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## Origin of unexpected magnetism in Cu-doped TiO<sub>2</sub>

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**Abstract** – Cu-doped TiO<sub>2</sub> has recently been found to exhibit unexpected room temperature ferromagnetism. In the present work, possible defect structures and the associated magnetism are calculated within the generalized gradient approximation using the projector augmented wave method (PAW). In particular, structures of the vacancy-Cu impurity complex are studied. Our results show that the magnetism is caused by: 1) the hybridization of *p-d* orbitals between the Cu and O ions, and 2) the spin polarization of the 3*d* orbital of Cu and of the 2*p* orbital of O ions.

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**Introduction.** – Recent discovery of room temperature magnetism in non-magnetic metal-oxide films, such as HfO<sub>2</sub> [1,2], In<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> [3] and Mg-doped AlN [4], has caused much attention [5,6]. Studies indicate that the magnetism could be the result of the interaction between the intrinsic defects and the doped ion. For example, in Mg-doped AlN films, the magnetism is a result of the tetrahedral MgN<sub>4</sub> complex [4], and in Cu-doped ZnO films, it is from the tetrahedral CuO<sub>4</sub> complex [7]. The basic mechanism responsible for the room temperature magnetism has yet to be established.

Room temperature dilute magnetic semiconductors (DMS) based on typical transition metal-doped TiO<sub>2</sub> thin films [8–11] had been initially thought to be produced by transition metal dopants such as Mn, Fe, and Co in the TiO<sub>2</sub> rutile phases [12]. However, it was later found that the reaction of the transition metal ions and the oxygen vacancies (*V*<sub>O</sub>) in Fe or Co-doped TiO<sub>2</sub> rutile phases played a more important role [13,14]. It was suggested that the magnetism found in transition metal-doped anatase TiO<sub>2</sub> thin films was due to a combination of short-range super-exchange coupling and long-range bound magnetic polaron percolation, such as found in the vanadium (V)-doped anatase phase [15], or from the super-exchange as in the cobalt (Co)-doped anatase phase [16]. For transition metal-doped rutile TiO<sub>2</sub> thin films, the magnetism in Co-doped rutile TiO<sub>2</sub> [17] comes

from the *p-d* interaction between the transition metal and oxygen ions, or from the coupling of two Fe ions, enhanced through the double exchange interaction of the oxygen vacancy in the Fe-doped TiO<sub>2</sub> rutile phase [13].

Although copper is non-magnetic in the bulk, magnetic moments of 1.5 μB/Cu were found in a Cu-doped TiO<sub>2</sub> film [18], with a copper concentration higher than 10%. Duhalde *et al.* suggested that the magnetism could be the result of a complex formed from a substitutional Cu impurity in a Ti site (Cu<sub>Ti</sub>) and an oxygen vacancy. This complex is similar to the magnetic one in other 3*d* transition metal-doped TiO<sub>2</sub> rutile thin films. Nevertheless, this suggestion has yet to be confirmed. In this paper, we investigate the mechanism responsible for the magnetism in Cu-TiO<sub>2</sub>, and the feasibility of its application to explain the unexpected magnetism of non-classical magnetic-transition metal-doped TiO<sub>2</sub> films in general.

**Calculations method.** – In the following, the configuration as well as associated electronic structure and magnetic properties of defects in non-classical magnetic-transition metal-doped TiO<sub>2</sub> films are studied via *ab initio* computer modeling, adopting the projected augmented wave (PAW) method [19] within the generalized gradient approximation [20]. The computation is performed using the VASP code [21,22] in a periodic supercell including 48 atoms (16 formula units), with a plane-wave

Table 1: Calculated formation energies and magnetic moments for single neutral defects and complexes.

	Formation energies (eV)	Magnetic moment ( $\mu\text{B}/\text{defect}$ )
$\text{Cu}_{\text{Ti}}$	7.666	0
$\text{Cu}_{\text{O}}$	4.820	0
$\text{V}_{\text{Ti}}$	15.922	0.961
$\text{V}_{\text{O}}$	6.574	0.965
$\text{Cu}_{\text{Ti}}\text{-V}_{\text{O}}$	3.946	0.997

cutoff energy of 400 eV, and  $K$ -points set according to a  $6 \times 6 \times 4$  Monkhorst-Pack  $K$ -mesh. Configuration relaxation is achieved by using the conjugate-gradient algorithm, with a tolerance of  $10^{-5}$  eV.

For pure rutile  $\text{TiO}_2$ , we use a tetragonal cell with space-group symmetry of  $P42/mnm$ , and lattice parameters  $a = b = 4.6123 \text{ \AA}$ ,  $c = 2.9504 \text{ \AA}$ . The resulting O ion is at the position (0.30358, 0.30358, 0), which agrees well with the results of ref. [23]. Several possible defect configurations are then considered, with the formation energy of a single neutral defect  $\Omega_f$  calculated according to [24,25]

$$\Omega_f = E_d - E_0 - \sum_i (n_i \mu_i), \quad (1)$$

where  $E_d$  and  $E_0$  are respectively the total energies of the supercell with and without the defects.  $n_i$  is the numbers of Ti, Cu and O atoms removed from the supercell, and  $\mu_i$  represents the corresponding chemical potentials. In the present calculation, the chemical potentials are governed by the conditions  $\mu_{\text{Ti}} + 2\mu_{\text{O}} \leq \mu_{\text{TiO}_2(\text{bulk,cal})} = -9.41 \text{ eV}$  and  $\mu_{\text{Cu}} + \mu_{\text{O}} \leq \mu_{\text{CuO}(\text{bulk,cal})} = -1.42 \text{ eV}$  to reflect the reductive chemical environment in the actual growth of the Cu-TiO<sub>2</sub> thin film [18].

**Results and discussion.** – The calculated formation energies and the associated magnetism for various defects are listed in table 1. It can be seen that single neutral defects, such as substitutional impurity copper at the titanium and oxygen sites ( $\text{Cu}_{\text{Ti}}$  and  $\text{Cu}_{\text{O}}$ , respectively), are non-magnetic. On the other hand, vacancy defects such as  $\text{V}_{\text{O}}$  and  $\text{V}_{\text{Ti}}$  are both found to be magnetic, with moments of  $0.965 \mu\text{B}/\text{supercell}$  and  $0.961 \mu\text{B}/\text{supercell}$ , respectively. However, these defects do not contribute significantly to the magnetization of Cu-TiO<sub>2</sub> films due to their low thermodynamic concentrations as a result of their large formation energies (table 1).

On the other hand, magnetic defect complexes such as  $\text{Cu}_{\text{Ti}}\text{-V}_{\text{O}}$ , have low formation energies (table 1) and may contribute significantly to the magnetic moments of doped TiO<sub>2</sub> thin films, similar to other TM-doped TiO<sub>2</sub> thin films [13], in which unexpected magnetism [4,7] is in every case induced by the defect complexes.

In the following, we consider defect complexes such as  $\text{Cu}_{\text{Ti}}\text{-V}_{\text{O}}$  and  $\text{Cu}_{\text{O}}\text{-V}_{\text{Ti}}$  (fig. 1(a)). In  $\text{Cu}_{\text{Ti}}\text{-V}_{\text{O}}$  defect complexes, the Cu ion replaces the Ti ion at the origin,

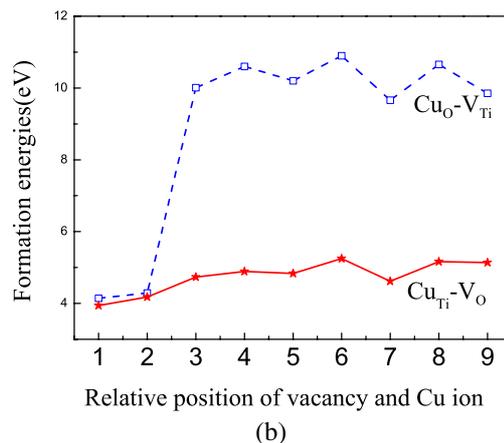
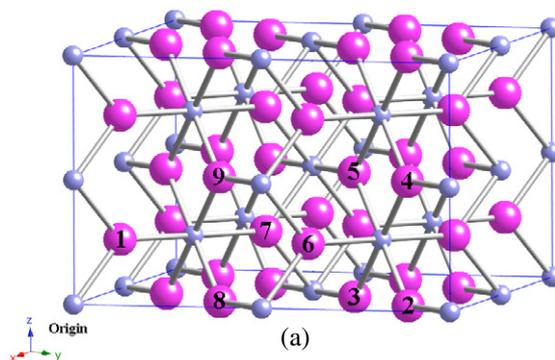


Fig. 1: (a) The relative position of  $\text{Cu}_{\text{Ti}}\text{-V}_{\text{O}}$  and  $\text{Cu}_{\text{O}}\text{-V}_{\text{Ti}}$ . (b) The energies of different positions of the vacancy relative to the doped-Cu ion at the origin.

and the vacancy is put at positions 1 to 9 in fig. 1. For the  $\text{Cu}_{\text{O}}\text{-V}_{\text{Ti}}$  defect pair, the configuration is similar, except that the copper impurity is at positions 1 to 9 with the vacancy is at the origin. In this way, nine configurations of every defect complexes  $\text{Cu}_{\text{Ti}}\text{-V}_{\text{O}}$  and  $\text{Cu}_{\text{O}}\text{-V}_{\text{Ti}}$ , respectively, are considered from fig. 1(a). The corresponding calculated total energies of the supercell are shown in fig. 1(b) as a function of the relative positions of the vacancy and the substituting Cu impurity ion. The results show that the most stable configurations of both  $\text{Cu}_{\text{Ti}}\text{-V}_{\text{O}}$  and  $\text{Cu}_{\text{O}}\text{-V}_{\text{Ti}}$  have the copper ion and the vacancy at nearest-neighbor positions at position 1 and the origin (fig. 1(a)). In the most stable configurations, the formation energy of the  $\text{Cu}_{\text{Ti}}\text{-V}_{\text{O}}$  complex is 0.3 eV lower than that of  $\text{Cu}_{\text{O}}\text{-V}_{\text{Ti}}$ , and is much lower than the formation energies of the magnetic defects  $\text{V}_{\text{Ti}}$  (15.9217 eV) and  $\text{V}_{\text{O}}$  (6.5741 eV (see table 1)). This suggests that  $\text{Cu}_{\text{Ti}}\text{-V}_{\text{O}}$  is the stable magnetic defect structure in Cu-TiO<sub>2</sub> thin films, a result that agrees well with that of Duhalde *et al.* [18].

The origin of magnetism in the  $\text{Cu}_{\text{Ti}}\text{-V}_{\text{O}}$  defect complex can be understood from its relaxed atomic configuration in fig. 2(a), in which attention is directed to the strong lattice distortion around the defect. The copper and four oxygen ions are seen to have moved towards the vacancy

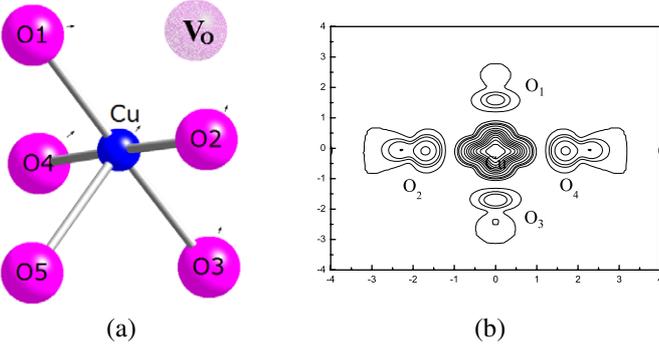


Fig. 2: (a) The dimensional structure in the complex structure CuO<sub>4</sub>, in which Cu and the most neighbouring four O ions attract each other. (b) The spin charge density of Cu-doped TiO<sub>2</sub> rutile phase; most of the spin density was localized in the complex structure CuO<sub>4</sub>.

during the relaxation. As a result, the Cu ion and the neighboring O atoms formed a CuO<sub>4</sub> complex, in which the O ions are non-coplanar (see fig. 2(a)).

The spin polarization of the CuO<sub>4</sub> complex as represented by the net spin charge density ( $\rho_{\text{up}} - \rho_{\text{down}}$ ) is calculated and shown in fig. 2(b). It is clear that the magnetic moment is localized between the copper ion and the neighboring oxygen ions. It is important that the direction of the lobes of the wave function for the Cu ions points toward the neighboring oxygen ions. It is further noted that the Cu and the neighboring O ions do not form covalent bonds due to the electron hybridization between the Cu and the O ions. As a result, the occupied states of Cu can interact effectively with the surrounding oxygen ions and induce stronger magnetic interactions. In our calculations, magnetic moments of  $0.55 \mu\text{B}/\text{Cu}$  and  $0.06\text{--}0.08 \mu\text{B}/\text{O}$  ions are obtained. As a result, the CuO<sub>4</sub> complex provides a magnetic moment of  $0.9 \mu\text{B}/\text{supercell}$ , which accounts for more than 90% of the  $0.997 \mu\text{B}/\text{supercell}$  seen. This suggests that the CuO<sub>4</sub> complex provides the most important contribution to the magnetic moments in the matrix.

To understand the role played by the impurity Cu ion in TiO<sub>2</sub>, we compare the spin density distributions of Cu<sub>Ti</sub>-V<sub>O</sub> and V<sub>O</sub>. In fig. 3, it can be seen that the magnetic moment of V<sub>O</sub> mostly comes from the two Ti ions ( $0.290\text{--}0.310 \mu\text{B}/\text{Ti}$  ion) as a result of the hybridization induced by the absence of the neighboring oxygen ion. Comparing fig. 2(b) with fig. 3, it can be seen that the magnetic moment in the complex defect Cu<sub>Ti</sub>-V<sub>O</sub> is mostly due to the impurity Cu ion, in contrast with V<sub>O</sub>, in which the magnetic moment is mostly due to the two Ti ions. The roles played by the impurity Cu in the magnetism of TiO<sub>2</sub> can be summarized as follows: Cu binds easily with an oxygen vacancy in TiO<sub>2</sub> to form the complex defect Cu<sub>Ti</sub>-V<sub>O</sub>, which relaxes to form a CuO<sub>4</sub> complex, in which the Cu ion is strongly magnetic.

The magnetic moment in the CuO<sub>4</sub> complex can also be understood by analyzing the energy levels shown in fig. 4.

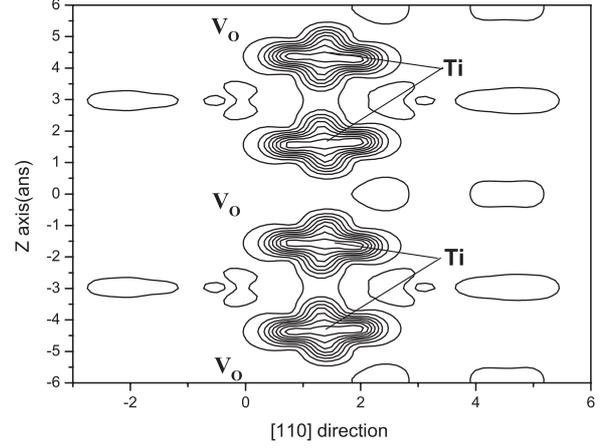


Fig. 3: The spin charge density of around the single neutral defect V<sub>O</sub>.

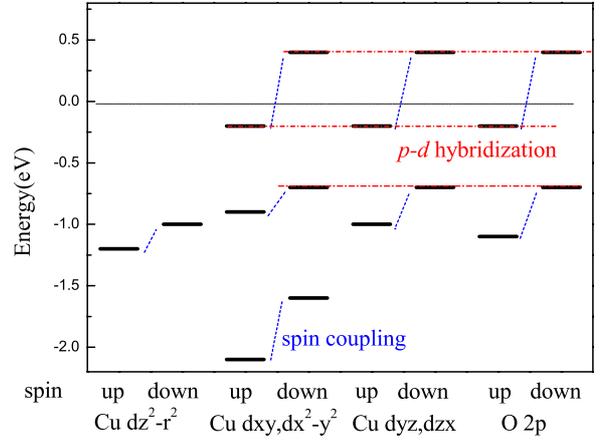


Fig. 4: The spin-polarized energy levels of the CuO<sub>4</sub> complex. The magnetic moment is due to the  $p$ - $d$  hybridization of the Cu  $3d$  orbitals with the O  $2p$  orbitals and the spin coupling of the lower-energy levels.

It can be seen that, instead of simply splitting into  $e_g$  and  $t_{2g}$  levels, the  $3d$  orbitals of the copper ions undergo a more complex change caused by the broken octahedral crystal field due to the absence of the neighboring oxygen ion. In particular, the  $x^2-y^2$  orbital is degenerate with the  $xy$  orbital, the  $yz$  orbital is degenerate with the  $zx$  orbital, and the  $z^2-r^2$  orbital has a different energy from the aforementioned orbitals, as shown in fig. 4. Such peculiar orbital splitting also occurs in the one-dimensional magnetic structure of Ca<sub>3</sub>Co<sub>2</sub>O<sub>6</sub> [26].

In fig. 4, the energy levels of the CuO<sub>4</sub> complex are divided into two groups, one situated near the Fermi level, and the other one lower. The group near the Fermi level is from the hybridized oxygen  $2p$  and the copper  $3d$  orbitals at energy levels of  $-0.8$ ,  $-0.2$  and  $0.4 \text{ eV}$ . We know by analyzing fig. 1 that this interaction is not sufficient to form a stable covalent bond, but the hybridization has changed the energy levels of both the  $2p$  orbitals of O and  $3d$  orbitals of Cu, providing part of the magnetization.

In the lower-energy group, the spin polarization of the 3*d* orbitals of Cu ions and 2*p* orbitals of O provide the rest.

**Conclusion.** – In conclusion, the magnetism in the Cu-doped TiO<sub>2</sub> film is likely to be from the interaction between the oxygen vacancy and the substitutional Cu impurity, which adopts the form of the non-regular magnetic complex CuO<sub>4</sub>, the magnetization of which is due to the hybridization of the Cu 3*d* orbitals with the O 2*p* orbitals, and the spin polarization of the 3*d* orbitals of Cu ions and 2*p* orbitals of O ions.

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