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# 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
[c] School of Physics, The University of Sydney, Sydney, New South Wales, Australia

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## ABSTRACT

We present a trend study of a large variety of dopants at the cation site in $Cu_2O$ (i.e. substituting Cu), focussing largely on the early 3*d*-, 4*d*-, and 5*d*-transition metals (TMs) in which many of them are known to be non-magnetic. We also include *s*-, *sp*- and $d^{10}$-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 3*d*-TM dopants exhibit a larger magnetic moment than most of the 4*d*- and 5*d*-TM dopants. From this trend study, we also find a correlation between their substitution enthalpy and associated interatomic relaxations. In particular, Ti-doped $Cu_2O$ 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 $Ti_2$:$Cu_2O$ 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 $Co_2$:$Cu_2O$.

## 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 ($T_c$) higher than 300 K. In particular, recent experimental [5,6] and theoretical [7–9] studies have shown that cuprous oxide, $Cu_2O$, has the capability of acting as a host material, giving rise to ferromagnetic semiconductors with room temperature $T_c$. This was first shown for Al (0.5%) and Co (5%) co-doped $Cu_2O$ films grown via pulsed laser deposition by Kale et al. [10]. The authors first found that mono-doped Co:$Cu_2O$ leads to a spin glass-like behaviour while (V, Co) and (Zn, Co) co-doped $Cu_2O$ quench this spin glass behaviour and do not show any appreciable ferromagnetism. It was only the (Al, Co):$Cu_2O$ system that exhibited a large magnetization at room temperature. Antony and co-workers approached the Co:$Cu_2O$ system from a different angle and investigated its magnetic properties at the nano-scale [11]. They used the sputtering-aggregation technique and prepared crystalline nanoclusters of Co:$Cu_2O$ 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 $Cu_2O$-based system that has shown much promise is the Mn:$Cu_2O$ system. Although it was first shown by Ivill et al. [12] that Mn:$Cu_2O$ exhibits ferromagnetic behaviour due to the binding of $Mn_3O_4$ secondary phases, Pan and co-workers found that Mn:$Cu_2O$ 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:$Cu_2O$ can indeed exhibit room temperature ferromagnetism [5,14]. With a dilute concentration of Mn (0.3–0.5%) in $Cu_2O$, Wei et al. demonstrated that a $T_c$ of more than 300 K could be achieved by reacting $Cu_2O$ with $Mn_2O_3$ at 923 K [14]. However, when the reaction temperature was increased to 1073 K, the $T_c$ was lowered to 215 K. Coupling both experimental and theoretical approaches, they have also found that in Mn:$Cu_2O$, Mn can take both substitutional and interstitial sites [12]. It was also proposed that the lowering of $T_c$ 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

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* Corresponding author. School of Physics, The University of Sydney, Sydney, New South Wales, Australia. Tel.: +61 2 935 15901; fax: +61 2 935 17726.
*E-mail address:* stampfl@physics.usyd.edu.au (C. Stampfl).

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ferromagnetic interactions in Co:$Cu_2O$ [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 atoms to cluster in Co:$Cu_2O$ [7]. Other transition metal TM-doped $Cu_2O$ systems were also studied by Sieberer et al. [7] in a trend study of magnetic Mn-, Fe-, Co- and Ni-doped $Cu_2O$ systems. Using the same theoretical approach, they find that for defect-free Co-doped $Cu_2O$, ferromagnetic alignment is favoured and the magnitude of this preference over anti-ferromagnetic alignment decreases quickly with increasing inter-Co distance. In the case of defect-free Mn-doped $Cu_2O$, the antiferromagnetic alignment is always dominant and extended (i.e. with increasing inter-Mn distance), indicating that Mn:$Cu_2O$ may not be a suitable candidate for spintronic applications [7]. However, the introduction of lattice 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 are likely to increase $T_c$. The authors conclude that magnetic interactions for Co:$Cu_2O$ are predominantly ferromagnetic and rather short-ranged, while those for Mn:$Cu_2O$ 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* 3*d* 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 $In_2O_3$ 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 $Cu_2O$ systems, we survey a wide range of both cationic and anionic dopants in $Cu_2O$. This trend study focuses on the early TM, namely the 3*d* (Ti, V and Cr), 4*d* (Zr, Nb and Mo), and 5*d* (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 $Ti_2$:$Cu_2O$ system as an example, we study the Ti dopant–dopant interaction as a function of the distance between the two Ti atoms in the $Cu_2O$ matrix and compare that to the late transition metal doped systems e.g. $Co_2$:$Cu_2O$.

## 2. Computational method

All DFT calculations are performed using the full-potential all-electron DMol$^3$ code [17,18]. The exchange-correlation functional is approximated using the GGA due to Perdew, Burke and Ernzerhof (PBE) [19]. The DMol$^3$ 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 $1 \times 10^{-6}$ Ha ($2.7 \times 10^{-5}$ eV), $3 \times 10^{-4}$ Ha/Bohr ($1.5 \times 10^{-2}$ eV/Å), and $3 \times 10^{-4}$ Bohr ($1.6 \times 10^{-2}$ 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 $Cu_2O$ 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-$Cu_2O$ 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 BCC and FCC 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 ($O_2$, $N_2$ and $F_2$). 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 DMol$^3$ 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, $E_{\text{sub}}$ for a dopant $X$ in $X$:$Cu_2O$ as,

$$E_{\text{sub}} = E^{X:\text{Cu}_2\text{O}} - E^{\text{Cu}_2\text{O}}_{\text{bulk}} + \sum_i \Delta N_i E_i, \tag{1}$$

whereby $E^{X:\text{Cu}_2\text{O}}$ and $E^{\text{Cu}_2\text{O}}_{\text{bulk}}$ are taken as the total energy of the doped system, $X$:$Cu_2O$ and stoichiometric reference bulk $Cu_2O$, 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 $O_2$ molecule or the normalized energy of $X$ in its reference state. For example, when $X$ = Ti, $E_{\text{Ti}}$ will assume the total energy of a bulk Ti atom while for $X$ = F, $E_{\text{F}}$ will take half the total energy of a $F_2$ molecule.

## 3. Results and discussion

### 3.1. Bulk copper oxide, $Cu_2O$

$Cu_2O$ crystallizes in a cuprite structure with space group $Pn\bar{3}m39$ [24]. There are two formula units of $Cu_2O$ 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. $Cu_2O$ 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