Theoretical study on the magnetic moments formation in Ta-doped anatase TiO$_2$

A Bupu$^1$, M A Majidi$^1$ and A Rusydi$^{2,3}$

$^1$Department of Physics, Faculty of Mathematics and Natural Sciences Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia
$^2$NUSNNI-NanoCore, Department of Physics, Faculty of Science, National University of Singapore, Singapore 117576, Singapore
$^3$Singapore Synchrotron Light Source, National University of Singapore, Singapore 117603, Singapore

Corresponding author’s email: aziz.majidi@sci.ui.ac.id

Abstract. We present a theoretical study on Ti-vacancy induced ferromagnetism in Ta-doped anatase TiO$_2$. Experimental study of Ti$_{1-x}$Ta$_x$O$_2$ thin film has shown that Ti-vacancies (assisted by Ta doping) induce the formation of localized magnetic moment around it, then, the observed ferromagnetism is caused by the alignment of localized magnetic moments through Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. In this study, we focus on the formation of the localized magnetic moments in this system. We hypothesize that on a unit cell, Ti-vacancy has caused four electrons from the surrounding oxygen atoms to become unpaired. These unpaired electrons then arrange themselves into a configuration with a non-zero net magnetic moment. To examine our hypothesis, we construct a Hamiltonian of the four unpaired electrons, incorporating the Coulomb intra- and inter-orbital interactions, in matrix form. Using a set of chosen parameter values, we diagonalize the Hamiltonian to get the eigenstates and eigenvalues, then, with the resulting eigenstates, we calculate the magnetic moment, $\mu$, by obtaining the expectation value of the square of total spin operator. Our calculation results show that in the ground state, provided that the ratio of parameters satisfies some criterion, $\mu \approx 4\mu_B$, corresponding to the four electron spins being almost perfectly aligned, can be achieved. Further, as long as we keep the Coulomb intra-orbital interaction between 0.5 and 1 eV, we find that $\mu \approx 4\mu_B$ is robust up to far above room temperature. Our results demonstrate that Ti vacancies in anatase TiO$_2$ can form very stable localized magnetic moments.

1. Introduction

Research on room temperature ferromagnetism (RTFM) in dilute magnetic semiconductors (DMS) has attracted much attention because of its potential for spintronics applications. Many studies on oxide DMS, such as TiO$_2$ and ZnO doped with transition metals or other elements [1–4], have successfully shown RTFM. Despite those facts, however, studies on the mechanisms of how the magnetic moments formed and aligned to lead to ferromagnetism in oxide DMS are still scarce.

For doped TiO$_2$, either cationic vacancies (Ti vacancies) or oxygen vacancies can play an important role in inducing ferromagnetism [3, 5]. An experimental study on anatase Ti$_{1-x}$Ta$_x$O$_2$ [6] shows that Ti vacancies are responsible for the observed RTFM by inducing formation of localized magnetic moments.
around the vacant sites. Furthermore, another study by Barman et al. [7] also suggests that Ti vacancies in Ti$_{1-x}$Ta$_x$O$_2$ act as magnetic centers. Ta atoms in Ta-doped anatase TiO$_2$ substitute Ti atoms in some sites of Ti. These substitutions cause distortion in some unit cells and lead to a situation in which a Ti atom cannot occupy its site, resulting in formation of a Ti vacancy. This situation makes Ta-doped anatase TiO$_2$ contain three types of unit cells: pure TiO$_2$ unit cells, TiO$_2$ with Ta replacing the Ti’s position and TiO$_2$ with the Ti site being vacant. It is this TiO$_2$ unit cell with the Ti site being vacant that is suspected to form the localized magnetic moment. Assuming such Ti-vacancy-induced magnetic moments exist, a recent theoretical study demonstrates that the Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction is likely responsible for the alignments of the magnetic moments to form the ferromagnetic order [8].

In this study, we develop a theoretical model and perform calculations to explain how Ti vacancies induce the formation of localized magnetic moments in Ta-doped anatase TiO$_2$ system. In each unit cell that contains a Ti vacancy, we argue that as a result of the breaking of Ti-O bonds due to the missing of Ti ion, the Ti vacancy creates four unpaired electrons in the surrounding oxygen sites. The unpaired electrons then interact with one another through repulsive Coulomb interactions. These interactions combined with Pauli exclusion principle can result in Hund’s couplings among spins of the four unpaired electrons, which eventually can lead to spin alignment among them. Previous studies [6, 7] indicate that there are three possible ways of spin alignment in this system, yielding the net magnetic moment of 0, 2 $\mu_B$, and 4 $\mu_B$. Since Ta-doped anatase TiO$_2$ has a pretty high $T_C$, a mean-field theory on ferromagnetism suggests that the high value of $T_C$ may be contributed by the high value of total magnitude of each constituent spin. It means that the four unpaired electrons may maximally align to form a net magnetic moment of 4 $\mu_B$. Here, we aim to find such an optimum condition when alignment of the unpaired electrons leads to a net magnetic moment of 4 $\mu_B$. Further, we would like to analyze the stability of the formed magnetic moments against temperature, especially at a room temperature and above it.

2. Model

As we aim to explain the role of Ti vacancy in creating a net localized magnetic moment in its corresponding unit cell, we isolate such a unit cell from the rest of the material and consider it as our system to study. Starting with the actual unit cell of TiO$_2$, we select a region where four oxygen atoms (red spheres) surround a titanium atom (blue sphere) marked with the black-dashed oval and pointed by

Figure 1. Unit cell of anatase TiO$_2$. The enclosed loop marked by the arrow shows the region we aim to explore.

Figure 2. (a) The considered block around Ti site. (b) Model of the block around a Ti-vacancy site.
The kinetic part of the Hamiltonian reads

\[ H = H_{\text{kin}} + H_{\text{int}}. \]  \hfill (1)

The kinetic part of the Hamiltonian reads

\[ H_{\text{kin}} = \sum_{m,m',\sigma} t_{m,m'} a_{m,\sigma}^\dagger a_{m',\sigma}. \]  \hfill (2)

Here, we assume that only one orbital from each oxygen atom containing the unpaired electrons is relevant to be considered in this model. The four electrons are assumed to be able to hop only within these four such orbitals. Within this restriction we define the size of the Hilbert space of our model. In equation (2), \( t_{m,m'} \) is the hopping parameter characterizing the energy associated with a hopping of an electron from site \( m \) to site \( m' \), \( a_{m,\sigma}^\dagger (a_{m,\sigma}) \) is creation (annihilation) operator each of which is associated with its basis orbital and spin orientation. \( t_{m,m'} \) is formally derived from

\[ t_{m,m'} = \int \phi_{m,\sigma}^\dagger (r) \left( -\frac{\hbar^2}{2m_{el}} \nabla^2 + V (r) \right) \phi_{m',\sigma} d^3r, \]  \hfill (3)

with \( m_{el} \) being the electron mass, \( V (r) \) the potential energy experienced by one electron due to the nearby atomic nuclei, and \( \phi (r) \) and \( \phi^\dagger (r) \) the single electron wave function and its conjugate corresponding to each oxygen’s atomic orbital at site \( m \) and \( m' \), respectively. The interaction part represents the Coulomb repulsive interaction between two electrons that, in second quantized form, reads as

\[ H_{\text{int}} = \sum_{m,m',m'',m'''} \frac{1}{2} U_{m,m',m'',m'''} \sum_{\sigma,\sigma'} a_{m,\sigma}^\dagger a_{m',\sigma'} a_{m'',\sigma'} a_{m'''}^\dagger, \]  \hfill (4)

with

\[ U_{m,m',m'',m'''} = \int \phi_{m,\sigma}^\dagger (r_1) \phi_{m',\sigma'}^\dagger (r_2) \frac{e^2}{|r_1 - r_2|} \phi_{m'',\sigma'} (r_2) \phi_{m'''} (r_1) d^3r_1 d^3r_2, \]  \hfill (5)

being the Coulomb interaction strength associated with a scattering of a pair of electrons initially at sites \( m'' \) and \( m''' \) scattered into sites \( m \) and \( m' \).

We further simplify the interaction part by restricting the scatterings of two electrons only to those with final occupied sites being the same as the initial ones, as we consider these to be the most dominant contribution. This restriction implies that there are only three possible conditions to be considered: (1) \( m = m' \) and \( m'' = m''' \); (2) \( m = m''' \) and \( m' = m'' \), but \( m \neq m' \); (3) \( m = m'' \) and \( m' = m''' \), but \( m \neq m' \). With
the above restriction, equation (4) is split into three terms as

\[
H_{\text{int}} = \sum_{m} \frac{1}{2} U \sum_{\sigma, \sigma'} a_{m, \sigma}^\dagger a_{m, \sigma} a_{m', \sigma'}^\dagger a_{m', \sigma'} + \sum_{m, m' \neq m'} \frac{1}{2} V_{m,m'} \sum_{\sigma, \sigma'} a_{m, \sigma}^\dagger a_{m', \sigma'} a_{m', \sigma} a_{m, \sigma'} + \sum_{m, m' \neq m''} \frac{1}{2} J_{m,m'} \sum_{\sigma, \sigma'} a_{m, \sigma}^\dagger a_{m', \sigma} a_{m', \sigma'} a_{m, \sigma'}. \tag{6}
\]

The first term of the above equation is the Coulomb intra-orbital interaction (with \(m = m' = m''\)) with \(U\) being the Coulomb intra-orbital parameter, while the last two terms are the Coulomb inter-orbital interactions with \(V_{m,m'}\) and \(J_{m,m'}\) being two different Coulomb inter-orbital parameters. Here, \(V_{m,m'}\) corresponds to scattering between two electrons initially occupying different orbitals with no exchange of orbitals after the scattering \((m = m''', m' = m)\), while \(J_{m,m'}\) corresponds to scattering with an exchange of orbitals after the scattering \((m = m'', m' = m'''\). Further rearrangement yields

\[
H_{\text{int}} = \sum_{m} \frac{1}{2} U \sum_{\sigma, \sigma'} n_{m, \sigma} n_{m, \sigma'} + \sum_{m, m' \neq m'} \frac{1}{2} V_{m,m'} \sum_{\sigma, \sigma'} n_{m, \sigma} n_{m', \sigma'} - \sum_{m, m' \neq m''} \frac{1}{2} J_{m,m'} \left( \frac{1}{2} + 2s_m \cdot s_{m'} \right), \tag{7}
\]

with \(n_{m, \sigma} = a_{m, \sigma}^\dagger a_{m, \sigma}\) being the occupation number operator of electron at site \(m\) with spin component \(\sigma\), and \(s_m = s_{m, \uparrow} \hat{x} + s_{m, \downarrow} \hat{y} + s_{m, \downarrow} \hat{z}\) being the spin operator of electron at site \(m\), with \(s_{m, \alpha} = (1/2) \sum_{\beta} a_{m, \alpha} a_{m, \beta} \sigma_{\alpha \beta}\), and \(\sigma_{\alpha \beta}\) elements of the \(\alpha\)-th component of the spin Pauli matrices. Note that from the above equation, \(J_{m,m'}\) is nothing but the Hund’s coupling parameter expected to lower the energy of the electrons occupying different sites with the same spin orientations. Hence, our full Hamiltonian

\[
H = \sum_{m, m', \sigma} t_{m,m'} a_{m, \sigma}^\dagger a_{m', \sigma} + \sum_{m} \frac{1}{2} U \sum_{\sigma, \sigma'} n_{m, \sigma} n_{m, \sigma'} + \sum_{m, m' \neq m'} \frac{1}{2} V_{m,m'} \sum_{\sigma, \sigma'} n_{m, \sigma} n_{m', \sigma'} - \sum_{m, m' \neq m''} \frac{1}{2} J_{m,m'} \left( \frac{1}{2} + 2s_m \cdot s_{m'} \right), \tag{8}
\]

comes up to be the well known extended Hubbard model with magnetic exchange interaction.

### 3. Method

With only four atomic orbitals, two possible spin orientations, and four electrons, the size of our Hilbert space is quite manageable to handle using exact diagonalization method. To proceed with this method, we first need to bring the Hamiltonian in equation (8) into matrix form by operating it on the 4-particle basis states, \(|\phi_i\rangle\). Here, the 4-particle basis states are all the possible configurations of the four electrons among the four \(p\) orbitals of the oxygen atoms surrounding the Ti vacancy. The total number of such states is \(8!/(4!4!) = 70\). The Hamiltonian matrix is constructed out of \(70 \times 70\) elements \(|\phi_i\rangle H |\phi_j\rangle\). Once the matrix is set up, we diagonalize it to obtain eigenstates and eigenvalues of the Hamiltonian. The diagonalization is done numerically using DSYEV routine of LAPACK (Linear Algebra Package). As our goal is to calculate the net magnetic moment of our system, we then use the eigenstates to calculate the ground-state expectation value of the square of total spin operator, \(\langle S^2 \rangle\), with \(S^2 = S \cdot S = (\sum_m s_m) \cdot (\sum_m s_m)\), and its corresponding thermodynamic averages for various temperatures.

Having obtained \(\langle S^2 \rangle\), we can extract the total spin \(S\) of the system using relation \(\langle S^2 \rangle = S(S + 1)\),
yielding

\[ S = \frac{-1 + \sqrt{1 + 4\langle S^2 \rangle}}{2}. \]  

(9)

The magnetic moment can then be calculated as

\[ \mu = gS\mu_B, \]  

(10)

with \( g \) being the Lande factor, which may be set to the free-electron value, \( g \approx 2 \).

Further, we also need to calculate the temperature dependence of the magnetic moment. For this purpose, we first take the thermodynamic averages of \( \langle S^2 \rangle \) as function of temperature as follows

\[ \langle S^2 \rangle (T) = \frac{1}{Z} \sum_i \langle S^2 \rangle_i e^{-\beta E_i}, \]  

(11)

where

\[ Z = \sum_i e^{-\beta E_i}, \]  

(12)

is the partition function, with \( E_i \) being the energy eigenvalue of state \( i \), and \( \beta = \frac{1}{k_B T} \), where \( k_B \) is the Boltzmann constant. Having this in hand, we then calculate the corresponding total spin as a function of temperature, \( S(T) \), by putting \( \langle S^2 \rangle (T) \) into equation (9). Then, the magnetic moment as a function of temperature is obtained by replacing \( S \) in equation (10) with \( S(T) \).

4. Results and discussion

To perform the computations, we need to specify the parameter values, \( t_{m,m'}, U, V_{m,m'} \) and \( J_{m,m'} \). There are some constraints in determining these parameters. Firstly, \( U, V_{m,m'} \) and \( J_{m,m'} \) may have to be small values as they describe the Coulomb interactions occurring between electrons occupying \( p \) orbitals which, unlike \( d \) orbitals, are not very localized. Secondly, according to equation (5), the intra-orbital Coulomb interaction coupling \( U \) has to be larger than the inter-orbital couplings \( V_{m,m'} \) and \( J_{m,m'} \). Furthermore, \( V_{m,m'} \), \( V_{m,m'} \) and \( J_{m,m'} \) may depend on the distance between sites \( m \) and \( m' \). Here, we set \( t_{m,m'} = t, V_{m,m'} = V \) and \( J_{m,m'} = J \) for \( m \) and \( m' \) located next to each other, while \( t_{m,m'} = t/2, V_{m,m'} = V/2 \) and \( J_{m,m'} = J/2 \) for \( m \) and \( m' \) located opposite to each other (see figure 2(b)).

Figures 3 and 4 demonstrate how we vary the parameters to explore how the magnitude of magnetic moment at the ground state depends on the parameters based on the considerations explained above. In figure 3, we present the magnetic moment (\( \mu \)) as a function of \( t/J \) while setting \( J = V \). We find that increasing \( t/J \) at fixed \( U/J \) decreases \( \mu \). However, the decrease in \( \mu \) with increasing \( V/J \) is insignificant. While, increasing \( U/J \) at fixed \( t/J \) or fixed \( V/J \) increases \( \mu \). The results presented in figure 3 show that to obtain maximum value of \( \mu \), we need to minimize \( t/J \) and maximize \( U/J \). The maximum value of \( \mu \) is reached when the ratio of \( t/J \) is small enough (\( \leq 0.2 \)). We obtain \( \mu = 3.995 \mu_B \), which is close to \( 4\mu_B \), when \( t/J = 0.2 \) and \( U/J = 10 \) with \( U = 1 \) eV and \( V = J \).

Figure 4 shows the calculated \( \mu \) as a function of \( V/J \). We use a constant ratio of \( t/J = 0.1 \) and \( U = 1 \) eV with \( U \geq J \). Our calculation shows that, at small values of \( U/J \), increasing \( V/J \) makes \( \mu \) decrease slightly on the order of 10^{-3}, whereas increasing \( V/J \) at higher value of \( U/J \) (\( U/J = 10 \)) does not change the magnitude of magnetic moment. Here, at \( U/J = 10 \), we obtain \( \mu = 3.998 \mu_B \). Thus, our overall result suggests that the maximum value of \( \mu \) can be achieved by requiring that \( U > J > t \). Our results are consistent with previous calculation by Peng et al. [9] and Qi et al. [10] which show that a Ti vacancy could generate a \( 4\mu_B \) magnetic moment.

From figure 3 we have found that the highest value of \( \mu \) requires \( t/J \) be as small as possible while \( U/J \) should be large. It may be also interesting to explore the other limit, that is for very high values of
Figure 3. Magnetic moment, $\mu$, as a function of $t/J$ for various $U/J$, with $U = 1$ eV and $J = V$, at $T = 0$.

Figure 4. Magnetic moment, $\mu$, as a function of $V/J$ for various $U/J$, with $U = 1$ eV and $t/J = 0.1$, at $T = 0$.

Figure 5. Magnetic moment, $\mu$, as a function of $t/J$ at various high values of $t/J$.

Figure 6. Magnetic moment, $\mu$, as a function of temperature with fixed ratio of parameters.

t/J. Figure 5 shows how $\mu$ evolves when $t/J$ is taken from 1 up to 6. At very high value of $t/J$, it appears that $\mu$ reduces exponentially to some finite values between 2 and 2.5 $\mu_B$. We argue that the non-vanishing value of $\mu$ is the consequence of keeping $J$ finite no matter how big the value of $t/J$ is.

Finally, we investigate the temperature dependence of $\mu$ for various $U$ with a fixed ratio among all the parameters. We use a constant ratio of $U : J : V : t = 1 : 0.1 : 0.1 : 0.01$ and vary the temperature from 25 to 400 K. As expected, increasing temperature would excite the energy of the electron spin at each oxygen site, that in turn, would destroy the spin alignment and decrease the total magnetic moment in the unit cell. Figure 6 shows our results for various values of $U$. When $U = 1$ eV and $U = 0.5$ eV we observe that $\mu$ does not change as temperature increases. $\mu$ only starts to fall off as a function of temperature if we reduce $U$ to $\sim 0.1$ eV or smaller. Furthermore, at the smallest chosen value of $U$, $U = 0.01$ eV, a full spin alignment corresponding to $\mu = 4\mu_B$ is not achieved even at an extremely low temperature. Another important observation is that, at room temperature, we find that for all values of $U$, provided $J > 0$, the
system always reveals a magnetic moment of the value $> 2\mu_B$.

5. Conclusions
We have developed a model and performed calculations to demonstrate that Ti vacancy, induced by Ta, in Ta-doped anatase TiO$_2$ leads to the formation of magnetic moment. The Ti vacancy causes the breaking of Ti-O bonds and generates four unpaired electrons hopping around the oxygen sites. The hopping integral $t_{m,m'}$ along with the Coulomb interactions among the electrons manifested in the parameters $U$, $V$ and $V'$, at the proper circumstances generate a maximum magnetic moment, $\mu \approx 4\mu_B$, at the ground state. In our simulation this condition is achieved when $U : J : V : t = 1 : 0 \cdot 1 : 0 \cdot 01$. As expected, temperature increase causes the magnetic moment to decrease, but this effect is only significant when $U$ is very small. At room temperature, the system always has a non-zero magnetic moment, provided $J > 0$. As we keep $U$ between 0.5 and 1 eV, the maximum magnetic moment of $\sim 4\mu_B$ is robust upto 400 K. Our results confirm our hypothesis that Ti vacancies in Ta-doped anatase TiO$_2$ induce the formation of magnetic moments, presuming the above proper circumstances of the parameters are met in the system.

Acknowledgement
We are very grateful to Universitas Indonesia for providing us a full funding for this project through PITTA Research Grant No. 2020/UN2.R12/HKP.05.00/2016.

References
[1] Pan H, Yi J B, Shen L, Wu R Q, Yang J H, Lin J Y, Feng Y P, Ding J, Van L H and Ying J H 2007 Phys. Rev. Lett. 99 127201
[2] Hu Y M, Li S S, Kuang C H, Han T C and Yu C C 2015 J. Appl. Phys. 117 17B901
[3] Zhang S, Ogale S B, Yu W, Cao X, Liu T, Ghosh S, Das G P, Wee A T, Greene R L and Venkatesan T 2009 Adv. Mater. 21 2282-71
[4] Choudhury B, Choudhury A and Borah D 2015 J. Alloys Compd. 646 692-8
[5] Wang X et al. 2014 Appl. Phys. Lett. 105 262402
[6] Rusydi A et al. 2012 Phil. Trans. R. Soc. A 370 4927-43
[7] Barman A R, Annadi A, Gopinadhan K, Lu W M, Ariando, Dhar S and Venkatesan T 2013 AIP Adv. 2 012148
[8] Majidi M A, Bupu A and Fauzi A D 2016 Physica B http://dx.doi.org/10.1016/j.physb.2016.08.031
[9] Peng H, Li J, Li S and Xia J 2009 Phys. Rev. B 79 092411
[10] Qi D C et al. 2013 Phys. Rev. B 87 245201