Structural, electronic, optical, and magnetic properties of Co-doped Cu_2O

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We investigate the magnetic properties of Co-doped Cu_2O. We studied first the electronic and structural properties of Cu_2O using the optimization of the lattice constant which is 4.18 Å. The calculated gap is found between 0.825 eV and 1.5 eV, these values are in good agreement with the experimental results. The Co atoms are inserted in Cu_2O by means of the density functional theory (DFT) using LSDA, LSDA + U, and LSDA + MBJ approximations in the WIEN2k code, based on the supercell model by setting up 12, 24, and 48 atoms in $(1\times1\times2)$, $(1\times2\times2)$, and $(2\times2\times2)$ supercells respectively with one or two copper atoms being replaced by cobalt atoms. The energy difference between the ferromagnetic and antiferromagnetic coupling of the spins located on the substitute Co has been calculated in order to obtain better insight into the magnetic exchange coupling for this particular compound. The studied compound exhibits stable integer magnetic moments of 2 μ_B and 4 μ_B when it is doped with 2 atoms of Co. Optical properties have also been worked out. The results obtained in this study demonstrate the importance of the magnetic effect in Cu_2O.

Keywords: Cu_2O, electronic structure, magnetic properties, optical properties

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1. Introduction

Recently, much effort has been put into exploring new semiconductors which can be suitable as hosts for a new DMS system because of the importance in their potential applications in spintronic devices and also for their importance in basic magnetism.

Cuprous oxide Cu_2O as p-type oxide-based diluted magnetic semiconductors (DMSs) is attracting increasing attention because of its advantages, such as simple structure and composition, no toxicity and low production cost. Its energy gap is 2.1 eV,[1,2] therefore it has been used in the field of solar cell,[3–6] photocatalytic water splitting[7–9] or photo degradation of pollution,[10,11] spin transistors,[12–15] and DMS.[16] Cu_2O has four different states depending on the various combinations of valence band holes and conduction band electrons.

Due to the important effect of the magnetic atom in the semiconductor, transition metals like Mn, Fe, Ni, and Co are doped into semiconducting oxide hosts such as Cu_2O, TiO_2, and ZnO to form diluted semi conducting material.[17] Large studies reported that the doping could improve the electronic, magnetic, and optical properties,[18,19] like Mn-, Fe-, Co-, and Ni-doped Cu_2O by Sieberer,[20] Mn-doped Cu_2O epitaxial films reported by Liu *et al.*[21,22] and Co-doped Cu_2O by Antony *et al.*[23] Kale *et al.* also found that Co-doped Cu_2O films could be ferromagnetic by co-doping with Al.[24] On the other hand, there are still some reports indicating that no sign of ferromagnetism is seen in Mn-doped Cu_2O films.[25]

In this paper, we did a systematical study on the structural and electronic properties of Cu_2O, and the main motivation of our work is to explore the possibility of inducing ferromagnetism in cuprous oxide by doping a few percent of cobalt atoms to understand and practice the spintronic or the electron spin. The other aspect is to investigate the optical properties such as reflectivity and refraction index of various compounds which is not studied as much as it should be despite the great importance in applications of optoelectronic materials.

All the properties are calculated theoretically by using the full potential linearized augmented plane wave (FL PLAW) within the density functional theory (DFT) with the local spin density approximation (LSDA), (LSDA+U) methods within density functional theory, we explicitly include the on-site Coulomb interaction term in the Hamiltonian, which describes strongly correlated systems which contain transition metal (3d electron) and LSDA + mBJ methods to use the modified Becke–Johnson potential (mBJ) to allow the calculation of band gaps with accuracy. Many useful results have been obtained and compared with other calculated or experimental ones. Our investigated results may offer theoretical data for the applications of Co-doped Cu_2O in magnetic or optoelectronic sides.

2. Computational details

Cu_2O crystallizes in a cubic structure with a lattice constant of $a = 4.2696$ Å and space group of $Pn3N$, its unit cell contains six atoms. The four copper atoms are situated in a face-centered cubic lattice and the two oxygen atoms are tetrahedral sites forming a body-centered cubic sub-lattice. The

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constants of lattice are $a = b = c$, and $\alpha = \beta = \delta = 90°$.[26]

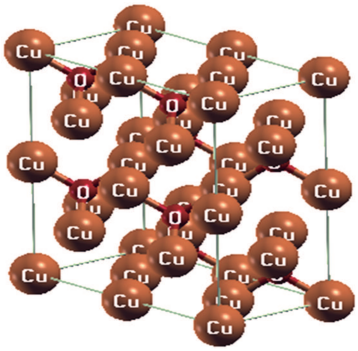


Fig. 1. (color online) The $1 \times 2 \times 2$ supercell of Cu_2O in cubic structure.

All the calculations are based on the supercell model. We chose to study $(1 \times 1 \times 2)$, $(1 \times 2 \times 2)$, and $(2 \times 2 \times 2)$ supercells which contain 12, 24, and 48 atoms, using mesh number of 100. The calculations were performed with wien2k code,[27] which is based on the density functional theory (DFT) with the LSDA, LSDA+U, and LSDA+mBJ approaches.

For the magnetic properties two kinds of doping concentrations are created by replacing one or two copper atoms with transition metal atoms. Two special arrangements are considered with the first transition metal atom being fixed at the site (0 0 0) and the second atom being put at the first or the second neighbor site.

3. Results and discussion

The optimized lattice constant of a pure Cu_2O and Co-doped Cu_2O is 4.18 Å, this result is in reasonable agreement with the experimental value.[28] We found almost the same in both cases because the Co radius is very close to the Cu one.

3.1. Electronic properties

In order to analyze the magnetic and the optical properties of Co-doped Cu_2O, we first investigate its electronic properties based on the optimization. The energy band structure and total density of states (DOS) of pure and Co-doped Cu_2O are shown in Figs. 2(a), 2(b), and 2(c). We chose to study $(1 \times 2 \times 2)$ superlattice model. The top of the valence band (VB) and the bottom of the conduction band (CB) are composed of Cu 3d and O 2p states respectively.

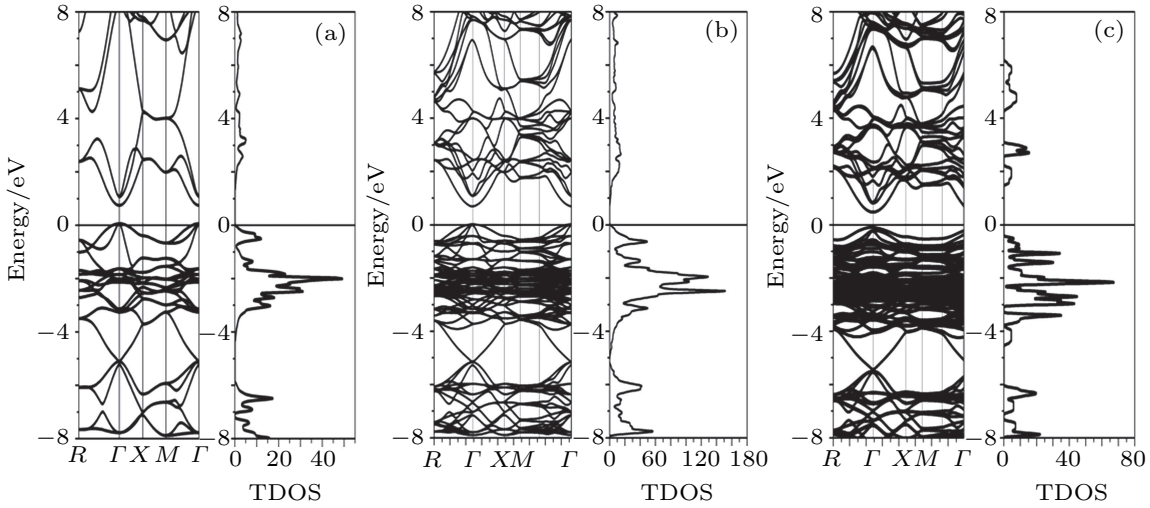


Fig. 2. The $1 \times 1 \times 1$ and $1 \times 2 \times 2$ total densities of states and band structure of pure Cu_2O [(a) and (b)], Co-doped Cu_2O (c).

We calculated the gap energy of a pure Cu_2O with LSDA and LSDA+mBJ approximations based on the density functional theory in order to find the best approximation for our study. The results are listed in Table 1.

Table 1. Values of calculated gap energy in Cu_2O obtained at the optimized lattice parameter $a = 4.18$ Å.

Gap energy/eV	LSDA	LSDA+MBJ	Exp value/eV
Cu_2O mono-crystal	1.33	1.324	2.1
$(1 \times 1 \times 2)$	1.931	2.160	
$(1 \times 2 \times 2)$	2.20	2.26	
$(2 \times 2 \times 2)$	1.220	1.454	
Other works	1.34 eV, 0.99 eV, and 1.8 eV (Ref. [29])		

In all cases, both LSDA and LSDA+mBJ calculations give values in good agreement with the experimental ones. So we chose the LSDA approximation for the rest of our work.

The total densities of states of Cu_4O_2, $Cu_{16}O_8$, and $Cu_{15}Co_1O_8$ are shown in Figs. 2(a), 2(b), and 2(c). In comparison with experimental data,[20,30,31] the total densities of states of all are made up of two groups of phonon states (low- and high-frequency states) separated by a gap. There is a distribution between −8 eV and 0 eV caused by the Co 4d states. The Co 4d and Cu 3d form a new orbital with O 2p which drives to a new distribution of energy of Co-doped Cu_2O and the conduction band moves to the Fermi level.[20]

The band structure of both pure and Co-doped Cu_2O present a direct band gap but for Co-doped Cu_2O our results

underestimate the real band gap of Cu_2O. The reason for the under-estimated band gap is the exchange–correlation energy; Co is a transition metal, the spin exchange between local spin states and the sp band result in the valence and conduction bands shifting to a low energy zone, and the shift of valence band is larger than conduction band,[32] so when the interaction between 4d of cobalt and 2p of oxygen increases, the band gap decreases as shown in Table 2.

Table 2. Values of calculated gap energy in Co-doped Cu_2O obtained at the optimized lattice parameter $a = 4.18$ Å.

Energy gap/eV	LSDA/eV	LSDA + U/eV	(LSDA + mBJ)/eV
$(1\times1\times2)$	0.115	0.258	1.585
$(1\times2\times2)$	0.232	0.107	1.90
$(2\times2\times2)$	0.112	0.101	1.30

3.2. Magnetic properties

As pointed out in the introduction, the idea developed in this work is to dope Cu_2O with impurities to change their properties. This approach can be followed to introduce magnetic elements into non magnetic semiconductors to make them magnetic. In this part we investigate the effect of the magnetic impurity in the Cu_2O structure. A study of Co inserted in Cu_2O with one or two copper atoms being replaced has been carried out but in this study the LSDA + U approximation was the best. The Hubbard U used in the magnetic properties of doped superlattices with value of $U_{\text{eff}} = U - J = 8.5$ eV was used too.[33] The results were calculated using 4% and 8% of cobalt concentration. The compound considered in this study exhibits a stable integer magnetic moment of 2 μ_B,[20] the results are given in Table 3.

In order to estimate the stability of the ferromagnetic (FM) against an anti-ferromagnetic (AFM) alignment of the spins, the energy difference between a ferromagnetic and an anti-ferromagnetic spin arrangement has been calculated for two Co atoms in $Co_2Cu_{14}O_8$. One Co atom was put at the origin (0 0 0), and the other one was assumed to occupy the (1/2, 1/2, 1/2) site. The ground state magnetic properties have been calculated using the total energy difference between FM and AFM ground state ($\Delta E = E_{\text{AFM}} - E_{\text{FM}}$). As shown in Table 4 the AFM state is lower than that of the FM state, so that indicates that the compound is more stable with FM alignment.[20,34]

Table 3. Values of total and partial magnetic moment of Co-doped Cu_2O.

112 supercell	LSDA	LSDA + U	LSDA + mBJ
MMT/(μ_B/cell)	2.00014	2.00046	2.000
On Co/(μ_B/atom)	1.61487	1.81043	1.88063
On O(μ_B/atom)	0.03048	0.02212	0.02028
122 supercell			
MMT	1.97694	2.00011	2.000
On Co	1.61368	1.98441	1.88832
On O	0.02281	0.00731	0.01121
222 supercell			
MMT	2.01714	2.00154	2.000
On Co	1.70322	1.88312	1.88121
On O	0.02216	0.00152	0.02001

Table 4. The magnetic coupling modes of two atoms of Co-doped Cu_2O in unit Rydberg.

Approximation	Supercell structure	E_{FM}	E_{AFM}	ΔE	Coupling
LSDA	$1\times1\times1$	–12473.52577	–12473.49544	+0.03032	FM
	$1\times1\times2$	–25992.44382	–25992.43331	+0.01051	FM
	$1\times2\times2$	–53030.33100	–53030.32115	+0.009849	FM
LSDA + mBJ	$1\times1\times1$	–12472.70891	–12472.70084	+0.00807	FM
	$1\times1\times2$	–25990.84125	–25990.83939	+0.01998	FM
	$1\times2\times2$	–53027.44250	–53027.39271	+0.04979	FM
LSDA + U	$1\times1\times1$	–12473.03589	–12473.06665	+0.03076	FM
	$1\times1\times2$	–25992.29765	–25992.29763	+0.00002	FM
	$1\times2\times2$	–53030.3338	–53030.3336	+0.0002	FM

3.3. Optical properties

The optical properties are studied through the dielectric function, refractive, index, reflectivity, and energy loss function. At low energy and considering only the electric dipole approximation, the total dielectric function is:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + \varepsilon_2(\omega), \tag{1}$$

where ε_1 is the real part of the complex dielectric function while ε_2 corresponds to the imaginary part. The imaginary part $\varepsilon_2(\omega)$ can be calculated from the momentum matrix element between the occupied and unoccupied wave functions within the selection rules while the real part $\varepsilon_1(\omega)$ of the complex dielectric function can be obtained using the Kramers–Kronig relationship.[35,36] The imaginary and real parts of the dielectric function $\varepsilon(\omega)$ are given respectively[36–40]

$$\varepsilon_2(\omega) = \left(\frac{4\pi^2 e^2}{m^2\omega^2}\right)\sum_{i,j}\int_k \langle i|M|j\rangle^2 f_i(1-f_i) \times \delta\left(E_{i,j} - E_{i,k} - \omega\right) \mathrm{d}^3k, \tag{2}$$

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} p \int_0^{\infty} \frac{\omega' \varepsilon_2(\omega')\, \mathrm{d}\omega'}{(\omega'^2 - \omega^2)}. \quad (3)$$

All other optical constants such as the refractive index $n(\omega)$, reflectivity $R(\omega)$, and energy loss $L(\omega)$ can be found using $\varepsilon_1(\omega)$, and $\varepsilon_2(\omega)$, where[36–40]

$$n(\omega) = \left[\frac{\varepsilon_1(\omega)}{2} + \frac{\sqrt{\varepsilon_1(\omega) + \varepsilon_2(\omega)}}{2} \right]^{1/2}, \quad (4)$$

$$L(\omega) = \frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2}, \quad (5)$$

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2. \quad (6)$$

The optical constants are calculated to study the influence of cobalt impurity on the optical properties of Cu_2O for $(1 \times 2 \times 2)$ supercell. The calculated real and imaginary parts of the dielectric function of pure and Co-doped Cu_2O are displayed in Fig. 3.

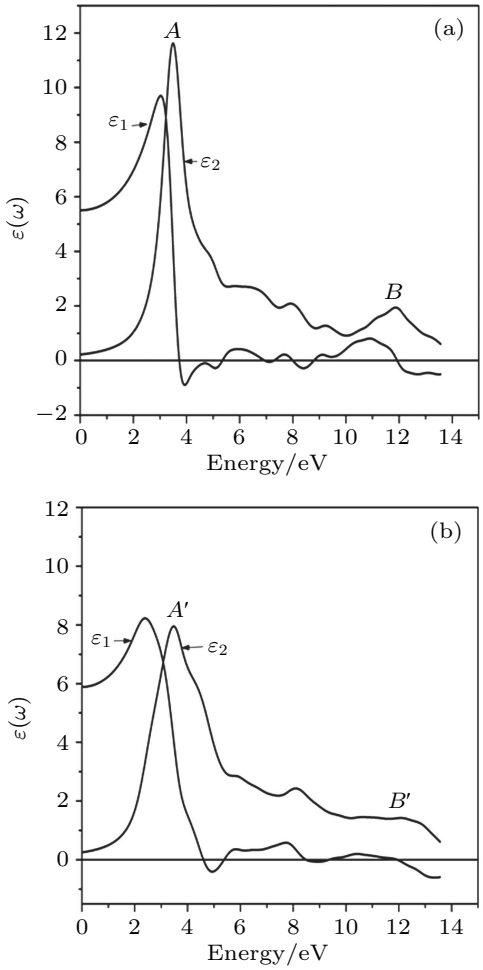


Fig. 3. Real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the dielectric function for (a) pure Cu_2O and (b) Co-doped Cu_2O.

The curve of the imaginary part $\varepsilon_2(\omega)$ for pure Cu_2O consists of two peaks: A (11.58, 3.5 eV) corresponds to the transition from Cu 3d states to the O 2p states at Γ point while the B (2, 11.85 eV) peak derives from transition from Cu 4s to O 2p states.[32] The A peak also appears in the curve of $\varepsilon_2(\omega)$ for Co-doped Cu_2O but with weaker intensities A' (7.94, 3.44 eV) and B' (1.41, 11.93 eV) vanishes due to the split of energy levels after the Co doping. The valence bands shifts to the Fermi level and the transitions are forbidden at higher energy level.

In the curve of $\varepsilon_1(\omega)$, the static dielectric constants at zero frequency limit of Cu_2O and Co-doped Cu_2O are 9.67 and 8.22 respectively. A negative distribution appears in (4 eV) and in (4.85 eV) respectively. It indicates that both Cu_2O and Co-doped Cu_2O show a metallic behavior in this frequency region.

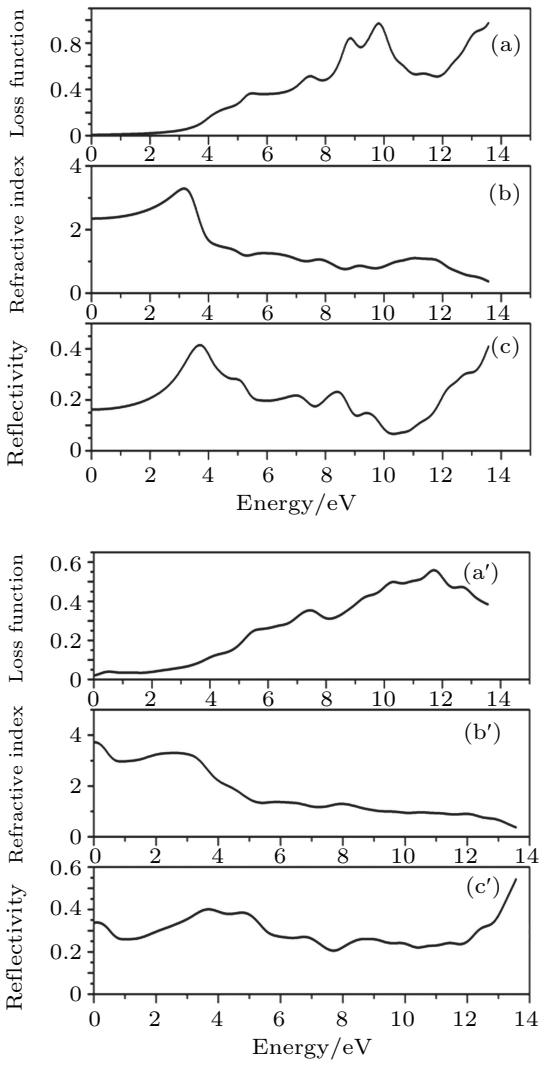


Fig. 4. The calculated electron energy loss spectrum $L(\omega)$ [(4a) and (4a′)], refractive index [(4b) and (4b′)], and the optical reflectivity $n(\omega)$ [(4c) and (4c′)] of $Cu_{16}O_8$ and $Cu_{15}Co_1O_8$.

The calculated values of the energy loss function, the refractive index, and the reflectivity of Cu_2O and Co-doped Cu_2O are shown in Figs. 4(a), 4(b), 4(c) and Figs. 4(a′), 4(b′), 4(c′) respectively. The loss function describes a fast electron traveling in a material; the higher value in $L(\omega)$ spectra represents the characteristic associated with plasma resonance.[40] The resonant energy loss are located at about (9.80 eV) for Cu_2O and about (11.76 eV) for Co-doped Cu_2O. In addition

the static refractive index $n(0)$ of pure Cu_2O is 2.5, while for Co-doped Cu_2O it is higher $(n(0) = 3.8)$. This increase is caused by the doping impurity.

4. Conclusion

In this study, the LSDA, LSDA+U, and LSDA+mBJ have been performed in order to analyze the electronic and magnetic properties of pure and Co-doped Cu_2O supercell. The results obtained indicate that the calculated electronic structure and magnetic properties are in good agreement with the experiments ones. The band gap is equal 1.9 eV for pure Cu_2O and 0.3 eV for Co-doped Cu_2O which are comparable with other experimental and calculated results. For the magnetic properties the substance shows a stable ferromagnetism with a total magnetic moment of 2 μ_B. Also the dielectric function and optical constants are calculated to study the influence of Co impurity on the optical properties of our compound and the results agree well with the experimental data.

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