

Lone Pairs at Surfaces

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Post transition elements such as Sn and In have two main oxidation states: the group (N) oxidation state (N=4 for Sn and N=3 for In) and the so-called N-2 state where formally the metal has a $5s^2$ valence electron configuration. Localised and stereochemically active lone pairs develop when post transition metals in the N-2 oxidation state occupy crystallographic sites lacking inversion symmetry. The lone pairs arise from hybridisation between anion states and occupied metal s states to give antibonding states close to the top of the valence band, which hybridise further with nominally empty metal p states. This mixing is only possible in non-centrosymmetric sites because s and p states are of opposite parity. There has been speculation over many years that lone pairs should develop at the surfaces of compounds of post transition metal compounds because surface sites of necessity lack inversion symmetry. However the unambiguous identification of surface lone pair surface states has proved elusive. In the present contribution we show that by comparing hard and soft X-ray photoemission spectra of $\text{In}_2\text{O}_3(111)$ it becomes obvious that a gap state seen previously is undoubtedly localised at the crystal surface. Moreover the state is seen to move toward the valence band edge in Sn-doped $\text{In}_2\text{O}_3(111)$, as expected from the higher nuclear charge of Sn as compared to In. The outcomes of calculations which have explored the local atomic configurations required to produce surface localised lone pairs surface states on $\text{In}_2\text{O}_3(111)$ and $\text{Sn-In}_2\text{O}_3(111)$ using density functional methods will be presented. The discussion will be extended to more recent work on SnO_2 . We will also discuss the implications of lone pair formation with respect to the application of oxides such as In_2O_3 and SnO_2 as transparent conducting oxides and as gas sensor materials.

References

1 Walsh, A., Payne, D. J., Egdell, R.G., Watson, G.W. Stereochemistry of post-transition metal oxides: revision of the classical one pair model. *Chem. Soc. Rev.* **40**, 4455 (2011).

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