



INVESTIGATION OF MAGNETIC STATES OF 3D TRANSITION METALS DOPED SnO AND SnO₂ COMPOUNDS BY USING *AB INITIO* ELECTRONIC STRUCTURE CALCULATIONS

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Abstract: Here we study the magnetic state of $\text{Sn}_{0.99}\text{M}_{0.01}\text{O}$ and $\text{Sn}_{0.99}\text{M}_{0.01}\text{O}_2$, where $\text{M} \equiv \text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu}$, by using *ab initio* electronic structure calculations. Present work suggests the magnetic ground state for all the compounds except $\text{Sn}_{0.99}\text{Sc}_{0.01}\text{O}$, $\text{Sn}_{0.99}\text{Sc}_{0.01}\text{O}_2$, and $\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_2$. The comparison of energy of the magnetic and local moment disorder (LMD) states suggests the absence of long range magnetic ordering in SnO based compounds except for $\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}$. However, SnO₂ based compounds are predicted to show long range magnetic ordering for all the magnetic compounds except for Co and Cu doped compounds. The hybridization between M 3d and O 2p orbitals are found to play crucial role in deciding the magnetic property of these compounds. The importance of these results in possible Spintronics applications is also discussed.

Keywords: Spintronics, Transition Metal, Magnetic Moment, Doping.

1. INTRODUCTION

Diluted magnetic semiconductors (DMS) have attracted a great deal of attention for last two decades because of the manifestation of magnetic long range ordering and their promising technological applications in the electronic industries. [1, 2, 3] DMS are materials that exhibit both ferromagnetism and useful semiconducting properties.

[4] Such materials which possess both the properties are also known as semimagnetic semiconductors. Spintronics could make integrated use of both charge and spin of electron. In the DMS, a small concentration of magnetically active atom (normally transition metals) is distributed at cation site of the host semiconductor. Such a system may have both semiconducting and magnetic properties. In other words we can say that DMS are characterized by the random substitution of the fraction of the original atoms by magnetic atoms. In traditional

electronics we used the charge carriers for conduction control but practical magnetic semiconductors would also allow control of quantum spin state (up or down). A material that exhibits these properties offers the exciting aspect of combining non-volatile magnetic storage and conventional semiconductor electronics in a single device. DMS have the existence of magnetic phenomena with a simple band structure. This unique property of DMS makes it as very popular in industrial and electrical physics. [4]

DMS have many interesting properties as mentioned above and hence many researchers are attracted towards this topic. Most of the work has been done on the metallic semiconductors like GaAs, GaN, InAs, etc. Relatively small amount of work has been carried out on the oxide semiconductors like ZnO, TiO₂, etc. In these compounds transition metals like Cr, Mn,

Fe and Co are doped. Very limited studies have been carried out to see the effect of doping of various 3d transition metals in the oxide semiconductors. Here we see the effect of doping of all the 3d transition metals on SnO and SnO₂ compounds in the dilute limit which are less explored. SnO and SnO₂ are wide band gap semiconductors having band gap of ~ 2.5 and 3.6 eV, respectively.[5, 6] SnO is used as a reducing agent and finds its role in the manufacture of copper-ruby glass.[7] SnO₂ is used as gas sensors. Thicker layers of SnO₂ doped with Sb or F ions are electrically conducting and used in electroluminescent devices.[8] Mn and Co doped SnO₂ doped are expected to be used in high voltage varistors.[9] The band gap of these materials lies in the optical and UV regions respectively. Any possibility of doping 3d transition metals in these compounds with ferromagnetic ordering has potential for fabricating spintronics devices.

Therefore we studied the oxide semiconductor SnO₂ which when doped with different transition metals from Sc to Cu results into dilute magnetic semiconductor. The same we tried with SnO also but in this case we do not found any long range ferromagnetic ordering (except Ti doped compound) which is essential for using DMS in electronics. We doped all the transition metal atoms (1%) into SnO and SnO₂ at Sn site and calculate the moment as well as total energy with nonmagnetic, magnetic and local moment disorder (LMD) calculations.

2. RESULTS AND DISCUSSIONS

2.1 Computational details

The nonmagnetic, magnetic and local moment disorder (LMD) calculations for transition metal doped SnO and SnO₂ oxide semiconductors have been carried out by using the Korringa-Kohn-Rostoker (KKR)-Green's function method.[10] Effect of doping is studied under (CPA). We have doped 1% of all the 3d transition metals (from Sc to Cu) at Sn site. The lattice parameters used for these calculations of SnO and SnO₂ are $a=b=7.17907$ Bohr, $c=9.14815$ Bohr and $a=b=8.95220$, $c=6.02125$ Bohr,

respectively corresponds to the tetragonal structure. The muffin-tin sphere radii used in the present work are $Sn=0.29913$, $O=0.28493$ in SnO and $Sn=0.22186$, $O=0.21127$ in SnO₂. Here the type of the relativistic treatment used is semi-relativistic treatment of core level. The exchange correlation functional used in the calculations is taken after Vosko, Wilk, and Nussair.[11, 12] The k-points used in both cases are 105. The self-consistency was achieved by demanding the convergence of the total energy to be smaller than 10^{-6} Red/cell.

2.2 Results

Let us first see the effect of doping of different transition metals in tin oxide (SnO). We doped one percent of transition metals in SnO and obtained the corresponding nonmagnetic, magnetic solutions. The energy difference between magnetic and nonmagnetic solutions along with the calculated magnetic moments are given in Table 1. It is evident from the table that the energy of magnetic solution is always less than that of nonmagnetic solution for every compound except Sc where magnetic solution does not exist. Thus doping Ti to Cu at Sn sites results in magnetic ground state with the formation of magnetic moment at Sn site. The nonexistence of the magnetic ground state of Sc doped SnO is quite surprising as in Sc atom there are two electrons in 4s orbital and one in the 3d orbital. Under pure ionic model Sn is in 2+ ionic state and Sc is replacing Sn atom thus it is expected that Sc should also be in 2+ state by removing 2 electrons from 4s orbital and hence left with one electron in the 3d which should have contributed in the formation of magnetic ground state. The nonexistence of magnetic ground state in Sc doped SnO suggests the breakdown of pure ionic model.

For rest of the compounds we found non-integral values of magnetic moments. If we consider the pure ionic model as mentioned above and assume the validity of Hund's first rule in the case of solid we would have got the integral values for the magnetic moments as shown in Table 1 and represented as expected moment. However in every case we

get the moment less than the expected moment. For Ti doped compound we get $\sim 1.5 \mu_B$ less moment whereas for V, Cr, and Mn doped compounds it is about $1 \mu_B$ less. For Fe and Co doped compounds calculated magnetic moments come out to be closer to the expected values. For other two compounds calculated moments are away from the expected one. These observations indicate that the Hund's first rule is only applicable to the Fe and Co based compounds and fails for other compounds. The failure is not surprising because this rule is valid for atoms. In the case of solids the magnetic states of a magnetic ion is decided by the competition between the Hund's energy and the crystal field energy. Thus our results suggest the domination of crystal field energy over the Hund's energy for all the compounds except Fe and Co doped compounds.

Table 1:

Dopant	M_{exp} (μ_B)	M_{obs} (μ_B)	ΔE_1 (meV)	ΔE_2 (meV)
Sc	1	0	0	0
Ti	2	0.5	-0.85	-0.49
V	3	1.9	-8.11	0.34
Cr	4	3.1	-26.17	1.22
Mn	5	4.2	-55.66	1.23
Fe	4	3.9	-53.30	1.16
Co	3	2.9	-29.33	1.68
Ni	2	1.7	-133.23	0.58
Cu	1	0.4	-0.57	0.39

The mere formation of magnetic moment at Sn sites for all the compounds except for Sc doped does not guarantee the existence of long range magnetic ground state. For any application to the electronic devices long range

magnetic ordering is the desirable property. Thus to study the existence of long range magnetic ordering we found the LMD solutions for all the compounds. The energy difference between magnetic and LMD solutions for each compound is given in Table 1. It is clear from the table that the energy corresponds to LMD solution is always less than that of the magnetic solution for every compound except Ti doped. This suggests existence of long range magnetic ordering for the Ti doped SnO only and for rest of the compound will not show any long range magnetic ordering.

Table 2:

Dopant	M_{exp} (μ_B)	M_{obs} (μ_B)	ΔE_1 (meV)	ΔE_2 (meV)
Sc	0	0	0	0
Ti	0	0	0	0
V	1	1.2	-393.96	-0.56
Cr	2	2.5	-26.01	-0.88
Mn	3	3.5	-1270.47	-1.63
Fe	4	1.5	-7.37	-1.38
Co	5	3.4	-6.58	1.73
Ni	4	2.3	-0.28	-3.48
Cu	3	1.4	-9.97	4.24

Now let us consider the doping effect of different transition metals into SnO₂. The energy difference between magnetic and nonmagnetic solutions along with the calculated magnetic moments are given in Table 2. From the table it is clear that the energy of magnetic solution is always less than that of nonmagnetic solution for all compounds except Sc and Ti doped compounds where magnetic solutions do not exist. Thus doping transition metals from Vanadium (V) to Copper (Cu) results into the magnetic ground state with formation of magnetic moment at Sn site. The nonexistence of magnetic ground state in Sc and Ti is obvious. In Sc and Ti atoms there are one and two electrons, respectively, in 3d orbital and two electrons in 4s orbital. Under pure ionic model, Sn is in 4+ ionic

state. On replacing Sn by Sc (Ti) will put Sc (Ti) in 4+ state. This ionic state will result in completely unfilled 3d orbitals for Sc and Ti ions resulting in nonexistence of magnetic ground state for Sc and Ti doped SnO₂.

As mentioned above, consideration of pure ionic model and Hund's first rule give rise to integral values of moment in this case also which has been given in Table 2. However, the observed moment for all the compounds from V to Cu are non-integral. For V doped compounds the moment is ~0.2 μ_B greater, for Cr, Mn and doped compounds it is ~0.5 μ_B greater. Surprisingly from Fe onwards the moment is less than that of expected one. For Fe doped material the observed moment is ~2.5 μ_B less, for Co, Ni and Cu doped compounds it is ~1.7 μ_B less. As discussed in case of SnO here also the crystal field energy dominates over the Hund's energy for all the compounds.

In order to study the possibility for the existence of long range magnetic ordering we have obtained the LMD solutions for all the compounds which show the existence of magnetic ground state. The energy difference between magnetic and LMD calculations is given in the Table 2. From the table it is clear except Co and Cu doped compounds the energy of magnetic solutions is always less than LMD solutions. Which implies that there exist long range magnetic ordering in V, Cr, Mn, Fe and Ni doped compounds. The Co and Cu doped SnO₂ compounds will not show the long range magnetic ordering.

3. CONCLUSIONS

Conclusively, we found the long range ferromagnetism in SnO₂ by doping only one percent of transition metals. But in the same case, Co and Cu doped SnO₂ shows the nonexistence of long range ferromagnetism. Also only Titanium (Ti) doped SnO shows the long range ferromagnetism. While in other transition metals case compound material behaves as a paramagnetic. One has to keep in mind that, in SnO there is a formation of

magnetic moment but it is not long range ferromagnetism. It may be possible by increasing the doping concentration than one percent but that will not be the dilute doping. This means that, dilute (1%) doping of transition metals in Tin Oxide (SnO) does not gives us the effective long range ferromagnetism. In short, we cannot make the diluted magnetic semiconductors with SnO as host but it is possible in SnO₂ by doping different transition metals except Co and Cu.

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