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DIGITAL OBJECT IDENTIFIER
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The article by Thorne Lay and Hiroo Kanamori is an interesting one. It discusses the energy released by the 1994 Northridge earthquake. The authors claim that the energy released was approximately five times as much as the 1906 San Francisco earthquake. However, they do not provide any references to support their claim. In fact, the 1906 earthquake released more energy than the 1994 earthquake. The authors' calculations are based on a model that is not supported by the data. Therefore, the parameters of the damage extend into the future when the released energy to that which became struck by the ball as its momentum ceased and passed energy to the struck item. Therefore the parameters of the damage extend into a new event. Perhaps calculations of one added that in while another's calculations did not. E.M.C.
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The origin of the electron distribution in SnO

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Gradient corrected density functional theory calculations have been performed on SnO in the litharge and idealized CsCl structures with the litharge structure in good agreement with experiment. The CsCl structured SnO has a spherical electron density whereas the litharge structured SnO has a nonspherical electron distribution. Such asymmetry is often attributed to a sterically active lone pair formed by the $5s^2$ electrons which does not take part in chemical bonding. However, analysis of the density of states and band structures indicates that the situation is more complicated. In CsCl structured SnO mixing of the Sn $5s$ with the oxygen $2p$ electronic states results in filled bonding and antibonding combinations. The antibonding combinations, at the top of valence band, can interact with Sn $5p$ to stabilize the structure, only when in the distorted litharge structure resulting in the asymmetric electron density. This is in contrast to the classical theory of hybridization of the tin $5s$ and $5p$ orbitals to form a ‘lone pair’ as the asymmetric electron distribution is the result of the tin–oxygen covalent interactions. © 2001 American Institute of Physics.
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INTRODUCTION

Elements toward the bottom of groups 14 can, in addition to displaying the +4 oxidation state expected for their group, display an oxidation state two lower.¹ Tin and lead form compounds with oxidation states of both +2 and +4 as is demonstrated by the occurrence of two oxides, PbO_2 and PbO and SnO_2 and SnO . Indeed all the elements from group 14 show an oxidation state of +2 with their reactivity reducing down the group. Carbon forms carbenes, but these are very reactive intermediates in organic chemistry. Silicon forms similar compounds but these are also highly reactive. Compounds of Ge, Sn and Pb are more stable. $GeCl_2$ reacts rapidly at 25 °C with Cl_2 forming $GeCl_4$ while $SnCl_2$ reacts slowly. $PbCl_2$ is stable and will only react with Cl_2 to form $PbCl_4$ under extreme conditions.² It is clear from this that the M(II) compounds for group 14 elements become more stable on moving down the group.

The +2 oxidation state is associated with the concept of an inert s^2 electron pair.³ This ‘lone pair’ is considered to form from hybridization of the s and p atomic orbitals with the s^2 electrons filling one of the resulting orbitals. This lone pair is considered to be chemically inactive, not taking part in the bond formation but sterically active.⁴ The hybridization causes the lone pair to lose its spherical symmetry and is projected out one side of the cation resulting in asymmetry in the metal coordination and distorted crystal structures.

The most commonly employed model for the lone pair is the electronic lone pair localization (ELPL) model⁵ which considers the crystal to be ionic with a nonrecoverable point charge located at the atoms core and a second point charge which responds to the crystal's electric field and represents the lone pair. The formation of the lone pair is thus considered to be purely an electrostatic phenomenon as the point charge responds to the asymmetric electrostatic field within the crystal. From these calculations the location of lone pairs

has been determined for distorted crystal structures⁶ but direct calculation of the stabilization of the crystal cannot be achieved. In addition these models provide no information on the electronic effects of the lone pairs on chemical reactivity and thus represent a mechanism of locating the lone pair once their existence has already been established.

The thermodynamically stable phase of SnO has a distorted tetragonal crystal structure⁷ known as the litharge structure with two formula units per unit cell and a $P4/nmm$ space group. The structure can be thought of as a $\sqrt{2} \times \sqrt{2}$ supercell of the CsCl structure [Fig. 1(a)]. The c -axis is then elongated with the layer of tin atoms split in half forming the structure shown in Fig. 1(b). Both the tin and oxygen are four coordinate in SnO rather than the eight coordination found in CsCl, with the oxygen at the center of a distorted tetrahedra. All four coordinating oxygens are on the same side of the lead with the lone pair occupying the position on the opposite side.

Not all Sn(II) compounds show this type of asymmetric structure. For example compounds of tin formed with the group 16 elements, SnX ($X=O, S, Se, Te$), change from highly distorted SnO through to cubic SnTe. It could be suggested that from the absence of a lone pair in SnTe that the formation and stability of the lone pair is not as simple as the hybridization arguments suggest, as this would imply lone pair formation for all Sn(II) compounds. Indeed previous calculations by us on PbO ⁸ indicated that this simplistic view is wrong with the majority (around 70%) of the Pb $6s$ character directly involved in chemical bonding with the oxygen.

Previous calculations have been made on the SnX ($X=O, S, Se, Te$) series using the density functional theory and tight binding.⁹ This study, although detailed in its investigation, only considered the observed crystal structures for the materials and thus could not comment on the origin of the lone pair formation for a given material. The full potential linear muffin tin orbital (FP-LMTO) approach has also

FIG. 1. Illustration of the structure of (a) CsCl structured SnO and (b) litharge structured SnO. Tin atoms are light, while oxygen atoms are dark.

been applied to the electronic structure of SnO.¹⁰ Although they calculated the band structure their main interest was vibrational frequencies and again they did not comment on the lone pair. In this study we directly compare the electronic structure of SnO in its thermodynamically stable phase (litharge), which shows a highly distorted Sn site, with the idealized CsCl structured SnO.

THEORETICAL METHODS

Our calculations are based on the density function theory (DFT) method as implemented in the code VASP.^{11–13} The Kohn–Sham equations¹⁴ were solved self-consistently using an iterative matrix diagonalization method with the exchange and correlation energy evaluated within the Generalized Gradient Approximation (GGA) using the parameterization of Perdew *et al.*¹⁵

The calculations were performed within periodic boundary conditions allowing the expansion of the crystal wave functions in terms of a plane wave basis set. To reduce the number of plane waves required to represent the oscillations of the valence orbitals near the core we have employed ultra-

TABLE I. Convergence test results showing the variation in volume and binding energy (per formula unit) for CsCl SnO and litharge SnO and a function of (a) plane wave cutoff and (b) k -point sampling density.

(a) Cutoff	CsCl SnO		Litharge SnO	
	Energy (eV/Sn)	Volume ($\text{\AA}^3/\text{Sn}$)	Energy (eV/Sn)	Volume ($\text{\AA}^3/\text{Sn}$)
300	−9.979	30.36	−11.543	37.36
400	−9.980	30.37	−11.544	37.25
500	−9.982	30.35	−11.547	37.32

(b) k -point grid	CsCl SnO		Litharge SnO	
	Energy (eV/Sn)	Volume ($\text{\AA}^3/\text{Sn}$)	Energy (eV/Sn)	Volume ($\text{\AA}^3/\text{Sn}$)
$6 \times 6 \times 6$	−9.983	30.33		
$8 \times 8 \times 8$	−9.980	30.37		
$10 \times 10 \times 10$	−9.977	30.38		
$4 \times 4 \times 4$	−11.544	37.23		
$6 \times 6 \times 6$	−11.544	37.25		
$8 \times 8 \times 8$	−11.544	37.24		

soft pseudo potentials^{16,17} (US-PP) to represent the valence-core interactions. The pseudo potentials were derived from scalar relativistic calculations with all of the electrons except the $5s^2$ of Sn considered to be part of the tin core and all except the $2s^2$ and $2p^4$ part of the oxygen core.

The forces on the atoms and the stress tensor were calculated using the Hellmann–Feynman theorem and used to perform a conjugate gradients or quasi-Newton relaxation until the forces on the atoms had converged to less than 0.01 eV/ $\text{\AA}$ and the pressure on the cell had equalized (a , b and c are allowed to relax within the constraint of constant volume).

Convergence of the calculation was checked by calculating the equilibrium structure for a number of plane wave energy cutoffs and a number of k -point grids, which were obtained using the Monkhorst–Pack¹⁸ method, and will be detailed in the next section.

OPTIMIZATION OF THE LATTICE VECTORS

Optimization in VASP was performed at constant volume but allowed the lengths (and angles) of the lattice vectors to vary within this constraint. This effectively equalizes the pressure in each direction and thus allows the calculation of the energy as a function of volume. From these data the equilibrium lattice vectors and bulk modulus were obtained with convergence of the calculation checked with respect to both the plane wave cutoff and the number of k -points.

To investigate the effect of the plane wave cutoff on the energy and equilibrium lattice vectors, we have evaluated the variation of the energy as a function of volume for three cutoffs—300 eV, 400 eV and 500 eV. For these calculations we used a k -point sampling grid of $8 \times 8 \times 8$ for the CsCl structure and $6 \times 6 \times 6$ for litharge structured SnO. The resulting equilibrium volume and energy for each cutoff are shown in Table I(a) and clearly show that the calculations are

TABLE II. Comparison of calculated and experimental structural properties of SnO.

Property	CsCl SnO	Litharge SnO	
	Calculated	Experimental	Calculated
Binding energy (eV/Sn)	-9.976	-	-11.544
Volume ($\text{\AA}^3/\text{Sn}$)	30.366	34.985	37.0
a ($\text{\AA}$)	3.120	3.803	3.8496
b ($\text{\AA}$)	3.120	3.803	3.8496
c ($\text{\AA}$)	3.120	4.838	5.0271
Sn (Z)	-	0.2382	0.2300
Sn-O distance ($\text{\AA}$)	8×2.702	4×2.224	4×2.245

well converged with a cutoff of 400 eV. To ensure accuracy all of the following calculations have been performed at this cutoff.

k -point testing was performed in a similar way. Using the chosen cutoff of 400 eV we performed calculations at three different k -point grids for each of the structures, $6 \times 6 \times 6$, $8 \times 8 \times 8$, and $10 \times 10 \times 10$ for CsCl SnO and $4 \times 4 \times 4$, $6 \times 6 \times 6$, and $8 \times 8 \times 8$ for litharge structured SnO [Table I(b)]. The calculations are well converged with the intermediate grids, so that further calculations were performed using k -point grids of $8 \times 8 \times 8$ for CsCl SnO and $6 \times 6 \times 6$ for litharge SnO.

Using a cutoff of 400 eV and k -point sampling of $8 \times 8 \times 8$ for CsCl structured SnO and $6 \times 6 \times 6$ for litharge SnO the equilibrium structures were calculated and are given in Table II along with experimental data where available. The binding energies clearly show that the calculations predict that the tetragonal phase is more stable than the cubic CsCl structure as expected for the thermodynamically stable phase. The predicted lattice vectors and the only free internal coordinate (the Z coordinate) are in good agreement with experimental observations⁷ for the tetragonal phase. The a vector is overestimated by only 0.3% while the c vector is overestimated by 3.9%. The overestimation of these parameters is typical for calculations performed within the generalized gradient approximation which tends to overcompensate for the overbinding of the local density approximation. As may be expected the length of weak bonds, such as interaction between the Sn-O layers, is overestimated more significantly than that of strong bonds leading to a somewhat larger error for the c lattice vector.

The electron densities calculated by VASP are shown for slices through planes containing Sn atoms in Fig. 2(a) for the CsCl structured SnO and Fig. 2(b) for litharge structured SnO. For CsCl structured SnO the electron density around the Sn is clearly spherical. In contrast, that of the tetragonal phase forms an enhanced density on the side of the Sn atom that points away from the SnO layers and toward each other. This asymmetric electron distribution could be attributed to the classical $5s^2$ lone pair which would thus be interpreted as directing the layered structure, i.e., stereo chemically active.

ELECTRONIC STRUCTURE OF SnO

To simplify the interpretation of the electronic structure, in addition to the total electronic density of states (EDOS)

FIG. 2. Electron density contour plot through a plane containing lead atoms. (a) Spherical distribution around the tin atoms in CsCl structured SnO and (b) distribution in litharge structured SnO showing the spherical-like electron density within the oxygen planes and the distorted distribution around the lead atoms below the oxygen planes. Contour levels are shown between 0 and $0.30e/\text{\AA}^3$ at $0.05e/\text{\AA}^3$ steps.

we have also calculated the partial (ion and l -quantum number decomposed) electronic density of states (PEDOS). These were obtained by projecting the wave functions onto spherical harmonics centered on each atom with a radius of $1.55 \text{ \AA}$ for both atom types and both structures (Fig. 3). These radii were chosen because they give rise to reasonable space filling, but the results (at least the qualitative aspects) are insensitive to a change of the radii. The total EDOS shows that CsCl structured SnO has no band gap with a low density of states across the Fermi energy indicating that it is

FIG. 3. Electronic density of states and partial electron density of states for (a) CsCl structured SnO and (b) litharge structured SnO.

semi-metallic while litharge structured SnO has a small band gap of 0.6 eV. This is in line with x-ray photoelectron spectroscopy¹⁹ which shows that on reduction of SnO₂, which has a band gap of 3.6 eV, additional features that are attributed to the Sn 5s states appear close to the Fermi level, giving rise to a much smaller gap between the occupied and unoccupied states. Recent photoemission spectra²⁰ has also studied the valence states of SnO and again show a small band gap with a significant contribution of the Sn 5s to the states just below the Fermi level.

The basic feature of the EDOS are similar for the two structures. The lowest energy bands correspond to O 2s (−18 to −16 eV). The next peak (between −9 and −6 eV) is derived mainly from the Sn 5s orbital. Finally, the third set of peaks from −6 eV to the Fermi energy is primarily due to the O 2p states with the Sn 5p orbitals responsible for the states above the Fermi level. This is broadly in line with a simple ionic model for SnO in which the two electrons

from Sn 5p have been transferred to the oxygen.

Detailed examination of the PEDOS, however, reveals that this is oversimplistic with significant mixing of the stated between −9 eV and the Fermi energy. The peak between −9 and −6 eV is found to be around 30%–50% O 2p in character indicating that the bonding has a high degree of covalency. The peaks between −6 and the Fermi energy can be divided into to different sets. At lower energy (−6 to −3 eV) are states primarily O 2p in origin with some mixing of the Sn 5p again indicating a small degree of covalency. The peak just below the Fermi level (−3 to 0 eV) is quite different. It gives rise to a high density of states at the Fermi energy and is composed of primarily O 2p character with the remaining Sn 5s character. This band appears to be the filled antibonding combination of the peak between −9 and −6 eV. The major difference between the two EDOS is in this area just below this Fermi surface; the filled antibonding states. In the case of litharge structured SnO there is addition mixing of the Sn 5p into these states which results in a shift of the density away from the Fermi energy indicating a stabilization effect. It is this shift in energy that gives rise to the small band gap and corresponds to the Sn 5s character seen experimentally just below the top of the valence band.^{19,20}

The difference between the two EDOS is close to the Fermi surface where there is some Sn 5s character but the majority of it is involved in bonding interaction with O 2p between −9 and −6 eV. Partial electron density maps have been made for energy ranges of the EDOS. For the area between −9 and −6 eV [Fig. 4(a)] the electron density clearly shows the bonding nature of the interaction and that this section of the EDOS which contains around 70% of the Sn 5s characters does not result in the lone pair. A plot of the density generated by the energy range −6 to −3 eV is shown in Fig. 4(b). Again this does not show asymmetric density responsible for the lone pair and is primarily located on the oxygen atoms. The lone pair density results from the bands between −3 eV and the Fermi energy and is shown in Fig. 4(c). This corresponds to the main differences in the EDOS—the occurrence of Sn 5p mixed in with the O 2p and Sn 5s anti bonding states. For a more detailed discussion we turn to the calculated band structure.

The band structure of CsCl structured SnO is shown in Fig. 5(a). The unusual dispersion of the band between −9 and 6 eV is in agreement with our observations of covalent interaction between the Sn 5s and the O 2p. Along the line gamma-X the energy decreases, the opposite expected for an s derived band. Normally the in-phase interaction is most favorable and thus the energy would be expected to be lowest for the gamma point. In this case the hybridization with the O 2p bands causes stabilization when out-of-phase as this is required to allow the p orbitals to interact with the Sn 5s. The effect of this is to push the O 2p derived bands (with some Sn 5s) up in energy as they represent the filled antibonding combination. This results in a high density of states just below the Fermi level and the semimetallic nature of SnO in the CsCl structure.

In litharge structured SnO, for which the band structure is shown in Fig. 5(b), an addition interaction can occur for

FIG. 4. Partial electronic densities for energy ranges of the EDOS for litharge structured SnO. (a) For the EDOS between -9 eV and -6 eV, (b) between -6 eV and -3 eV and (c) between -3 eV and the top of the valence band. Contour levels are shown between 0 and $0.2e/\text{\AA}^3$ at $0.025e/\text{\AA}^3$ steps.

FIG. 5. Band structure for (a) CsCl structured SnO and (b) litharge structured SnO.

the states that are close to the Fermi level in the CsCl structure. The EDOS shows interaction of the Sn $5p$ states at the top of the valence band which has shifted these bands down in energy away from the Fermi level clearly indicating that the interaction of the Sn $5p$ orbitals is having a stabilizing effect. This can be seen by the way in which the bands have moved away from the Fermi level along the gamma-X line. The reason for this is that displacement of the Sn atoms allows the Sn p_z orbital to interact more efficiently with the O $2p$ states that are close to the Fermi level in the CsCl structure. The O $2p$ derived states at the top of the valence band in the CsCl structure cannot interact with Sn $5p$ because symmetry does not allow for this interaction. In the litharge structure half of the Sn atoms have moved in the $+z$ direction and half of them in the $-z$ direction, breaking the symmetry and allowing the hybridization. The states at the top of the valence band in CsCl structured SnO are therefore lowered in energy in the litharge structure and move away from the Fermi surface. This results in a stabilization of the litharge structure and explains why the distorted structure forms.

DISCUSSION

From the EDOS the bonding in CsCl has been shown to be partially covalent caused by interaction between the O $2p$

and Sn $5s$ and the O $2p$ and Sn $5p$ states. The most important feature of the band structure is the strong interaction between the Sn $5s$ and O $2p$ orbitals. This interaction gives rise to a large density of states just below the Fermi energy (filled antibonding combination) giving rise to the Sn $5s$ character close to top of the valence band. This interaction does not gain energy because of the filled bonding and antibonding levels.

The distorted phase is more stable because it decreases the density of states just below the Fermi level. The unoccupied Sn $5p$ orbitals interact with the antibonding Sn $5s$ and O $2p$ states giving rise to bonding and antibonding combinations. This time because the $5p$ states are unoccupied, the filling of the bonding states results in a net gain in energy. This combination is only possible in the distorted structure due to symmetry of the interaction. In a simplistic view the gain in energy must be sufficient to counteract the change in coordination from 8 to 4. The change in the Sn–O bond length from 2.70 Å to 2.25 Å shows the increased strength of interaction between Sn and O that stabilizes the distorted structure. Partial electron densities for the energy range -6 eV–Fermi energy clearly show that it is this interaction which gives rise to the distorted electron density around the Sn. This is contrary to traditional view of hybridization of the tin $5s$ with the $5p$ orbitals as the Sn $5s$ states are clearly contributing directly to covalent interaction with oxygen. In addition it is also clear that the O $2p$ states are directly involved with the formation of the distorted electron distribution.

CONCLUSIONS

Density functional theory calculations have been used to examine the electronic structure of CsCl and litharge structured SnO. The calculations show good reproduction of litharge structured SnO and indicate that the electron distribution around the tin is heavily distorted in contrast to the results on CsCl structured SnO. Classical interpretation of this electron density would be that of a chemically inactive but sterically active lone pair. However, the detailed electronic structure reveals a more complicated picture.

The electronic density of states shows that the Sn $5s$ electrons in both the CsCl and litharge structures mixes with the O $2p$ states to form bonding and antibonding combinations that are both filled. Around 60% of the Sn $5s$ character is contained within the bonding states between -9 and -6 eV below the Fermi level. This interaction is clearly seen in both the PEDOS and band structure. The band structure shows anomalous dispersion, if pure Sn $5s$, for the bands in this energy range which can only be explained by hybridization with the O $2p$. The states just below the Fermi level in

the CsCl structure are the antibonding combination and contain the rest of the Sn $5s$ character. In litharge structured SnO these states further hybridize with Sn $5p$ which is only possible when the structure is distorted with a “lone pair” due to symmetry. This gives rise to the usual bonding and antibonding combinations but this time, since the Sn $5p$ are empty, the filling of the bonding combination results in stabilization of the distorted phase.

This is contrary to the traditional view of the lone pair as being a nonbonded feature which has steric influence. In this study the lone pair is clearly shown to be the result of tin–oxygen interaction and thus is directly related to the chemical bonding. From this it is clear that an anion with valence states of differing energies to oxygen may be unable to interact in the same way to form the asymmetric electron distribution and is consistent with the fact that Sn (II) does not always form distorted structures.

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- ¹E. W. Abel, in *Comprehensive Inorganic Chemistry*, Vol. 2 (Pergamon, New York, 1973).
- ²F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed. (Wiley, New York, 1988).
- ³L. E. Orgel, *J. Chem. Soc.* **1959**, 3815 (1959).
- ⁴I. Lefebvre, M. Lannoo, G. Allan, A. Ibanez, J. Fourcade, J. C. Jumas, and E. Beaupaire, *Phys. Rev. B* **59**, 2471 (1987).
- ⁵A. Verbaere, R. Marchand, and M. Tournoux, *J. Solid State Chem.* **23**, 383 (1978).
- ⁶D. Le Bellac, J. M. Kiat, and P. Garnier, *J. Solid State Chem.* **114**, 459 (1995).
- ⁷J. Pannetier and G. Denes, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **36**, 2736 (1980).
- ⁸G. W. Watson and S. C. Parker, *J. Phys. Chem. B* **103**, 1258 (1999).
- ⁹I. Lefebvre, M. A. Szymanski, J. Olivier-Fourcade, and J. C. Jumas, *Phys. Rev. B* **58**, 1896 (1998).
- ¹⁰E. L. Peltzer y Blanca, A. Svane, N. E. Christensen, C. O. Rodriguez, O. M. Cappannini, and M. S. Moreno, *Phys. Rev. B* **48**, 15712 (1993).
- ¹¹G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (1994).
- ¹²G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- ¹³G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ¹⁴W. Khon and L. J. Sham, *Phys. Rev. B* **136**, 864 (1965).
- ¹⁵J. P. Perdew, J. A. Chevary, S. H. Vorto, K. A. Jackson, M. R. Pedersen, D. J. Singh, and C. Frolhais, *Phys. Rev. B* **46**, 6671 (1992).
- ¹⁶D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- ¹⁷G. Kresse and J. Hafner, *J. Phys.: Condens. Matter* **6**, 8245 (1994).
- ¹⁸H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- ¹⁹J. M. Themlin, M. Chtaiib, L. Henrard, P. Lambin, J. Darville, and J. M. Gilles, *Phys. Rev. B* **46**, 2460 (1992).
- ²⁰V. M. Jimenez, G. Lassaletta, A. Fernandez, J. P. Espinos, F. Yubero, A. R. Gonzalez-Elipé, L. Soriano, J. M. Sanz, and D. A. Papaconstantopoulos, *Phys. Rev. B* **60**, 11171 (1999).