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Origin of ferromagnetism in Cu doped rutile TiO_2 - An *ab-initio* approach

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ABSTRACT

Origin of room temperature ferromagnetism in copper doped rutile TiO_2 has been studied by varying both copper concentrations as well as oxygen vacancies. *Ab-initio* calculations have been carried out within the framework of density functional theory. Copper atom has been doped at two different positions to study the effect of distance between the dopants for ferromagnetism in TiO_2 system. Spin polarized density of states calculation has been performed for each system and the induced magnetic moment has been calculated along with the total free energy and Fermi energy. Spin-spin interaction studies have been performed for two copper doped at Ti site ($Ti_{22}Cu_2O_{48}$) as well as two oxygen vacancies along with Cu doping at Ti site ($Ti_{22}Cu_2O_{46}$). Spin-spin interaction results have been analyzed to understand the possibility of ferromagnetism in the copper doped rutile TiO_2. It has been found that copper doped system with adjacent oxygen vacancies gives ferromagnetic ordering.

1. Introduction

Recently, dilute magnetic semiconductors (DMS) based upon TiO_2 have drawn lots of attention of the researchers due to its potential application in solar cell, opto-electronic, magneto-optic devices [1–4]. High dielectric constant and high refractive index of rutile-TiO_2 make it preferred choice for electronic and optical purposes [5]. TiO_2 nanomaterials are widely used as photocatalysts in industrial scale because of its high catalytic efficiency, stability, cost efficiency and environmentally benign nature [6]. Magnetic properties along with intrinsic semiconducting properties can be used for better storage and swift response in electrical devices [7]. This property of ferromagnetic-semiconductors makes them suitable choice for spintronics application [8]. Pristine TiO_2 is a wide-band-gap semiconductor with band gap of ~3 eV [9]. Due to this band gap it can only absorb in UV region but with the incorporation of defects it can be tuned to absorb in the visible part of the spectrum [10]. This large band gap can be reduced by doping TiO_2 with Cu because this doped system has some added states at the top of the valence band [11]. Photocatalytic activity of TiO_2 has been studied by co-doping Mo and Cu in TiO_2 [12]. Numerous studies have been done on defect induced ferromagnetism in oxides (like TiO_2, ZnO, MgO, SnO_2 etc.) [13–17]. However, in TiO_2 it has been shown both theoretically and experimentally that both cation vacancies [18] as well as anion vacancies [19] can induce room temperature ferromagnetism. Copper being a non magnetic element, Cu doped TiO_2 will give a direction for the study of room temperature ferromagnetism (RTFM) in wide-band- gap semiconductors. Copper doped TiO_2 can be used as a photocatalytic agent [20] and it also shows bacterial inactivation properties [21]. Duhalde et al., showed that a magnetic moment of about 1.5 μ_B can be induced per Cu dopant with one oxygen vacancy in (TiO_2) [22]. However, Torres et al. proposed that Cu doped at Ti site generates a ferromagnetic behavior [23]. Hau et al., observed room temperature ferromagnetism in copper doped TiO_2 thin films. Further, they reported that the ferromagnetic coupling strongly depends upon distance between the dopants and also the magnetism decreases with high dopant concentration [24]. S. A. Ahmed [25] carried out the magnetic measurements for Cu doped TiO_2 prepared by solid state technique and concluded that ferromagnetic property in TiO_2 system is an intrinsic character. Furthermore, magnetic study carried out by Xu et al., for pristine and Cu doped rutile TiO_2 is in agreement to this results and concluded that oxygen vacancies are responsible for inducing ferromagnetism in this system [26]. Despite of all these studies the origin of ferromagnetism in Cu doped TiO_2 system is yet not clear and the results are sometimes self contradictory. Hence, it needs further study to understand the process in detail.

In the present work, we have performed a first principle calculation under the framework of density functional theory. Possibilities of inducing ferromagnetic properties have been studied by considering the different TiO_2 system (i.e. $Ti_{24-n}Cu_nO_{48-m}$, n and m have been assigned values 0, 1, 2, 3 as required in different configurations). Different concentrations of Cu doping and oxygen vacancy have been considered along with the doping distance of two Cu atoms for complete

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understanding of the process.

2. Computational methodology

Ab-initio calculations under the framework of Density Functional Theory (DFT) have been employed using VASP (Vienna *ab-initio* Simulation Package) Code, along with MedeA Simulation Package [27–30]. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange and correlation [31] method has been followed to study the system. Periodic boundary conditions have been introduced along all the basis vectors. A 2 × 2 × 3 super cell with 72 atoms is build by multiplying the tetragonal unit cell of rutile TiO_2 with optimized lattice constants of a = b = 4.59 Å and c = 2.95 Å and α = β = γ = 90°. The structure in each case has been geometrically relaxed until the maximum value of the unbalanced inter-atomic force component (Hellman-Feynman force) is less than 0.02 eV/Å. TiO_2 system having different atomic concentration ($Ti_{24-n}Cu_nO_{48-m}$) and different doping distance have been taken for detailed understanding of the process. For $Ti_{22}Cu_2O_{46}$ system (~3 at. % Cu doping has been considered along with oxygen vacancies (V_O)), two Ti atoms have been substituted with two Cu atoms and two oxygen atoms are removed from adjacent site of Cu in the pristine $Ti_{24}O_{48}$ structure. Similarly, corresponding changes have been made in TiO_2 system for generating other systems taken under consideration. In all the cases, V_O have been created adjacent to the doped atom as it is more stable [22]. Two different positions have been fixed for the doping of Cu atom, one at near distance (~3.5 Å) and other one at long position (~6.5 Å). To study the doping of three atoms, two different cases have been considered, varying the dopant at middle position. In all calculations, 400 eV mesh cut-off energy has been taken into account to expand the plane wave basis set and 10^{-5} eV tolerance has been fixed as stopping criteria of the self-consistent loop to reach the electronic ground state. The Brillouin zone (BZ) of the super cells has been divided by 4 × 4 × 4 Monkhorst-Pack (MP) k-points [32]. Each system has been structure optimized and spin polarized density of states have been calculated along with the induced magnetic moment, Fermi energy and free energy. The ground state energies of ferromagnetic and anti-ferromagnetic ordering have been compared after considering the spin - spin interaction study in the spin polarized condition. The free energies of the different spin polarized systems are compared to get the stability information for corresponding parallel and anti-parallel spin state. Ferromagnetic ordering has been achieved by enforcing all the spins to align in one direction and G-type anti-ferromagnetic state has been achieved for calculating anti-ferromagnetic state.

3. Results and discussion

Origin of room temperature ferromagnetism (RTFM) in Cu doped rutile TiO_2 has been studied for different dopant concentrations. Both the effects of Cu doping and oxygen vacancies (V_O) have been considered by varying the number of Cu atoms as well as oxygen vacancies. In reality, there are many defects disorders incorporated in TiO_2 matrix during its synthesis; e.g., oxygen vacancies, metal vacancies, metal interstitials, formation of Ti^{3+}, formation of O^- etc [6]. Among them defects due to oxygen vacancies are most common intrinsic defects in the system as the defect formation energy for TiO_2 system with V_O is less [18]. For this reason we have studied the Cu doped TiO_2 systems with oxygen vacancies. Different positions have been chosen for substitution of Cu atoms at Ti site in TiO_2 super cell. Sites for two Cu atom doping at short distance (1, 2 site, labeled as 'S') and for long distance, (1, 3 site, labeled as L) has been chosen as shown in Fig. 1.

The optimized distance between the two Cu atoms doped in $Ti_{22}Cu_2O_{48}$ is found 3.57 Å for short position and 6.51 Å for long position. Similarly, for three Cu doped system (i.e., $Ti_{21}Cu_3O_{48}$) two different cases have been considered, one at the near site (1, 2, 4) and other at long site (1, 3, 4) varying the dopant at middle position as marked in Fig. 1. The details of the optimized distance, induced magnetic moment, defect formation energy and Fermi energy shift in different Cu doped TiO_2 systems have been tabulated in Table 1.

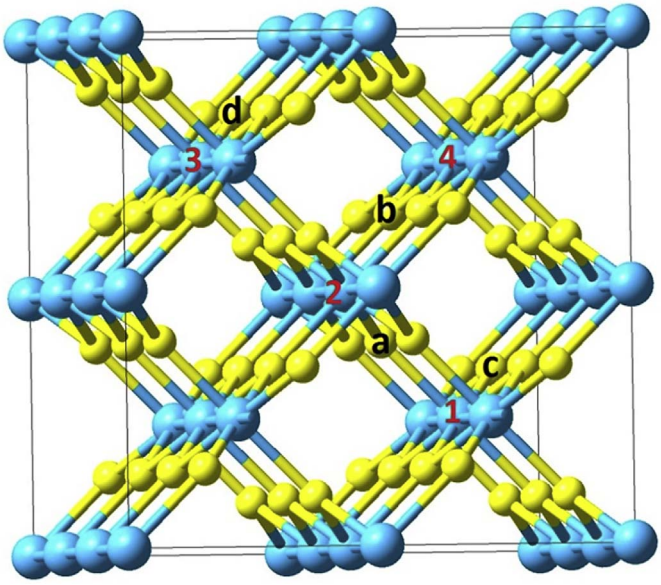

Fig. 1. Structure of pristine TiO_2 showing positions of doped Cu and Vo. The blue spheres and yellow spheres represent Ti and O atom respectively in the 72 atom super cell of TiO_2.

Table 1
The optimized distance, induced magnetic moment, defect formation energy and Fermi energy shift with respect to pristine TiO_2.

TiO_2 System	Position of doped copper	Position of oxygen vacancy	Cu–Cu distance (Å)	Magnetic Moment (μ_B)	Defect formation Energy (eV)	Fermi energy Shift (eV)
$Ti_{23}CuO_{48}$	2	NA	NA	1.45	12.04	1.23
$Ti_{23}CuO_{47}$	2	a	NA	1.01	18.61	1.72
$Ti_{23}CuO_{46}$	2	a, b	NA	0.91	28.76	2.81
$Ti_{22}Cu_2O_{48}$	1, 2	NA	3.57	1.26	24.49	1.12
$Ti_{22}Cu_2O_{47}$	1, 2	a	3.58	1.39	29.71	1.17
$Ti_{22}Cu_2O_{46}$	1, 2	a, c	3.48	0.65	34.41	1.69
$Ti_{22}Cu_2O_{48}$	1, 3	NA	6.51	1.68	24.33	1.08
$Ti_{22}Cu_2O_{46}$	1, 3	c, d	6.51	1.96	33.71	1.59
$Ti_{21}Cu_3O_{48}$	(1,2); (2,4); (1,4)	NA	3.57; 3.57; 4.59	0.14	36.93	1.0
$Ti_{21}Cu_3O_{48}$	(1,3); (3,4); (1,4)	NA	6.50; 4.59; 4.59	2.36	36.80	0.96

Doping of one Cu atom in TiO_2 produces a significant magnetic moment in TiO_2. The Cu atom has $4s^13d^{10}$ as the valence electronic configuration and when Ti^{4+} is substituted by Cu it becomes Cu^{2+} [33]. Substitution of Cu^{2+} in place of Ti^{4+} and generation of an oxygen vacancy lead to charge neutrality of the local environment [25]. Though Copper ions can be present in two major oxidation states, Cu^+ and Cu^{2+}, but for substitution of Cu^{2+} in place of Ti^{4+} in TiO_2 matrix, generally Cu^{2+} is predominant in absence of any complex forming ligand having high affinity for Cu^{2+} [34]. Magnetic moment is generated in non magnetic TiO_2 matrix, due to an unpaired electron in Cu^{2+}. The magnetic moment of Cu^{2+} ion polarizes the oxygen atoms in its neighboring atmosphere. When these neighboring oxygen atoms are removed, the contribution from these atoms decreases leading to overall decrease in net magnetic moment. After creating oxygen vacancy, magnetic moment decreases to 1.01 μ_B and 0.91 μ_B for single V_O and two V_O respectively from 1.45 μ_B in case of Cu doping without vacancy. The substitution of two Cu atoms at short position (i.e., 1, 2