to behave like a bulk C-doped SnO_2. This case does not produce magnetism (Fig. 3) since the exchange splitting in the s as well as in the p orbitals of the C atom is absent. The PDOS shows that the (001) surface has small surface states just below E_F, which is in agreement with previous theoretical calculations.[21] A small peak, which is induced by the subsurface C p orbitals just above E_F, can also be seen. The PDOS also shows hybridization between the p orbitals of C, Sn, and O atoms, particularly near E_F. We can then conclude that C does not induce magnetism when located at the subsurface O(II) positions due to the lack of empty minority p spin states, as opposed to the surface O(I) positions.

Figure 1 illustrates that each O atom is surrounded by three Sn atoms and each atomic layer consists of O-Sn-O units which have a total of 16 valence electrons. A simple electron counting suggests that when an O atom is replaced by a C atom, the total number of valence electron changes to 14 and hence induces holes in the system. At the (001) surface, the O atoms are not surrounded by three Sn atoms but by two Sn atoms. Hence, magnetism at SnO_2 (001) in this case is driven simultaneously by a surface effect (low coordination) and unpaired electrons. Calculations with two C located at the O sites show that the magnetic moment increases, suggesting that hole doping enhances magnetism. In bulk C-doped SnO_2 the C atom bonds directly to the three Sn atoms, which allow the 6 valence electrons to delocalize on the states associated to the bonds and reduce their Coulomb repulsion, leaving empty the localized state of the C atom, as can be seen in Fig. 2 (c) and Fig. 3 (b). In the surface, however, the number of bonds is reduced to two, which leaves two localized states, as can be seen in Fig. 2 (a). The two electrons which are not associated to the bonds follow then Hund's rules to reduce again their Coulomb repulsion and occupy each state with parallel spins, which gives a total magnetic moment of 2.00 μ_B/C.

Finally, similar calculations were also performed for different layers of SnO_2 and we always found that the C atom can only induce magnetism at the surface layers and the magnetic moment is only localized at the surface and subsurface atoms.

In summary, first-principles calculations showed that C induces a large magnetic momment at the SnO_2 (001) surface. The magnetic moment, which is localized at the surface and subsurface atoms, was mainly contributed by the C atom and partially by the O atoms. When the C atom was located at the subsurface O sites it did not show magnetism. The possible origin of magnetism was discussed in terms of surface bonding. Further work would be necessary to investigate similar phenomena at other semiconductor surfaces. We hope our results stimulate further experimental verification.

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