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Electronic and optical studies of Cu_2O with oxygen defects: A DFT approach

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ABSTRACT

Systematic examination of Cu_2O super cell with and without oxygen defects by using DFT method in SIESTA package. Structural, electrical, optical and HOMO-LUMO properties of Cu2O super cell was analyzed by Generalized Gradient Approximation (GGA). From the band structure, we observed that the removal of oxygen tends to decrease the band gap. The electronic properties such as HOMO-LUMO energy level, ionization potential and electron affinity were studied in DFT method. It was observed that the absorption coefficient was decreased with increasing of oxygen vacancies.

Keywords: Cu_2O super cell; DFT; optical properties; band structure; DOS; HOMO-LUMO level

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INTRODUCTION

Cuprous oxide (Cu_2O) has wide application in the field of solar energy conversion and photo catalytic water splitting. Cuprous oxide is one of the p-type semiconductors because the copper vacancies are negatively charged and mostly oxygen is intersitial. Cuprous oxide (Cu_2O) band gap was 2.17 eV [1]. Theoretical calculation of the Cu_2O shows a small band gap is in the range of 0.5 eV to 0.8 eV. The photoconductivity is limited by minority carrier recombination; it was caused by defect trap states. Here we use density functional theory method for simulation, mainly focus on determination of inter-atomic forces and vibration spectra of nano- structures. The oxygen vacancy contributes to band gap widening because the oxygen vacancy easily affects the electronic structure [2]. X-ray photoelectron spectroscopy is used for analysing the electronic structure and bonding of Cu_2O and it gives the good result for the valence-band states. The choice of exchange-correlation functional is a crucial issue for surface calculation. Generalized gradient approximations (GGA) can give very much better dissociation energies [3] and are now widely used in molecular calculations; there is strong evidence that they also give much better adsorption energies [4].

COMPUTATIONAL DETAILS

Full geometry optimization of Cu_2O super cell of with and without oxygen defects parameters are calculated by DFT method with the help of SIESTA package. The basis set is completely optimized the Cu_2O super cell and studied all the parameters. Double zeta basis type has been used for Cu_2 and O atoms. The convergence criteria for self consistent field calculation [5] are 10^{-5} on the total energy. For band structure calculation 3 x 3 x 2 monk horst pack grid was used to sample the brillouin zone [6]. Meshcutoff for the SCF calculation [7] was set to 140 Ry. The optical excitation calculation is performed within the energy range of 0 to 5 hartrees with 0.02eV broadening value. For optical calculation 1x1x1 optical mesh is used with 0.02 eV optical broadening.

RESULTS AND DISCUSSION

3.1 Structures of Cu_2O, $1Cu_2O$, $2Cu_2O$, $3Cu_2O$ for 36 atoms

The Cu_2O structure was analysed in two forms namely with and without oxygen defects and its computational details were approached by using density functional theory (DFT). Optimizing the electronic structure of Cu_2O super cell by using first principle density functional theory (DFT) with the help of standard generalized gradient approximation (GGA) and local density approximation (LDA) [8]. The energy obtained for pure Cu_2O was -46361.74128 eV. The removal of one oxygen from the super cell ($1Cu_2O$) makes defects which tend to decrease the stability of the structure. The obtained energy for ($1Cu_2O$) structure is -45925.55527 eV. When two oxygen vacancies are created in the structure ($2Cu_2O$), the structure was not stable because of increase in oxygen vacancies. The obtained energy for ($2Cu_2O$) structure is -45489.33608 eV. When the super cells have three oxygen vacancies ($3Cu_2O$) this results more F centre are formed and cluster becomes more unstable. The energy obtained for ($3Cu_2O$) is -45053.11037 eV [10]. The energy obtained for exchange correlation, kinetic energy is shown in the table 1[9].

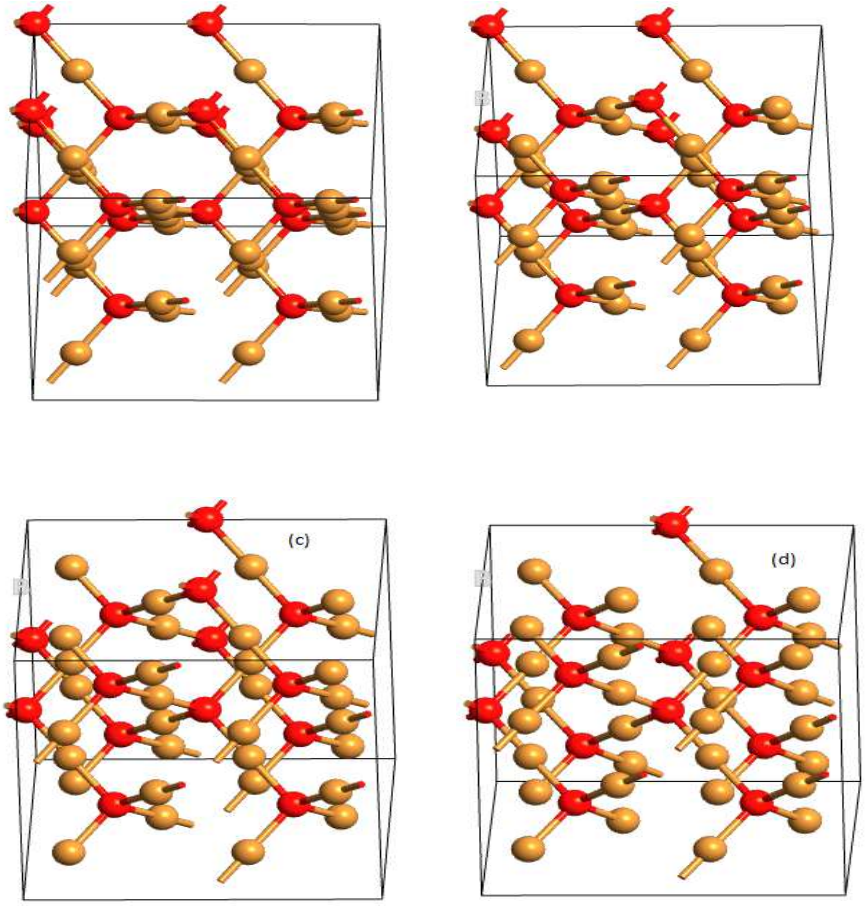

Fig.1. Optimized Structures of Cu_2O, $1Cu_2O$, $2Cu_2O$, $3Cu_2O$ for 36 atoms

Table 1: Total Energy of exciting structure of Cu_2O, $1Cu_2O$, $2Cu_2O$, $3Cu_2O$ for 36 atoms

System Name	Exchange Correlation (eV)	Kinetic Energy (eV)	Electrostatic Energy (eV)	Entropy-Term	Total energy (eV)
Cu_2O	-9331.87397	48166.84954	-85196.7168	-0.00002	-46361.74128
$1Cu_2O$	-9230.23442	47865.99071	-84561.31156	0	-45925.55527
$2Cu_2O$	-9128.49158	47564.51011	-83925.35461	0	-45489.33608
$3Cu_2O$	-9026.7569	47263.10928	-83289.46273	-0.00002	-45053.11037

3.2 Band Structures of Cu_2O, $1Cu_2O$, $2Cu_2O$, $3Cu_2O$

We observed that the Cu_2O is a direct band gap semiconductor, In theoretical calculation, the electronic structure of Cu_2O have low band gap in the range of 0.5 eV to 0.8 eV [1] is shown in Fig (2). The experimental value is comparatively greater than the theoretical value, the density functional theory method usually under estimated by the band gap because of the well known problem in GGA approximation [10, 11]. The band gap is observed for Cu_2O structure was 3.70 eV. Removal of one oxygen atom from the super cell changes and band gap obtained for this

structure is 7.58 eV was shown in fig.2(b). When two oxygen are removed from the structure, we observed dispersion in the valence band and obtained the band gap of 8.80 eV was shown in fig.2(c). For three oxygen vacancy in the super cell band gap obtained was 9.07 eV [11]. Therefore further removal of oxygen atom from the super cell, produce more dispersion in the conduction band in the structure. Therefore, band gap is reduces due to valence band has more localized states due to the oxygen vacancy.

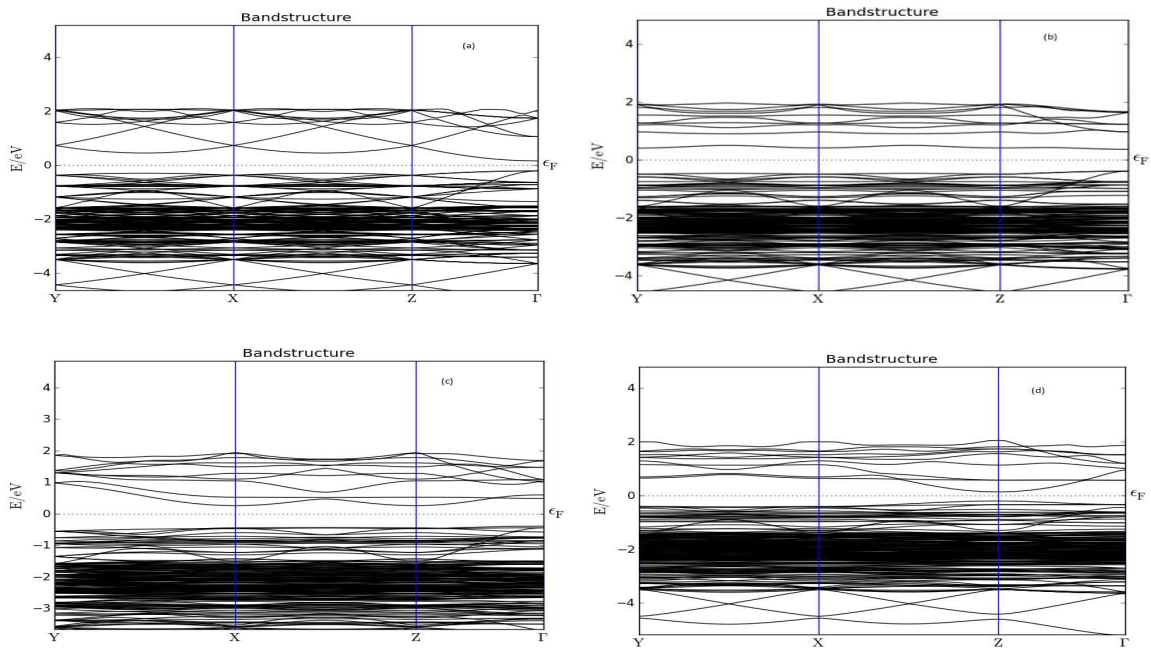

Fig.2 Band Structures of Cu_2O, $1Cu_2O$, $2Cu_2O$, $3Cu_2O$

Table 2: Band gap energy of Cu_2O, $1Cu_2O$, $2Cu_2O$, $3Cu_2O$

System Name	Chemical potential (eV)	HOMO value (eV)	LUMO Value (eV)	Fermi energy (eV)	Band gap (eV)
Cu_2O	-3.089645	-2.12E-01	1.58E-01	-3.09E+00	3.70E-01
$1Cu_2O$	-2.987486	-3.94E-01	3.64E-01	-2.99E+00	7.58E-01
$2Cu_2O$,	-3.03545	-3.93E-01	4.87E-01	-3.04E+00	8.80E-01
$3Cu_2O$	-3.184963	-3.37E-01	5.70E-01	-3.18E+00	9.07E-01

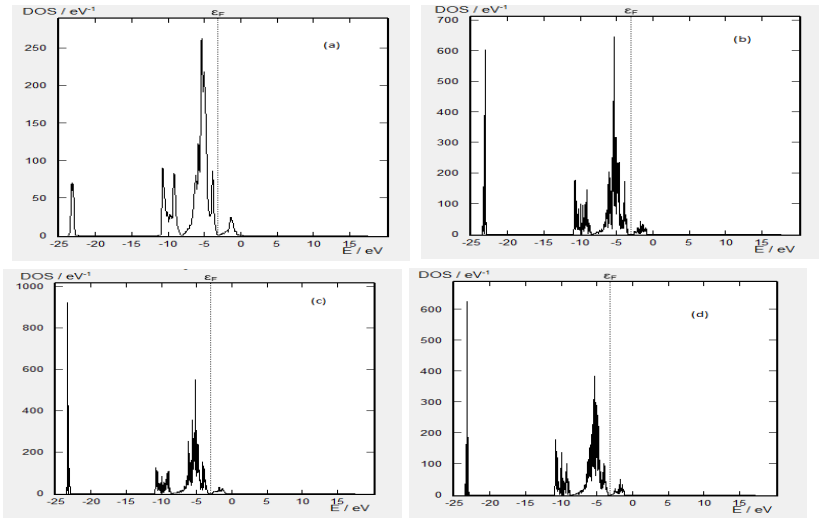

Fig 3: Density of states for Cu_2O, $1Cu_2O$, $2Cu_2O$, $3Cu_2O$

3.3 Density of States

The Strong peak is observed above the Fermi level and it shows, both the valence and conduction band states are equal in pure Cu_2O super cell. In fig 3(a) two major peaks are observed below the Fermi level is in the range of

-25 ev to 0 eV with the highest number of states per eV. In fig 3(c), cu_2o cluster with two oxygen vacancies, this results the further increase in the acceptor level. The important thing is same number of states remains when one more oxygen is getting removed. Hence we undoubtly know here, when the oxygen is removed from the Cu_2O super cell, it increases in the acceptor level states. These results lead to the formation of f centres.

3.4 Optical property

Fig4. Shows a shift in the absorbance peaks when oxygen defects increased in the Cu_2O super cell. This is because, Cu_2O is generally a p-type semiconductor and hence hole concentration increases in oxygen deficient. This can also be attributed in the reduction of electron concentration from the super cell. It also signifies an increase in energy band gap with the increase of oxygen vacancies.

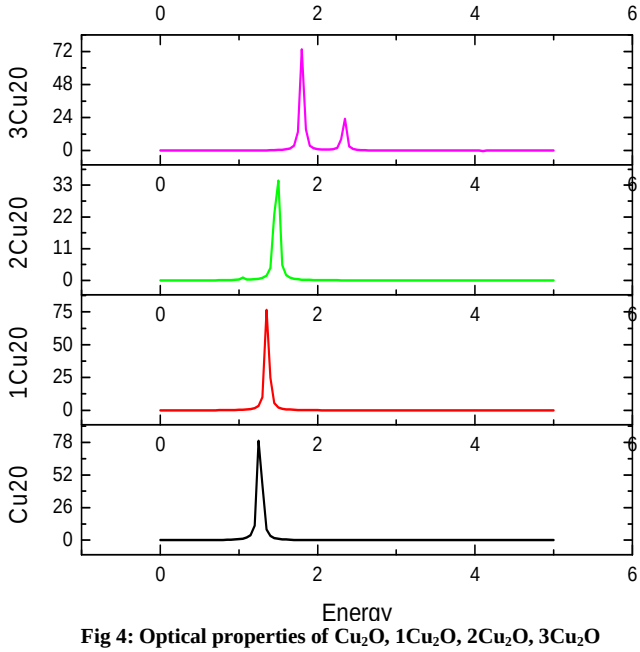

Fig 4: Optical properties of Cu_2O, $1Cu_2O$, $2Cu_2O$, $3Cu_2O$

3.5 Electron density and HOMO - LUMO

The visualization of electron density gives the better indication of molecular size, From the electronic structure of Cu_2O super cell HOMO and LOMO levels are absorbed, the corresponding HOMO and LOMO values are listed in the tabular column table (2), for Cu_20 super cell. The absorbed energy level is -2.12 eV and 1.58 eV respectively the further removal of oxygen the band gap is reduced.

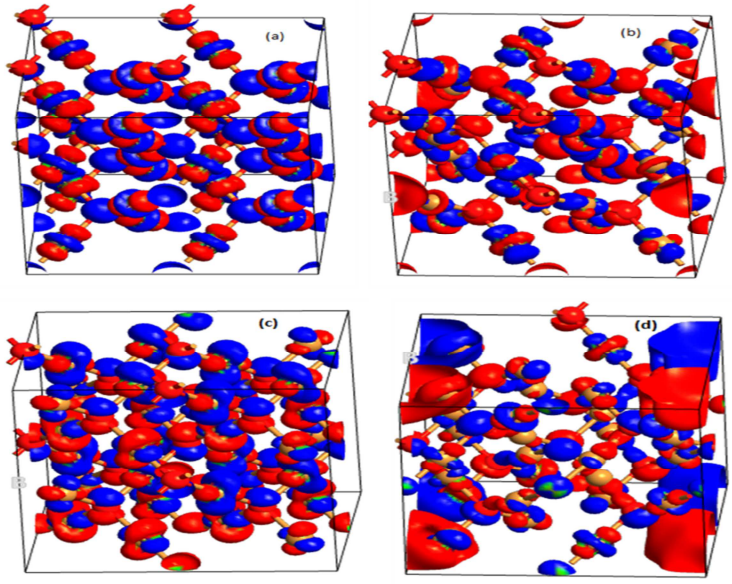

Fig 5: HOMO and LUMO for states Cu_2O, $1Cu_2O$, $2Cu_2O$, $3Cu_2O$

The more electro negativity gives the greater share of electrons in a bond. At the time of chemical reaction the electrons flow from higher electron density place to lower electron density place, therefore the partial charges are take the important role for determining a the molecule where will react. The total electron densities of Cu2O practically present in a spherical distribution around the atoms, but the difference were obtained quite small and spherically symmetric around the oxygen atom [11].

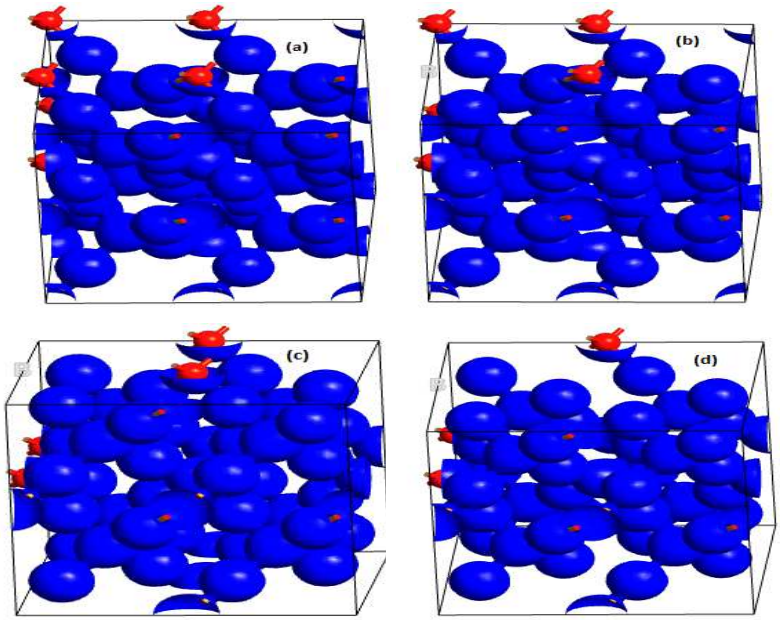

Fig 6: Electron density for Cu_2O, $1Cu_2O$, $2Cu_2O$, $3Cu_2O$

CONCLUSION

Thus Cu_2O super cell of with and without oxygen defects were analysed by using density functional theory (DFT). The obtained results show different energy levels, band structure and its optical properties. From the density of states (DOS) spectrum points out, donor level is increases with increasing of the oxygen vacancies. It was observed, that the HOMO-LUMO energy levels were decreased with increase in oxygen defects.

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