Early transition metal dopants in cuprous oxide: To spin or not to spin

Aloysius Soon a, Joel Wallman c, Bernard Delley b, Catherine Stampfl a,c,*

a Department of Materials Science & Engineering, Yonsei University, Seoul, Republic of Korea
b Paul-Scherrer-Institut, Villigen PSI, Switzerland

Abstract

We present a trend study of a large variety of dopants at the cation site in Cu2O (i.e. substituting Cu), focussing largely on the early 3d-, 4d-, and 5d-transition metals (TMs) in which many of them are known to be non-magnetic. We also include s-, sp- and d-band metals for comparison. We find that doping with sp-elements results in zero spin moment while dopants with a partially filled d-band show a stronger tendency to magnetize and 3d-TM dopants exhibit a larger magnetic moment than most of the 4d- and 5d-TM dopants. From this trend study, we also find a correlation between their substitution enthalpy and associated interatomic relaxations. In particular, Ti-doped Cu2O appears to be an interesting system, given its “peculiar” ability to exhibit a spin moment when doped with a non-magnetic substituent like Ti. We also find that the interaction between two doped Ti atoms in Ti2:Cu2O is predominantly antiferromagnetic, and interestingly (and unexpectedly), this interaction rapidly declines as a function of inter-dopant distance, as in the case for the magnetic late-TM dopants like Co2:Cu2O.

Crown Copyright © 2013 Published by Elsevier B.V. All rights reserved.

1. Introduction

The recent discovery of high-temperature ferromagnetism in magnetically doped semiconductors has fuelled much effort to develop a reliable approach to control and design magnetic semiconductor-based devices for practical applications in spintronics technology [1–4]. It has been proposed that hole-doped, wide-band-gap semiconductors are favourable for achieving a Curie temperature (Tc) higher than 300 K. In particular, recent experimental [5,6] and theoretical [7–9] studies have shown that cuprous oxide, Cu2O, has the capability of acting as a host material, giving rise to ferromagnetic semiconductors with room temperature Tc. This was first shown for Al (0.5%) and Co (5%) co-doped Cu2O films grown via pulsed laser deposition by Kale et al. [10]. The authors first found that mono-doped Co:Cu2O leads to a spin glass-like behaviour while (V, Co) and (Zn, Co) co-doped Cu2O quench this spin glass behaviour and do not show any appreciable ferromagnetism. It was only the (Al, Co):Cu2O system that exhibited a large magnetization at room temperature. Antony and co-workers approached the Co:Cu2O system from a different angle and investigated its magnetic properties at the nano-scale [11]. They used the sputtering-aggregation technique and prepared crystalline nano-clusters of Co:Cu2O at a doping level of 5%. It was shown that for a cluster size ranging from 4 to 8 nm, it was then possible to achieve a ferromagnetic ordering up to temperatures of 400 K. Another Cu2O-based system that has shown much promise is the Mn:Cu2O system. Although it was first shown by Ivill et al. [12] that Mn:Cu2O exhibits ferromagnetic behaviour due to the binding of Mn3O4 secondary phases, Pan and co-workers found that Mn:Cu2O exhibits very weak ferromagnetism at very low temperatures (about 5–25 K) [13]. The authors noted that due to the multivalency of Mn, it was very challenging to characterize the oxidation state of Mn in this system, though their results suggest a lack of O/Mn secondary phases in their sample. It was only recently that several studies showed that Mn:Cu2O can indeed exhibit room temperature ferromagnetism [5,14]. With a dilute concentration of Mn (0.3–0.5%) in Cu2O, Wei et al. demonstrated that a Tc of more than 300 K could be achieved by reacting Cu2O with Mn2O3 at 923 K [14]. However, when the reaction temperature was increased to 1073 K, the Tc was lowered to 215 K. Coupling both experimental and theoretical approaches, they have also found that in Mn:Cu2O, Mn can take both substitutional and interstitial sites [12]. It was also proposed that the lowering of Tc at higher reaction temperatures was due to the antiferromagnetic super-exchange between substitutional Mn through the lattice O atoms.

In an attempt to understand these experimental findings, Sieberer et al. investigated the effects of impurity clustering and
ferromagnetic interactions in Co:Cu2O [7]. They performed first-principles density-functional theory (DFT) calculations, using projector augmented waves (PAW) as a basis within the generalized gradient approximation (GGA). It was shown that strong ferromagnetic coupling between the Co atom-pair in this system is mediated via an unconventional mechanism of occupying previously unoccupied energy levels, not requiring partially filled states like in the case of double-exchange or p–d coupling. Strong dimer binding energies were also found, indicating the favourability of Co defects, such as the copper and oxygen vacancies, can change the magnetic interactions of the dopants and bring about long-range ferromagnetism. It is proposed that copper vacancies may be incorporated to increase Tc. The authors conclude that magnetic interactions for Co:Cu2O are predominantly ferromagnetic and rather short-ranged, while those for Mn:Cu2O are fairly extended and antiferromagnetic, which can be changed by the presence of defects such as vacancies.

So far, experimental and theoretical investigations have focused on mid-to-late magnetic 3d TM dopants. In fact, relatively few studies have been conducted with early TM (and other non-magnetic elements) dopants in other semiconducting materials, such as (V, Cr, Ti) doped In2O3 and Ti:ZnO [15,16]. Thus, to offer a first step towards a microscopic understanding of the electronic and magnetic properties of early TM-doped Cu2O systems, we survey a wide range of both cationic and anionic dopants in Cu2O. This trend study focuses on the early TM, namely the 3d (Ti, V and Cr), 4d (Zr, Nb and Mo), and 5d (Hf, Ta and W) metals. However, for comparison, we also explore other dopants at the Cu site such as Mg, Al, Ca, Zn and Au, and dopants C, N and F at the O site, which are examined in less detail. In addition, using the Ti2:Cu2O system as an example, we study the Ti dopant–dopant interaction as a function of the distance between the two Ti atoms in the Cu2O matrix and compare that to the late transition metal doped systems e.g. Co2:Cu2O.

2. Computational method

All DFT calculations are performed using the full-potential all-electron DMOl3 code [17,18]. The exchange-correlation functional is approximated using the GGA due to Perdew, Burke and Ernzerhof (PBE) [19]. The DMOl3 code uses numerically defined local orbital functions as variational basis sets. The main idea is to solve the free atom exactly for the given functional, and then use variation functions to take into account the response of the atom to various molecular or other environments [17,18]. For this work, the DNP basis set is used. The wave functions are expanded in terms of a double-numerical quality localized basis set that explicitly incorporates polarization functions and scalar-relativistic corrections. The DNP basis set has been successfully used to describe other systems containing transition metals (see e.g. Refs. [20–23]). The quality of the basis set is also influenced by the atomic localization radius. In all calculations, we employ a global cutoff radius of 9 Bohr. With this setup, the total energy, force on the atoms, and displacements are converged to within 1 × 10−6 Ha/(2.7 × 10−5 eV), 3 × 10−4 Ha/Bohr (1.5 × 10−2 eV/Å), and 3 × 10−4 Bohr (1.6 × 10−2 Å), respectively, in the DFT self-consistent cycles. The Brillouin-zone integrations are performed using a Monkhorst–Pack (MP) grid of 12 × 12 × 12 for all face-centred cubic (FCC) and body-centred cubic (BCC) bulk metals, and 12 × 12 × 8 for the hexagonally-closed packed (HCP) metals. This results in a total of 56 special k-points in the irreducible Brillouin-zone (IBZ) for FCC and BCC metals, and 76 special k-points in the IBZ for HCP metals. The corresponding MP grid for the doped Cu2O systems, described using a (2 × 2 × 2) 48-atom supercell, is 6 × 6 × 6, giving rise to 28 special k-points in the IBZ. In this work, only the neutral charge states for all doped-Cu2O systems are considered.

Convergence tests for the calculations of metallic systems are performed. When the atomic radial cutoff is increased from 9 to 11 Bohr, the cohesive energy of the bulk materials varies by less than 32 meV. Similarly, using denser k meshes of (14 × 14 × 14) for FCC and BCC structures and (14 × 14 × 12) for HCP structures changes the cohesive energy by less than 2 meV per atom (except for zinc, which changes by 12.3 meV per atom). Spin-unrestricted calculations using non-spherical densities are performed to study the atomic and molecular species (O2, N2 and F2). To achieve excellent numerical accuracy, the atom radial cutoff for the calculation of both the atomic and molecular species is increased to 20 Bohr, with the largest basis set available in the DMOl3 code. For cationic substitutions, one Cu atom per supercell (out of the 32 Cu atoms in the supercell) is replaced with a dopant to give a concentration of 3.13%, which is well within the experimental doping regime. Replacing one oxygen atom per supercell gives an anionic dopant concentration of 6.25%.

Considering element-rich conditions, we define the substitution enthalpy, E sub for a dopant X in X:Cu2O as,

$$E_{\text{sub}} = E_{\text{X:Cu}_2\text{O}} - E_{\text{Cu}_2\text{O}} + \sum_i \Delta N_i E_i,$$

whereby $E_{\text{X:Cu}_2\text{O}}$ and $E_{\text{Cu}_2\text{O}}$ are taken as the total energy of the doped system, X:Cu2O and stoichiometric reference bulk Cu2O, respectively. $\Delta N_i$ (for species i = Cu, O or X) is the change in the number of Cu, O and X atoms, bearing a positive (negative) value when the species i is added to (removed from) the system. For cationic substitutions, $\Delta N_{\text{Cu}} = -1$ and $\Delta N_{\text{O}} = 0$ while for anionic substitutions, $\Delta N_{\text{Cu}} = 0$ and $\Delta N_{\text{O}} = -1$. For i = Cu, O or X, $E_i$ corresponds to the total energy of a bulk Cu atom, half the total energy of an O2 molecule or the normalized energy of X in its reference state. For example, when $X = Ti$, ETi will assume the total energy of a bulk Ti atom while for $X = F$, EF will take half the total energy of a F2 molecule.

3. Results and discussion

3.1. Bulk copper oxide, Cu2O

Cu2O crystalizes in a cuprite structure with space group Pn̅m3̅m [24]. There are two formula units of Cu2O in this unit cell with two inequivalent atoms: an O atom at (0,0,0) and a Cu atom at (1/4,1/4,1/4), as shown in Fig. 1a. Each Cu atom is linearly coordinated to two oxygen atoms, and all oxygen atoms are tetrahedrally surrounded by four Cu atoms. Cu2O is a direct band-gap p-type semiconductor, with a calculated band gap of 0.46 eV (see Fig. 1b and c), in agreement with other reported DFT values [8,21,22]. The well-established experimental value [25] is 2.17 eV and is typically significantly larger than that obtained by both the generalized-gradient (DFT-GGA) and local-density (DFT-LDA) approximation. We found the optimized lattice constant, bulk modulus, and enthalpy of formation for cuprous oxide to be 4.32 Å, 103.7 GPa, and
1.24 eV, respectively, as previously reported [20–22]. The corresponding experimental values are 4.27 Å, 112 GPa, and 1.75 eV. The theoretical enthalpy of formation, $H_{\text{Cu}_2O}$ [21,22], was found to be considerably smaller than the experimental value and this can, in part, be attributed to the overestimation of the binding energy of the oxygen molecule. The optimized lattice constant of bulk copper (neglecting zero-point vibrations) was calculated to be 3.65 Å, which agrees very well with the established experimental value of 3.61 Å [25]. The computed bulk modulus and cohesive energy are 194 GPa and 3.44 eV, being in excellent agreement with the experimental values of 137 GPa and 3.49 eV, respectively [25]. The slight overestimation of the lattice constant and the underestimation of the bulk modulus are in line with analogous studies for other transition metals.

### 3.2. Properties of bulk metals and molecules

The substitution enthalpy, $E_{\text{sub}}$ given by Eq. (1) depends on the atomic energy of the dopants. In addition, the distortion induced in the Cu$_2$O lattice to accommodate the dopant will, in general, depend on the size of the dopant. Therefore, in order to insure that the dopants are consistently defined, the atomic energies and bulk properties are calculated (or molecular properties where applicable) for all the elements studied and the results are used to analyse the properties of the doped systems.

We find that the overall trend is in good qualitative agreement with other ab initio calculations using the same GGA-PBE functional [26–30]: The largest deviation of the calculated unit cell volume is for calcium, at −5.38%, while the deviation is within ±3.5% for all other materials. The calculations underestimate the volume for all early 3d and all 5d TMs, but overestimate the volume for late 3d and all 4d TMs. As reported in other works [26], the bulk modulus is overestimated for materials where the lattice constant is underestimated and vice versa, (except for Zr). This inverse dependence is expected from the fact that the bulk modulus depends inversely on the volume. However, there appears to be no relation between the magnitude of the deviation in the volume and the magnitude of the deviation in the bulk modulus. The deviation from the experimental cohesive energy ranges from −22%, for zinc, to 18%, for tantalum. The cohesive energy is underestimated for all late transition metals examined, while overestimated for the early 5d TMs.

For the three considered molecules (i.e. N$_2$, O$_2$, and F$_2$), their binding energies are overestimated by about 0.5 eV, while their bond lengths are very slightly overestimated. The present calculations are consistent with previous calculations, namely, substantially overestimating the binding energy and slightly relaxing the bond length. Note that the trends in the substitution enthalpy (i.e. relative energy differences) for anions in Cu$_2$O (given by Eq. (1)) should not be substantially affected by the tendency to overestimate the binding energy of the molecule.

### 3.3. Geometrical distortions

To investigate doping concentrations in the experimental regime, (2 × 2 × 2) supercells (i.e. containing 48 atoms), with the lattice constant fixed at the optimised bulk value, are set up with the dopant atom at the centre of the supercell. For cations, this gives a substitution of 3.13% of the copper atoms, while for anions this gives a 6.25% substitution of the oxygen atoms. In particular, for the studied TM dopants, Table 1 lists the distance between the dopant atom and the first and second nearest neighbours, as well as the relative change in bond lengths from the pure Cu$_2$O host.

In the case of early TMs, the TM–Cu bond length ($d_{\text{NN}}$) is shorter than the Cu–Cu bonds in the pure Cu$_2$O host. This has been noted in other studies [7], where the proposed explanation is that the deviation from the d$^{10}$ configuration results in stronger TM–Cu bonds. In the case of the late TMs (d$^{10}$), namely Zn and Au, the TM–Cu bond length is longer than the Cu–Cu bonds in pure Cu$_2$O, which can be attributed to the filled d$^{10}$ shells inhibiting d$^{10}$–d$^{10}$ repulsion. However, there are anomalies in the distortion if it is merely considered in terms of a deviation from a d$^{10}$ configuration. For the early 3d TMs, we find the distortion decreases as the occupation of the 3d shell increases, whereas for 4d and 5d TMs, the distortion increases as the occupation of the 4d and 5d shell increases.

Fig. 2 shows the plot of the substitution enthalpy, $E_{\text{sub}}$, of the dopant (calculated using Eq. (1)) and the deviation in the distance from the first and second nearest neighbours from the equivalent bond lengths in pure Cu$_2$O. The values of $E_{\text{sub}}$ and the deviations in the distances are listed in Table 1. $\Delta d_{\text{NN}}$ denotes the deviation of the distance between the dopant and its first nearest neighbour relative to the Cu–O separation of 1.869 Å in pure Cu$_2$O. For cationic substitutions, there are two nearest neighbour O atoms, while for anionic substitutions there are four nearest neighbour Cu atoms.

### Table 1

<table>
<thead>
<tr>
<th>Transition metals</th>
<th>$d_{\text{NN}}$ (Å)</th>
<th>$\Delta d_{\text{NN}}$ (%)</th>
<th>$d_{\text{NN}}$ (Å)</th>
<th>$\Delta d_{\text{NN}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>1.94</td>
<td>3.8</td>
<td>3.02</td>
<td>−1.2</td>
</tr>
<tr>
<td>V</td>
<td>1.92</td>
<td>2.5</td>
<td>3.02</td>
<td>−1.1</td>
</tr>
<tr>
<td>Cr</td>
<td>1.96</td>
<td>4.9</td>
<td>3.05</td>
<td>−0.10</td>
</tr>
<tr>
<td>Zn</td>
<td>1.93</td>
<td>3.4</td>
<td>3.07</td>
<td>0.56</td>
</tr>
<tr>
<td>Zr</td>
<td>2.07</td>
<td>10.5</td>
<td>3.04</td>
<td>−0.39</td>
</tr>
<tr>
<td>Nb</td>
<td>2.00</td>
<td>6.9</td>
<td>3.00</td>
<td>−1.7</td>
</tr>
<tr>
<td>Mo</td>
<td>2.00</td>
<td>4.8</td>
<td>2.94</td>
<td>−3.7</td>
</tr>
<tr>
<td>Hf</td>
<td>1.96</td>
<td>7.2</td>
<td>3.00</td>
<td>−1.8</td>
</tr>
<tr>
<td>Ta</td>
<td>2.00</td>
<td>4.0</td>
<td>2.94</td>
<td>−3.6</td>
</tr>
<tr>
<td>W</td>
<td>1.94</td>
<td>1.4</td>
<td>2.92</td>
<td>−4.4</td>
</tr>
<tr>
<td>Au</td>
<td>2.02</td>
<td>8.3</td>
<td>3.08</td>
<td>0.75</td>
</tr>
<tr>
<td>$E_{\text{sub}}$ (eV)</td>
<td>−0.608</td>
<td>0.364</td>
<td>0.118</td>
<td>0.198</td>
</tr>
</tbody>
</table>

**Fig. 1.** (a) Crystal structure of Cu$_2$O. Cu atoms are represented by the larger spheres; smaller spheres represent O atoms; (b) shows the partial density-of-states (PDOS) of Cu$_2$O while its electronic band structure is shown in (c).
\[ \Delta d_{\text{NN}} \text{ denotes the deviation in the distance between the dopant and its second nearest neighbour relative to the Cu–Cu separation of 3.052 Å in pure Cu}_2\text{O for cation substitutions, and the O–O separation of 3.748 Å in pure Cu}_2\text{O for anion substitutions. For cationic substitutions, there are 12 second nearest neighbour Cu atoms and for anionic substitutions there are 8 second nearest neighbour O atoms. The qualitative trends (as shown in Fig. 2) in the substitution enthalpy for a dopant and the deviation in nearest neighbour separations required to accommodate the dopant are very similar, particularly when examining similar dopants. The exceptions to the similarity in trends of } E_{\text{sub}} \text{ are the anionic substituents, which have more unfavourable substitution enthalpies due to the high energy cost of creating the V}_\text{O}.\]

### 3.4. Electronic and magnetic structures

The partial density-of-states (PDOS) for 12 of the doped Cu\(_2\)O lattices are shown in Figs. 3 and 4. Most of the doped Cu\(_2\)O systems investigated were found to be non-magnetic, with the exceptions of Ti-, V-, Cr-, Nb-, Mo-, Ta- and W-doped Cu\(_2\)O resulting in a spin-polarized TM:Cu\(_2\)O system. The total magnetic moment per unit cell, the magnetic moment on the dopant atom and the magnetic moment on each of the two adjacent oxygen atoms for these elements are calculated from the Mulliken charge population and given in Table 2. It can be seen that the magnetic moments of the 3d TM-doped systems are greater than those of the 4d and 5d TM-doped ones, even though intrinsically most of these dopants themselves are known to be non-magnetic (e.g. Ti).

As can be seen from the PDOS in Figs. 3 and 4, the contributions from the dopant states near the Fermi level are highly localised, residing in the outermost, partially occupied \(d\) band of the dopant, resulting in highly localised spin-split impurity bands. This, however, is not seen for the doped systems with dopants having partially occupied \(s\) or \(p\) bands. Hence, we find that typically doping with \(sp\) elements results in zero spin moment while dopants with a partially filled \(d\) band show a stronger tendency to magnetize. The only dopants which result in a semiconducting state are Al and Au, for which the calculated DFT-PBE band gaps are 0.41 and 0.47 eV respectively, consistent with reported results [31].

Comparing with the PDOS of Ti-, V- and Cr-doped Cu\(_2\)O (Fig. 3a–c), the occupation of the 3\(d\) band increases gradually, approaching an almost half-filled \(d\) shell stepwise. This progressive occupation of the 3\(d\) band largely accounts for the increasing magnetic moment seen in these systems (see Table 2). The total magnetic moment of Cr-doped Cu\(_2\)O is comparable with that of Mn-doped Cu\(_2\)O [7]. However, due to the smaller on-site exchange integral, the magnetisms of 4\(d\) and 5\(d\) TM-doped Cu\(_2\)O are weaker than that of the corresponding 3\(d\) TM-doped Cu\(_2\)O. This is most prominent for non-magnetic Zr- and Hf-doped Cu\(_2\)O systems. The PDOS for Mo- and W-doped Cu\(_2\)O (Fig. 4c and f, respectively) demonstrate half-metallic character, which may present promising applications such as a polarisation diode if unwanted secondary phases do not form in these systems.

To further investigate the effective magnetic interaction between substitutional dopants, we use the Ti\(_2\):Cu\(_2\)O system as an example and study the energy difference between a ferromagnetic (FM) and an antiferromagnetic (AFM) spin arrangement for two Ti atoms in the 48-atom supercell of the Cu\(_2\)O matrix, corresponding to 6.7% doping. The first Ti atom is positioned at the middle of the supercell (1/2,1/2,1/2), while the other Ti atoms position is varied according to the next nearest neighbour of the first (as in Fig. 5a). The PDOS of these Ti\(_2\):Cu\(_2\)O systems are also calculated, with that of the third nearest neighbour shown in Fig. 5b. In addition, given that Cu\(_2\)O is known to be substoichiometric (i.e. contains copper vacancies, V\(_\text{Cu}\)) [22], we also study the energy differences and magnetic interactions of Ti\(_\text{Cu}\) and V\(_\text{Cu}\) again as a function of their inter-
defect distance, as shown in Fig. 5c and d. In this case, the position of $V_{\text{Cu}}$ follows that as shown in Fig. 5a. For the Ti$_2$:Cu$_2$O system, both the AFM and FM configurations are thermodynamically more stable than the singly doped Ti:Cu$_2$O, with the AFM spin arrangement being marginally more stable (30 meV/Ti or less). In fact, generating a copper vacancy, $V_{\text{Cu}}$, with a singly Ti-doped system (i.e. TiCu$^+$ + $V_{\text{Cu}}$) is also found to be energetically more favourable than the singly doped case, but less favourable than the doubly doped Ti$_2$:Cu$_2$O system. It can be seen from Fig. 5c that it is energetically most favourable for the Ti atoms to be close to each other at next-nearest-neighbour cation sites (position 2 in Fig. 5a). Relative to the energy of this favoured configuration, positions 1, 3, 4 and 5 are 44, 42, 70 and 114 meV less favourable. This suggests that the Ti dopants prefer close-distance interactions (i.e. pairing) rather than being far apart from one another, similar to what has been found for Co in Cu$_2$O [7]. With regards to the calculated magnetic moments (in Fig. 5d), we see that the magnetic moment decreases rather quickly with respect to the decreasing distance between Ti atoms, and that the preference of AFM versus FM becomes rapidly smaller for greater distances, indicating that perhaps, like in the case of Co$_2$:Cu$_2$O [8,9], the magnetic interactions are also not carrier mediated. As seen in the PDOS (Fig. 5b), the Fermi level is located in the energy gap of the Cu$_2$O host matrix for the down-spin states, and inside the Ti 3$d$ states for the up-spin states, rendering no Cu$_2$O host states at the Fermi level which is required for the long-range magnetic interactions between the localized magnetic moments, as in Mn$_2$:Cu$_2$O [7]. To further our understanding of these magnetic interactions, detailed calculations of their charged states would be required to determine whether these charged states are energetically favoured as a function of their formation energies [32].

4. Conclusions

The characteristics of doped Cu$_2$O lattices (for the neutral charge state) have been investigated by DFT calculations, and it has been found that early transition metal doping results in ground state magnetic effects. However, the majority of the early TMs have unfavourable formation energy.

We find that doping Cu$_2$O with sp elements results in zero spin moment while TM dopants with a partially filled d band show a stronger tendency to magnetize. It is observed that 3d early non-magnetic TM dopants yield a larger magnetic moment than that of early 4d and 5d TM dopants. Interestingly, we propose Ti-doped Cu$_2$O to be studied further, given its favourable substitution enthalpy and its ability to exhibit a spin moment when doped with a non-magnetic substituent like Ti. Doping with Mo and W also warrant further investigation due to the half-metallic nature of the resultant lattice. We find that for the doubly doped Ti$_2$:Cu$_2$O system, anti-ferromagnetic spin arrangement is thermodynamically
preferred and is found to be more stable than the singly doped case. However, their magnetic interactions weaken rather quickly as the distance between the two Ti atoms increases, suggesting that this magnetic interaction is not carrier mediated as suggested from the calculated PDOS.

One direction in which such an investigation might proceed is to perform DFT calculations on doping Ti in the interstitial sites and for various possible charged states, as well as the consideration of the interaction between more than two Ti atoms. In particular, we stress that one may be required to go beyond standard DFT (e.g. within DFT + U, using hybrid DFT functionals etc.) as investigated recently for point defects in Cu₂O [33].

Acknowledgement

The authors gratefully acknowledge support by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF Grant No. 2011-8-0952), as well as the Australian Research Council (ARC). Computational resources have been provided by the Australian National Computational Infrastructure (NCI).

References