eV above the VBM. The oxygen vacancy generates the peak at 1.4 eV above the VBM, which is associated with different coupling between the Sn vacancy and oxygen vacancy in the $(V_{\text{Sn}}-V_{\text{O}})$ defect pair. Note that observed half-metallic behavior of the DOS may be important for spintronic applications.

IV. CONCLUSIONS

In summary, we find that hydrogenated tin vacancies and their complexes with oxygen vacancies form paramagnetic centers with g tensor value in the range of 1.89–1.94. The paramagnetic properties also arise from doping of the V_{Sn} or double defect $(V_{\text{Sn}}-V_{\text{O}})$ with fluorine, which enriches

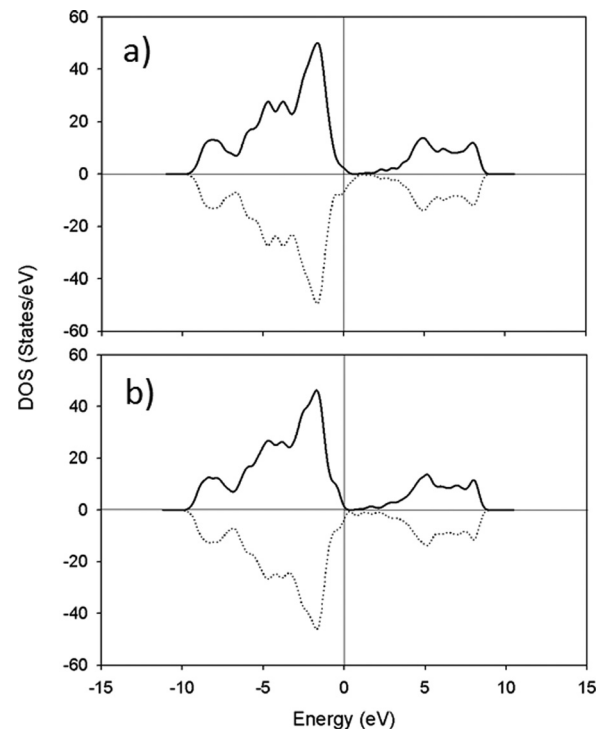


FIG. 3. Total DOS for (a) V_{Sn}^{-1} and (b) $(V_{\text{Sn}}^{-3}-V_{\text{O}}^{+2})$ defect complexes. Solid and dotted lines show density of states for spin up and spin down, respectively.

system with an odd electron. The corresponding EPR signals has been recorded by diverse groups at various temperatures from the tin dioxide structures prepared by different techniques, which points out on the abundance and stability of the corresponding defects in tin dioxide material. The important consequence from this finding is that Sn vacancies may exist in SnO₂ in significant amount of about 10^{17} cm^{-3} . This fact is at variance with negligible V_{Sn} concentration predicted by DFT calculations based on the estimation of defects equilibria from their formation energy. In contrast with isolated bulk case, the oxygen vacancy may stabilize in the singly ionized charge state in the $(V_{\text{Sn}}-V_{\text{O}})$ complex.

Further calculations of g tensor with background charge model and hybrid PBE0 functional are underway, which aim at clarifying the role of hydrogen impurity as indispensable part of this paramagnetic complex. The results may be important for the discussion about the abundance of uncontrolled hydrogen impurities in SnO₂. We will examine the coupling between such centers, which may be the reason for the experimentally observed room temperature ferromagnetism in undoped SnO₂.

ACKNOWLEDGMENTS

This work was supported by FP7-PEOPLE Marie Curie International Incoming Fellowship Program (project MOEBIUS). Computational resources were provided by the CSC—IT Center for Science, Espoo, Finland.

- ¹A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, and H. Pettersson, "Dye-sensitized solar cells," *Chem. Rev.* **110**, 6595–6663 (2010).
- ²B. Lewis and D. Pain, "Applications and processing of transparent conducting oxides," *MRS Bull.* **25**(8), 22–27 (2000).
- ³*Solid State Gas Sensing*, edited by G. Sberveglieri (Springer, New York, 2009), p. 337.
- ⁴C. Kilic and A. Zunger, "Origins of coexistence of conductivity and transparency in SnO₂," *Phys. Rev. Lett.* **88**(9), 095501 (2002).
- ⁵A. Singh, A. Janotti, M. Scheffler, and C. Van de Walle, "Sources of electrical conductivity in SnO₂," *Phys. Rev. Lett.* **101**, 055502 (2008).
- ⁶P. Agoston, K. Albe, R. Nieminen, and M. Puska, "Intrinsic n -type behavior in transparent conducting oxides: A comparative hybrid-functional study of In₂O₃, SnO₂, and ZnO," *Phys. Rev. Lett.* **103**, 245501 (2009).
- ⁷E. Konstantinova, I. Pentegov, A. Marikutsa, M. Romyantseva, A. Gaskov, and P. Kashkarov, "EPR study of nanocrystalline tin dioxide," *Phys. Status Solidi C* **8**(6), 1957–1960 (2011).
- ⁸A. Kar, S. Kundu, and A. Patra, "Surface defect-related luminescence properties of SnO₂ nanorods and nanoparticles," *J. Phys. Chem. C* **115**, 118–124 (2011).
- ⁹M. Ivanovskaya, P. Bogdanov, G. Faglia, P. Nelli, G. Sberveglieri, and A. Taroni, "On the role of catalytic additives in gas sensitivity of SnO₂-Mo based thin film sensors," *Sens. Actuators B* **77**, 268–274 (2001).
- ¹⁰D. Popescu, J. Herrmann, A. Ensueque, and F. Bozon-Verduraz, "Nanosized tin dioxide: Spectroscopic (UV, VIS, NIR, EPR) and electrical conductivity studies," *Phys. Chem. Chem. Phys.* **3**(12), 2522–2530 (2001).
- ¹¹C. Canevali *et al.*, "Mechanism of sensing NO in argon by nanocrystalline SnO₂: Electron paramagnetic resonance, Mossbauer and electrical study," *Sens. Actuators B* **100**, 228–235 (2004).

- ¹²N. Chiodini, C. Canevali, F. Morazzoni, R. Scottia, and C. Bianchi, "Defect chemistry in ruthenium-supported tin dioxide: A spectromagnetic approach," *Int. J. Inorg. Mater.* **2**(4), 355–363 (2000).
- ¹³N. Özcan, T. Kortelainen, V. Golovanov, T. T. Rantala, and J. Vaara, "Electron spin resonance parameters of bulk oxygen vacancy in semiconducting tin dioxide," *Phys. Rev. B* **81**, 235202-10 (2010).
- ¹⁴G. Rahman, V. Garcia-Suarez, and S. Hong, "Vacancy-induced magnetism in SnO₂: A density functional study," *Phys. Rev. B* **78**, 184404 (2008).
- ¹⁵W. Oo, S. Tabatabaei, M. McCluskey, J. Varley, A. Janotti, and C. Van de Walle, "Hydrogen donors in SnO₂ studied by infrared spectroscopy and first-principles calculations," *Phys. Rev. B* **82**, 193201 (2010).
- ¹⁶J. Varley, H. Peelaers, A. Janotti, and C. Van de Walle, "Hydrogenated cation vacancies in semiconducting oxides," *J. Phys.: Condens. Matter* **23**, 334212–334219 (2011).
- ¹⁷C. Canevali, N. Chiodini, P. Di Nola, F. Morazzoni, R. Scotti, and C. Bianchi, "Surface reactivity of SnO₂ obtained by sol-gel type condensation interaction with inert, combustible gases, vapor-phase H₂O and air, as revealed by electron paramagnetic resonance spectroscopy," *J. Mater. Chem.* **7**(6), 997–1002 (1997).
- ¹⁸P. Di Nola, F. Morazzoni, R. Scotti, and D. Narducci, "Paramagnetic point defects in SnO₂ and their reactivity with the surrounding gases. Part 1.—Interaction of oxygen lattice centers with vapor-phase H₂O, air, inert and combustible gases, as revealed by electron paramagnetic resonance spectroscopy," *J. Chem. Soc., Faraday Trans.* **89**(20), 3711–3713 (1993).
- ¹⁹N. Hong, N. Poirot, and J. Sakai, "Ferromagnetism observed in pristine SnO₂ thin films," *Phys. Rev. B* **77**(3), 033205 (2008).
- ²⁰A. Sundaresan, R. Bhargavi, N. Rangarajan, U. Siddesh, and C. Rao, "Ferromagnetism as a universal feature of nanoparticles of the otherwise nonmagnetic oxides," *Phys. Rev. B* **74**, 161306(R) (2006).
- ²¹E. Frolova and M. Ivanovskaya, "Structural defect formation in inorganic sol-gel derived oxides," *Defects Diffus. Forum* **242–244**, 143–158 (2005).
- ²²V. Milman, B. Winkler, J. A. White, C. J. Pickard, M. C. Payne, E. V. Akhmatkaya, and R. H. Nobes, "Electronic structure, properties, and phase stability of inorganic crystals: A pseudopotential plane-wave study," *Int. J. Quant. Chem.* **77**, 895–910 (2000).
- ²³P. E. Blöchl, "Projector augmented-wave method," *Phys. Rev. B* **50**, 17953–17979 (1994).
- ²⁴M. Marsman, J. Paier, A. Stroppa, and G. Kresse, "Hybrid functionals applied to extended systems," *J. Phys.: Condens. Matter* **20**, 064201 (2008).
- ²⁵D. Vanderbilt, "Soft self-consistent pseudopotentials in a generalized eigenvalue formalism," *Phys. Rev. B* **41**, 7892–7895 (1990).
- ²⁶M. Mäki-Jaskari, T. T. Rantala, and V. Golovanov, "Computational study of charge accumulation at SnO₂ (110) surface," *Surf. Sci.* **577**, 127–138 (2005).
- ²⁷J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R., Pederson, D. J. Singh, and C. Fiolhais, "Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation," *Phys. Rev. B* **46**, 6671–6687 (1992).
- ²⁸M. Viitala, O. Cramariuc, T. T. Rantala, and V. Golovanov, "Small hydrocarbon adsorbates on SnO₂(110) surfaces: Density functional theory study," *Surf. Sci.* **602**, 3038–3042 (2008).
- ²⁹E. Kadantsev and T. Ziegler, "Implementation of a DFT based method for the calculation of Zeeman g -tensor in periodic systems with the use of numerical and Slater type atomic orbitals," *J. Phys. Chem. A* **113**(7), 1327–1334 (2009).
- ³⁰E. van Lenthe, A. van der Avoird, and P. E. S. Wormer, "Density functional calculations of molecular g -tensors in the zero order regular approximation for relativistic effects," *J. Chem. Phys.* **107**, 2488 (1997).
- ³¹C. Freysoldt, J. Neugebauer, and C. G. Van de Walle, "Fully *ab initio* finite-size corrections for charged-defect supercell calculations," *Phys. Rev. Lett.* **102**, 016402 (2009).