People's Democratic Republic of Algeria

Ministry of Higher Education and Scientific Research Scientifique

Mohamed Boudiaf University of M'sila

FACULTY OF TECHNOLOGY
DEPARTMENT OF ELECTRONICS
N°: 2024/…….…….

1985
جامعة محمد بوضياف - المسيلة
Université Mohamed Boudiaf - M'sila

FIELD: SCIENCE AND TECHNOLOGY
BRANCH: ELECTRONICS
SPECIALIZATION: MICROELECTRONICS

Thesis Presented for the Achievement
of the Academic Master's Degree

Presented by:

- Chennafi said
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Title :

Contribution to the study of the structural, Electronic and optical properties of CuO and Cu_2O materials by CASTEP

Defended before the jury composed of:

Dr. Bentoumi miloud	**Université M'sila**	**President**
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Dr. Moufdi hadjab	**Université M'sila**	**Examiner**

Academic Year: 2023/2024

Dedicate

Humans do not live in isolation from the rest of humanity. At every stage of life, there are people deserving of our remembrance and dedication. My heartfelt dedications go to my dear father, my precious mother, my beloved brothers, and sisters, whom I pray to God to grant health and well-being. Special greetings to Ghayth and Youssef, and to my friends, each by name, and to my dear colleagues at work, each by name, whom I testify have supported and accompanied me.

Chennafi said

Dedicate

To the one who encouraged me to persist throughout my life, to the most influential man in my life, my dear father. To the one I rise with and rely on, to the kind-hearted soul, my beloved mother, and my dear siblings, as well as to the rest of my family and friends, each by name.

Laboukhi Mohamed lamine

Acknowledgement

First and foremost, we would like to thank Almighty ***ALLAH*** *for granting us the health and patience to complete this work.*

We also want to express our deep gratitude to our supervisor ***Professor BOUCHAMA Idris****, for initially proposing this topic and for his continuous follow-up throughout the preparation of this thesis, as well as for his ongoing advice and feedback.*

We would also like to extend a special and heartfelt thank you to ***Dr. Fayza Benlakhdar*** *for the tremendous efforts she has made for us. May Allah grant her health and well-being.*

Additionally, we thank all the members of the Jury: ***Dr Bentoumi Miloud*** *President and* ***Dr Moufdi hadjab*** *Examiner for agreeing to review this work, as well as all our teachers from the Electronics Department, University of Msila.*

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General introduction

General introduction

Numerical simulation through physical modeling is increasingly prevalent across various domains, spanning from solid-state physics to molecular chemistry. The advent of more powerful processors has facilitated the implementation of intricate calculation techniques, enhancing the precision of reported experimental findings. Notably, density functional theory (DFT) stands out among the theories that have significantly advanced solid-state physics. Developed by Hohenberg, Kohn, and Sham in the 1960s and 1970s, DFT aims to characterize the fundamental state of a system, with its numerical application becoming feasible due to technological progress. Consequently, numerical simulation has emerged as a valuable tool for investigating divers' physical properties, by passing the need for traditional experimentation. These computational approaches offer swifter and more cost-effective alternatives to physical trials. Moreover, they enable the manipulation of various material parameters, facilitating separate investigations into their effects on compound properties. Thus, digital methods present the opportunity to analyze any compound beforehand [1].

A comprehensive understanding of various properties like structural, mechanical aspects, and band structure behavior of a material is crucial for assessing its potential applications. Specifically, optical properties such as absorption, spontaneous emission, and stimulated emission of photons, along with parameters like optical refractive index, dielectric function, and optical conductivity, are of paramount significance for both the analysis and production of sought-after semiconductor components [2].

The scientific community's interest in copper oxidation for diverse applications has been spurred by its gentle chemical requirements, non-toxic nature, and the surface's effectiveness compared to alternative surfaces [3]. In our work we are interested in the study of the structural properties, optical and electronic properties of cupric oxide CuO and cuprous oxide Cu_2O by CASTEP.

CASTEP is a shared-source academic and commercial software package which uses density functional theory with a plane wave basis set to calculate the electronic properties of crystalline solids, surfaces, molecules, liquids and amorphous materials from first principles. CASTEP permits geometry optimization and finite temperature molecular dynamics with implicit symmetry and geometry constraints, as well as calculation of a wide variety of derived properties of the electronic configuration [4].

This dissertation is structured into three chapters distributed as follows:

In the chapter one, we will introduce the fundamental principles of Density Functional Theory (DFT). This theory holds significant importance in both quantum physics and chemistry, offering a robust framework for modeling and forecasting the electronic characteristics of atomic and molecular systems. Unlike traditional approaches that focus on individual electron positions and movements. DFT revolves around describing the system's energy primarily through electron density.

In the subsequent chapter, we delve into the investigation of the physical attributes of CuO (cupric oxide) and Cu_2O (cuprous oxide) materials, encompassing a diverse array of features such as their structural, electronic, and optical properties.

Ultimately, it is customary for a work of this nature to conclude with an examination of theoretical scenarios. The third chapter will focus on the analysis of various outcomes derived from our calculations using the CASTEP simulator, pertaining to the structural, optical, and electronic properties of copper oxides CuO and Cu_2O. We will interpret and compare these results within the framework of the methods outlined in the theoretical section.

As a conclusion, the overarching summary will encapsulate the principal findings and insights garnered from this study.

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Chapter I

Density Functional Theory

(DFT)

Chapter I

Density Functional Theory (DFT)

I.1 Introduction

Density Functional Theory (DFT) was initially proposed by Hohenberg and Kohn, with further development by Kohn and Sham by (Parr, Robert G, 1983) [1]. Despite initial skepticism, DFT has become a widely used computational method for predicting and analyzing electronic properties of materials [1].

In addition to DFT, several other ab initio codes are available for simulating and predicting material properties, including Quantum Espresso, Abinit, Castep, and VASP [2-5]. These codes have been extensively employed in studying various material types, such as metals, semiconductors and insulators.

DFT has been the primary tool for quantum mechanical simulation of periodic systems (P. Edwards *et al.*, 2013) [6]. Computational tools like DFT and other ab initio codes have played a crucial role in advancing material science research, enabling the design of materials with desired properties Robert R *et al.*, 1986) [7].

In conclusion, the development and applications of DFT and other ab initio codes have significantly contributed to material science research, leading to new discoveries and advancements in the field.

I.2 Schrödinger's equation

The Schrödinger equation is essential in the non-relativistic quantum description of crystalline or molecular systems. It serves as the foundation for this formalism and can be simplified through various approximations for ease of solution. To tackle the multi-body problem in quantum mechanics, the following Schrödinger equations [8,9] must be solved:

$$H\Psi = E\Psi \qquad \text{(I.1)}$$

Where E is the total energy of the system and Ψ is the wave function of the system.

H: Hamiltonian

The total Hamiltonian, denoted as H, is the Hamiltonian of the quantum system under study. In the non-relativistic case, it is written in the form:

Where:

TN: Kinetic energy of the nuclei:

$$H = T_N + T_e + V_{e-e} + V_{N-N} + V_{e-N} \tag{I.2}$$

$$T_N = \frac{-\hbar^2}{2M}\sum_k \Delta_k \tag{I.3}$$

T_e: Kinetic energy of the electrons:

$$T_e = \frac{-\hbar^2}{2m}\sum_i \Delta_i \tag{I.4}$$

V_{e-e}: Electron-electron interaction potential:

$$V_{e-e} = \frac{1}{2}\sum_{i,j\neq i} U_{ij} = \frac{1}{2}\sum_{i,j\neq i} \frac{e^2}{4\pi\varepsilon_{0|\vec{r}_i-\vec{r}_j|}} \tag{I.5}$$

V_{N-N}: Nuclei-nuclei interaction potential:

$$V_{N-N} = \frac{1}{2}\sum_{k,l\neq k} U_{kl} = \frac{1}{2}\sum_{k,l\neq k} \frac{e^2 Z_k Z_l}{4\pi\varepsilon_{0|\vec{R}_k-\vec{R}_l|}} \tag{I.6}$$

V_{e-N}: Electron-nuclei interaction potential:

$$V_{e-N} = \sum_{i,k} U_{ik} = \sum_{i,k} \frac{Z_k e^2}{4\pi\varepsilon_{0|\vec{R}_k-\vec{r}_i|}} \tag{I.7}$$

In an effort to simplify the notation, the spin coordinate was excluded. Nevertheless, the electrons' spin degree of freedom impacts the wave function.

I(r,t) and R(r,t), and therefore must be accounted. For stationary processes, the time-independent Schrödinger equation can be expressed as follows:

For electrons:

$$(-\hbar^2/2m)\nabla^2\Psi(r) + V(r)\Psi(r) = E\Psi(r) \tag{I.8}$$

For nuclei:

$$(-\hbar^2/2M)\nabla^2\Phi(R) + U(R)\Phi(R) = ER\Phi(R) \tag{I.9}$$

Where:

- ħ is the reduced Planck's constant;
- m is the mass of an electron;
- M is the mass of a nucleus;
- ∇^2 is the Laplacian operator.

Where V(r) represents the electron potential energy in terms of its spatial coordinates, U(R) represents the nuclear potential energy in terms of its spatial coordinates, E represents the total energy of the electron system and ER represents the total energy of the nuclear system.

Note: The equations provided assume a non-relativistic framework and neglect the spin-spin interactions between electrons and nuclei.

Where H is the Hamiltonian operator, Ψ is the wave function, E is the energy of the system, and the subscript "t" is omitted since the equation describes stationary states.

The total Hamiltonian operator (T H) for a system with multiple interacting particles, consisting of N nuclei and M electrons, can be obtained by adding the t. Total kinetic energy operator (T T) and the operator describing all Coulomb interactions (T V) in the Schrödinger equation.

The Hamiltonian operator plays a critical role in quantum mechanics as it describes the total energy of the system and is utilized to predict its time evolution.

The Schrödinger equation is essential in non-relativistic quantum mechanics for describing the behavior of crystalline or molecular systems. It encompasses the total energy of the system through the non-relativistic Hamiltonian operator, which includes the kinetic energy and Coulomb interactions. Solving the Schrödinger equation yields energy levels and wave functions that capture the system's dynamics.

The wave function must account for electron spin coordinates, introducing additional complexity. However, exact solutions are impractical for large systems due to the increasing number of particles. Consequently, simplifications are employed, such as the Born-Oppenheimer approximation, Density Functional Theory, and Hartree-Fock method (D. A. McQuarrie, 2007) [10].

The electromagnetic interaction becomes challenging for systems with numerous atoms and electrons, like solids with billions of nuclei and valence electrons. Without further simplification, solving the problem would be infeasible. Three common levels of simplification are the Born-Oppenheimer approximation, Density Functional Theory or Hartree-Fock approximation, and the approximations resulting from equation solving [11, 12].

I.2.1 Born Oppenheimer approximation

The Born-Oppenheimer approximation is a widely used technique in quantum mechanics to simplify the solution of the Schrödinger equation. This method assumes that the motion of the atomic nuclei is much slower than the motion of electrons, so the kinetic energy of the nuclei is neglected, and the Coulomb energy remains constant. Thus, the nuclei are considered to be stationary while the electrons move in their field. This approximation allows the separation of the electronic and nuclear motions, and the electronic Hamiltonian He is defined to describe the electronic behavior in the field of the nuclei. Using this Hamiltonian, the Schrödinger equation can be written to solve for the electronic wave function. The Born-Oppenheimer approximation is a fundamental concept in quantum chemistry and has many practical applications in molecular spectroscopy and electronic structure calculations [13,14] With Born-Oppenheimer approximation:

Schrödinger equation simplification:

$$\nabla^2\Psi(r,R) + (2\mu/\hbar^2)(E - V(R))\Psi(r,R) = 0 \tag{I.10}$$

Electron motion decoupling from nuclear motion:

$$\Psi(r,R) = \psi(r)R(R) \tag{I.11}$$

Nuclear kinetic energy term is neglected:

- T(R) ≈ 0
- Electron term:
- Electron wave function:
- ψ(r)
- Nuclear term:
- Nuclear wavefunction:
- R(R)

Electrostatic interaction between nuclei becomes constant:

$$V_{N-N} = constant \tag{I.12}$$

Electron-nucleus interaction potential is approximated as an external potential independent of nuclear positions:

$$V_{e-N} = V_{ext} \tag{I.13}$$

Electronic Hamiltonian:

$$H_e = T_e + V_{ext} \tag{I.14}$$

Second level of approximation:

Hartree-Fock method (approximation on wave functions):

$$\nabla^2\psi_i(r) - 2\mu/\hbar^2\sum[V_{ext} + \sum(J(r) - K(r))]\psi_i(r) = \varepsilon_i\psi_i(r) \tag{I.15}$$

Density Functional Theory (approximation on Hamiltonian):

$$H_e[\rho(r)] = T_e[\rho(r)] + V_{ext} + \int \rho(r')v(r,r')dr' + Exc[\rho(r)] \tag{I.16}$$

The decoupling technique of separating electron and nucleus movements is an important approximation method in quantum mechanics for addressing N-body problems. This technique is discussed in academic works like "Introduction to Quantum Mechanics" by (D. J. Griffiths *et al.*, 2018) [15] and "Quantum Mechanics: Concepts and Applications" by (N. Zettili *et al.*, 2003) [16]. However, obtaining analytical solutions for the Schrödinger equation for electrons is challenging, except in simple cases like hydrogen. To overcome this challenge, various approximation techniques are utilized, as mentioned in the aforementioned sources.

I.2.2 Approximation of Hartree and Hartree.Fock

I.2.2.1 Hartree approximation

The Hartree-Fock approximation simplifies the behavior of multi-electron systems in quantum mechanics. It assumes that each electron moves independently in a mean field created by the other electrons and nuclei. By reducing the complex N-electron system to a single-electron system, the Hamiltonian can be expressed as the sum of the Hamiltonians for each electron. This approximation is widely studied and discussed in academic works such as "Introduction to Quantum Mechanics" by [15] and "Quantum Mechanics: Concepts and Applications" by [16]. The wave function of the entire electronic system is the product of the individual wave functions of each electron multiplied by their corresponding energies. The Hamiltonian for such a system is given by:

$$H = \Sigma_{i=1}{}^{N} h(i) \tag{I.17}$$

Where h is the single-electron Hamiltonian.

$$\Psi(x_1; x_2; \ldots\ldots; x_N) = \varphi_i(x_1)\varphi_j(x_2)\ldots\ldots\ldots\ldots\varphi_k(x_N) \tag{I.18}$$

This equation represents the electronic wave function Ψ for a system of N electrons. The wave function is expressed as a product of single-electron wave functions φi, φj, ..., φk, where each wave function depends on the coordinates x1, x2, xN of the corresponding electron. This equation describes the spatial distribution of the electrons in the system, with each φ representing the probability amplitude of finding an electron at a specific position.

I.2.2.2 Hartree-Fock approximation

According to the article "Quantum Mechanics of Many-Electron Systems" by (P. A. M. Dirac, 1929) [17], the Hartree field can be used to break down a multiple equation into an equational system for a single electron. However, as [17] explain, the Hartree field neglects the exchange of any two particles, which means that the total wave function must be antisymmetric if the electron is a fermion. To address this, Fock suggested using Pauli's exclusion principle to correct the electron wave function, as mentioned in the article by [17], which can be expressed as a Slater determinant.

$$\Psi(r_1, r_2, \ldots, r\square) = 1/\sqrt{N}! \begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) & \phi\square(r1) \\ \phi_1(r_2) & \phi_2(r_2) & \phi\square(r_2) \\ & . & . \\ & . & \\ \phi_1(r\square) & \phi_2(r_n) & \phi\square(r_n) \end{vmatrix} \qquad (I.19)$$

The results of this approximation are good, but they are only applicable to small molecules with few electrons.

I.3 Functional Density Theory (DFT)

The energy of an electronic system can be expressed in terms of the density of the ground state, denoted as ρ(r), which forms the basis of the density function. The theoretical model developed by Thomas and Fermi in 1920, which replaces the calculation of the wave function dependent on 3N spatial coordinates with a simpler function, the electron density that depends only on 3 spatial coordinates, is the origin of the DFT (Functional Density Theory). Hohenberg and Kohn, as well as Kohn and Sham, made significant contributions to the field in the 1960s. The Thomas-Fermi model is a remarkable concept in the field of quantum mechanics, as it simplifies the complex calculation of the electron density. The details on this model are available in the works of Thomas and Fermi (1927), (Hohenberg and Kohn, 1964) [18], and (Kohn and Sham, 1965) [19].

Let us recall that the electron density, ρ(r), in an electronic system represents the number of electrons per unit volume in a given state (or the probability of finding an electron in a unit volume). It can be defined as:

$$\rho(r) = |\Psi(x_1, x_2, \ldots, x_N)|^2 \qquad \text{(I.20)}$$

Here, Ψ represents the wavefunction of the system, and N represents the total number of electrons. The electron density ρ(r) approaches zero as r tends to infinity, and when integrated over all space, it equals the total number of electrons N:

$$\int \rho(r)dr = N \qquad \text{(I.21)}$$

In 1964, Hohenberg and Kohn introduced two theorems to establish a mathematical framework for earlier concepts. These two theorems form the basis of the current form of DFT (Density Functional Theory).

I.3.1 Thomas-Fermi model

The work of Hohenberg and Kohn (1964) [18] initiated the development of density functional theory in 1964 and 1965. Their publications introduced two theorems that are considered the cornerstone of DFT.

- **First theorem:**

The relationship between the total energy E of an electronic system's ground state and its density ρ(r) under a specific external potential Ve(r) was established through a theorem [18]. According to this theorem, knowing the electron density enables the determination of all wave functions. Consequently, a ground-state electron density functional denoted by E[ρ(r)] is utilized to represent the total energy E of an electronic system interacting in an external potential [18].

- **Second theory:**

Every multiparticle system has a total functional energy, the minimum corresponding to the ground state. Ground-state particle density confirms:

According to the work of Hohenberg and Kohn (1964) [18], the actual density of the ground state is the one that minimizes the energy E. In fact, all other properties of the system are also dependent on this density. Vibration analysis is a method that is commonly employed to calculate the ground state energy of an electronic system when it is subjected to an external potential.

I.3.2 Hohenberg.Kohn theorems

The fundamental formalism of Density Functional Theory (DFT) applies to systems with multiple interacting particles that evolve in an external potential, and is rooted in the Hohenberg-Kohn theorem (Hohenberg & Kohn, 1964) [18]. The Hohenberg-Kohn theorem is based on two underlying theorems that provide a framework for DFT, making it a widely applicable tool for studying electronic structure and properties of materials (Kohn & Sham 1965) [19].

- **Theorem I**

According to this theorem, the electron density function (r) is sufficient to determine all electronic properties of a system. This means that the ground state electron density 0(r) and the external potential Vext(r) have a direct correspondence, and similarly, the wave function of the ground state background(r) and background(r) also correspond. The energy functional E [ρ, Vext] can be written as an integral consisting of two parts. The first part is the integral of the external potential Vext multiplied by the electron density ρ(r):

$$E[\rho, V_{ext}] = \int V_{ext}\rho(r)dr + FHK[\rho] \tag{I.22}$$

In this equation, FHK[ρ] represents the universal HK functional that combines the universal terms of electron kinetic energy T(ρ) and the potential energy due to electron-electron interaction Ve-e. It can be written as:

$$FHK[\rho] = T[\rho] + V_e - e[\rho] \tag{I.23}$$

The second theorem of Hohenberg and Kohn attempts to answer the question of how to determine whether any density is that of the ground state, given that it is known that the electronic density of the ground state is sufficient to obtain all the properties of this state.

- **Theorem II**

This theorem demonstrates that the energy functional E is minimal when any electron density corresponds to the electron density of the ground state background(r).

In this theorem, the energy functional E[ρ(r)] that provides access to the ground state energy is minimized when the electron density exactly matches that of the ground state.

$$E = minE[\rho(r)] \tag{I.24}$$

In other words, according to the first theorem, a test wave function and a test Hamiltonian are both defined for a test electron density. From this, we can establish a correspondence between the wave function of the variational principle and the electronic density versions.

However, an important problem remains to be solved: how to rewrite an exact analytical formulation of the FHK functional for an interacting N-electron system?

I.4 Kohn and Sham equations

The description of kinetic energy and electron-electron interactions in terms of electron density is a challenging mathematical problem when considering a system of interacting electrons in motion. In an attempt to solve this problem, Kohn and Sham introduced a theoretical approach, known as the Kohn-Sham equations (Kohn and Sham, 1965) [19]. This approach replaces the actual electronic system with a hypothetical system, in which each electron behaves independently and is only influenced by an effective potential, the Kohn-Sham potential. The potential comprises both the external potential caused by the nuclei and the potential induced by the influence of other electrons on the electron of interest.

K-S (Kohn-Sham) reformulated the energy functional of the real system based on the fictitious system. The reformulated energy functional is expressed as:

$$E[\rho(r)] = T_0[\rho(r)] + V_{\mathrm{ee}}[\rho(r)] + V_{\mathrm{ex}\text{⍰}}[\rho(r)] + Exc[\rho(r)] \quad \text{(I.25)}$$

In this expression, $T_0[\rho(r)]$ represents the kinetic energy of non-interacting particles, $V_e[\rho(r)]$ represents the classical Coulomb contribution known as the Hartree energy, and $Exc[\rho(r)]$ is the exchange-correlation functional.

The total energy (E) is given by:

$$E = [T[\rho] - T_0[\rho]] + V[\rho] + V_{\mathrm{ee}}[\rho] + V_{\mathrm{ex}\text{⍰}}[\rho] \qquad \text{(I.26)}$$

Where $V[\rho]$ is the external potential term and $[\rho]$ is the density-density interaction term.

The exchange-correlation potential (V_{ext}) is calculated from the derivative of the exchange-correlation energy functional (Exc) with respect to the electron density ($\rho(r)$):

$$V_{\mathrm{ex}\text{⍰}} = \partial EX[\rho(r)]/\partial\rho(r) \qquad \text{(I.27)}$$

$$(HKS(r) - \varepsilon_{\mathrm{i}})\phi_{\mathrm{i}}(r) = 0 \qquad \text{(0.1)}$$

By introducing the Kohn-Sham framework, the Schrödinger equation is transformed into N single-electron Schrödinger equations, commonly known as the Kohn-Sham equations:

Here, HKS is the Kohn-Sham Hamiltonian, N represents the number of electrons, and $\mathcal{E}_i$ are the eigenvalues. The Kohn-Sham Hamiltonian is defined as:

$$HKS = -\nabla^2 + V_eff(r) \qquad \text{(I.29)}$$

The effective potential (V_eff(r)) is given by:

$$V_eff(r) = V_classical[\rho(r)] + V_{\mathrm{ee}}[\rho(r)] + V_ext[\rho(r)] + V_{\mathrm{ex}\square}[\rho(r)] \qquad \text{(I.30)}$$

The electron density ($\rho(r)$) is determined from the N single-electron wave functions $\phi_i(r)$:

$$\rho[r] = \sum \phi_{\mathrm{i}}(r)^2 \qquad \text{(I.31)}$$

Where the sum runs from i = 1 to N.

I.4.1 Exchange and correlation energy approximations

I.4.1.1 Local density approximation (LDA)

The exchange-correlation energy of an inhomogeneous electron system can be determined using a method based on the assumption that the electron density is constant in each infinitesimal volume that makes up the actual system (J. P. Perdew, 1981) [20]. The exchange energy of the density of each volume is then estimated using the exchange energy obtained from a uniform electron gas (J. P. Perdew *et al.*, 2008) [21]. This estimated exchange energy is considered as the exchange energy of the corresponding density. The total energy of exchange-correlation of the system can be expressed as the sum of the exchange energies of all the infinitesimal volumes of the system. The equation is:

$$Exc = \int \rho(r)\varepsilon xc[\rho(r)]dr \qquad \text{(I.32)}$$

In this equation, $\varepsilon xc[\rho(r)]$ represents the exchange-correlation energy density for a homogeneous electron gas. It can be decomposed into the exchange energy density ($\varepsilon x[\rho(r)]$) and the correlation energy density ($\varepsilon c[\rho(r)]$):

$$\varepsilon xc[\rho(r)] = \varepsilon x[\rho(r)] + \varepsilon c[\rho(r)] \qquad \text{(I.33)}$$

The exchange energy density ($\varepsilon x[\rho(r)]$) and the correlation energy density ($\varepsilon c[\rho(r)]$) correspond to the exchange and correlation contributions of a homogeneous electron gas, respectively. The Dirac exchange function precisely identifies the analytical expression of exchange energy:

$$\varepsilon x(r) = Cx\rho^{3} \quad \text{(I.34)}$$

Where:

$$Cx = -(3/4\pi)^{(}1/3) \quad \text{(I.35)}$$

The exchange energy density ($\varepsilon x[\rho(r)]$) and the correlation energy density ($\varepsilon c[\rho(r)]$) correspond to the exchange and correlation contributions of a homogeneous electron gas, respectively. The Dirac exchange function precisely identifies the analytical expression of exchange energy:

I.4.1.2 Generalized Gradient Approximation (GGA)

According to a scientific article by (J. P. Perdew *et al.*, 1996) [22], the Local Density Approximation (LDA) considers the density at a given point r, but in real systems, the density is not homogeneous throughout space, which makes it more practical to include a correction that considers the rate of change of r. To address this issue, the Generalized Gradient Approximation (GGA) introduces a correction to the exchange-correlation energy functional that takes into account the local charge concentrations and their gradients. The GGA functional is defined in a general form that allows for a more accurate calculation of electronic properties in real systems with spatially inhomogeneous densities.

The exchange-correlation functional is expressed in terms of the electron density (ρ) and its gradient ($\nabla\rho$) according to the following equation:

$$E_{GGA}[\rho] = \int \rho(r)\varepsilon_{GGA}[\rho(r), \nabla\rho(r)]d^{3}r \quad \text{(I.36)}$$

In this equation, εGGA[$\rho(r)$, $\nabla\rho(r)$] represents the generalized exchange-correlation energy (GGA) depending on both the electron density and its gradient.

Often, the contributions for exchange (εx) and correlation (εc) are separately developed in the GGA functional.

$$GGA[\rho, \nabla\rho] = GGA[\rho, \nabla\rho]x + GGA[\rho, \nabla\rho]c \quad \text{(I.37)}$$

Where GGA[ρ,$\nabla\rho$]x corresponds to the exchange contribution, and GGA[ρ,$\nabla\rho$]c corresponds to the correlation contribution. The GGA functional can also include other terms and coefficients denoted as Zxc. Additionally, the electron density ($\nabla\rho$) can represent the gradient of the electron density with respect to spatial coordinates.

According to a research paper by (B. Hammer *et al*., 1999) [23], there exist various forms of exchange-correlation (Exc) functionals in density functional theory. Among these, the functionals developed by Perdew and Wang (PW91), Perdew and Becke (B88), and Burke and Ernzerhof have gained popularity due to their accuracy and ease of implementation. These functionals are commonly used for electronic structure calculations in different fields of science and engineering.

I.5 Solving the Kohn-Sham equation

The Kohn-Sham equation is a fundamental equation in density functional theory (DFT) that describes the behavior of non-interacting electrons in an effective potential. The equation can be written as:

$$[-1/2\nabla^2 + v_eff(r)]\psi_i(r) = \varepsilon_i\psi_i(r) \tag{I.38}$$

Where ψ_i(r) is the wave function of the i-th electron, ε_i is its energy, and v_eff(r) is the effective potential, which is a sum of the external potential and the Hartree and exchange-correlation potentials. The Hartree potential is given by:

$$v_H(r) = \int \rho(r')/|r - r'|dr' \tag{I.39}$$

Where ρ(r) is the electron density. The exchange-correlation potential is a functional of the electron density and is typically approximated using density functionals such as the local density approximation (LDA) or the generalized gradient approximation (GGA).

The process of solving the Kohn-Sham equation involves finding the eigenvalues and Eigen functions through numerical methods such as the self-consistent field (SCF) method or direct minimization. The SCF method iteratively solves the Kohn-Sham equation until self-consistency is achieved, meaning that the electron density matches the density used to calculate the effective potential. Detailed information on the Kohn-Sham equation and its solutions in density functional theory (DFT) calculations can be found in various research papers and textbooks. Some relevant references include "Density Functional Theory: A

Practical Introduction" by (J. A. Steckel *et al.*, 2009) [24], as well as the research papers by Kohn and Sham (1965) [19] and Hohenberg and Kohn (1964) [18].

I.6 Pseudo-potential methods and plane waves

I.6.1 Introduction

Pseudo potential methods and plane wave basis sets are widely used in solid-state physics and materials science to study the electronic structure of materials. Pseudo potential methods are a class of approximations used to simplify the calculation of electronic structure in solids, while plane wave basis sets are used to represent the wave functions of electrons in a crystalline solid.

Pseudo potential methods were first introduced in the 1950s and have since become a powerful tool for studying electronic structure in materials. The basic idea of pseudo potential methods is to replace the complicated atomic potentials that describe the interaction between electrons and atomic nuclei with a simplified potential that only includes the core electrons. This simplification reduces the computational cost of electronic structure calculations and allows for the study of larger and more complex systems. One of the earliest works in this field was by Hohenberg and Kohn in 1964 [18], where they presented their density functional theory (DFT) and its application to solids.

Plane wave basis sets, on the other hand, are a type of basis set used to represent the wave functions of electrons in a crystalline solid. The wave functions are expanded in terms of plane waves, which have a well-defined momentum and wavelength, and are periodic in space. The use of plane wave basis sets allows for the accurate description of electronic structure in materials, particularly in the case of metals and semiconductors.

One of the earliest works on this topic was by (F. Bloch 1929) [25], who developed the concept of Bloch waves to describe the wave functions of electrons in a crystalline solid.

The combination of pseudo potential methods and plane wave basis sets has proven to be a powerful tool for the study of electronic structure in materials. This approach is commonly used in software packages such as Quantum ESPRESSO and VASP to simulate and analyze materials at the atomic scale. The accuracy of these methods has been continuously improved over the years, and they are now widely used in the field of materials science.

In conclusion, the combination of pseudo potential methods and plane wave basis sets has become a powerful tool for the study of electronic structure in materials. The development of these methods was influenced by early works of Hohenberg and Kohn, and

Bloch. These methods are now widely used in software packages such as Quantum ESPRESSO and VASP to simulate and analyze materials at the atomic scale.

I.6.2 Bloch Theorem (the plane wave approach)

The Bloch theorem, first introduced by Felix (F. Bloch, 1928) [26], is a fundamental principle in the study of periodic structures. It relates the electronic wave function in a crystalline solid to its periodic potential. According to the Bloch theorem, the wave function of an electron in a periodic potential can be written as a product of a plane wave and a periodic function, which is known as the Bloch function. The plane wave represents the free electron propagation, while the periodic function describes the periodicity of the crystal lattice. The Bloch theorem is expressed mathematically as:

$$\Psi(r+R) = e^{(ik\cdot R)}\psi(r) \tag{I.40}$$

Where ψ (r + R) is the wave function at a point shifted by a lattice vector R, e(ik·R) is a phase factor, k is the wave vector, and ψ(r) is the wave function at the original point. This equation shows that the wave function of an electron in a crystal has the same form at any two points that differ by a lattice vector R. The wave function is periodic with respect to the lattice, and its periodicity is characterized by the wave vector k.

The Bloch theorem has important implications for the electronic structure of solids. It explains why the energy bands in a crystal are formed, and why they have the periodicity of the lattice. The electronic states in a crystal are labeled by their wave vectors, which are restricted to a Brillouin zone, the first Brillouin zone being the primitive cell of the reciprocal lattice. The band structure of a crystal can be calculated by solving the Schrödinger equation for the Bloch functions. The Bloch theorem has been used extensively in the study of semiconductors, metals, and insulators, and is the basis for many important concepts in solid-state physics, such as the Fermi surface, the density of states, and the effective mass approximation.

I.6.3 Sampling of the first Brillouin zone

The Brillouin zone (BZ) is a periodic region in reciprocal space that encompasses wave vectors k with the same periodicity as the crystal lattice. The first Brillouin zone (FBZ) is the smallest region enclosing the origin and a single unit cell of the lattice. Sampling the FBZ is crucial in electronic band Monk Horst-Pack method utilize a uniform grid of k-points

(H. J. Monkhorst *et al.*, 1976) [27], while the Matthiessen-Paxton method employs a smearing function for broadening the k-point grid (M. Methfessel *et al.*, 1989) [28].

The choice of sampling scheme and the number of k-points significantly affects accuracy and efficiency. More complex band structures or precise calculations of properties like density of states or optical properties require denser k-point sampling (G. Kresse *et al.*, 1996) [29].

In summary, accurate electronic band structure calculations necessitate sampling the FBZ, where the choice of sampling scheme and number of k-points impacts accuracy and efficiency. Equation:

The k-point mesh is defined as follows:

$$\Gamma = (1/N_{1,1}/N_{2,1}/N_3) \tag{I.41}$$

Where N1, N2, and N3 are the number of k-points along each reciprocal lattice vector in the Brillouin zone [27].

The total number of k-points required to sample the Brillouin zone is given by:

$$N = N_1 x N_2 x N_3 \tag{I.42}$$

Where N is the total number of k-points [27].

Another important concept is the weight of each k-point, which is determined by the size of the Brillouin zone and the number of k-points used for sampling. The weight of a k-point is given by:

$$W_k = (1/VBZ)x(2\pi)^3/N \tag{I.43}$$

Where VBZ is the volume of the Brillouin zone.

I.6.4 Ecut-off energy

The cut-off energy (Ecut) is a crucial parameter in density functional theory (DFT) calculations of electronic band structures and related properties. It determines the size of the basis set used to expand the electronic wave functions as plane waves.

Choosing a sufficiently high Ecut is vital for accurate results in properties like total energy, density of states, and optical properties. However, excessively high Ecut values increase computational costs, while insufficient values introduce significant errors.

Methods such as convergence testing involve calculating properties for increasing Ecut values until convergence to a stable value is achieved (S. Baroni *et al.*, 2001) [30].

Another approach is the extrapolation method, where properties are extrapolated to the limit of infinite Ecut (D. Vanderbilt, 1990) [31].

The appropriate value of Ecut depends on the system's size, complexity, and desired accuracy, with larger systems and higher accuracy requirements generally necessitating higher Ecut values [5].

In summary, selecting an appropriate value of Ecut is crucial for accurate and efficient DFT calculations of electronic band structures and related properties.

The plane wave basis set is defined as follows:

$$\Psi(r) = \sum GC(G)exp(iG \cdot r) \qquad \text{(I.44)}$$

Where Ψ(r) is the electronic wave function at position r, G is a reciprocal lattice vector, C(G) is the expansion coefficient for wave vector G, and the sum is over all reciprocal lattice vectors G within a sphere of radius Ecut centered on the origin of the reciprocal space [5].

I.7 CASTEP Simulation tool

CASTEP (Computer Aided Simulation of Thermochemistry and Energy of Materials) is a powerful computational tool for the simulation of materials at the atomic level. It is a widely used code for first-principles electronic structure calculations based on density functional theory (DFT). CASTEP can simulate a variety of properties of materials, such as crystal structures, electronic structures, optical and magnetic properties, and chemical reactions.

CASTEP uses a plane-wave basis set to expand the electronic wave functions and a pseudo potential approximation to describe the ion-electron interaction. The code can handle both periodic and non-periodic boundary conditions, making it suitable for the simulation of surfaces, interfaces, and nanoparticles.

One of the key features of CASTEP is its ability to perform calculations at different levels of theory, such as the local density approximation (LDA), generalized gradient approximation (GGA) and hybrid functional. The code also includes several advanced features, such as the calculation of phonon dispersions and the simulation of solid-state NMR and EPR spectra.

CASTEP is user-friendly and can be run through a graphical user interface or via command-line interface. The code is maintained and updated regularly, and it has an active user community that provides support and shares expertise.

In summary, CASTEP is a powerful tool for the simulation of materials at the atomic level. It is widely used in academia and industry and provides a broad range of simulation capabilities for the study of various properties of materials.

I.8 Conclusion

In conclusion, density functional theory (DFT) has become an essential tool for studying the electronic structure and properties of materials. DFT provides a rigorous theoretical framework for understanding the behavior of electrons in materials and has been successful in predicting a wide range of properties. Its accuracy and efficiency have made it a popular method for studying large-scale systems, and it has been used to design new materials with specific functionalities for applications in energy conversion, storage, and catalysis. However, DFT also has its limitations, and further improvements are needed to address certain types of materials and properties, such as strongly correlated materials and excited states. Despite its limitations, DFT continues to be a valuable tool for materials science research, and its ongoing development is expected to lead to new discoveries and insights into the behavior of materials.

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Chapter II

Physical properties of CuO and Cu_2O materials

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Physical properties of CuO and Cu_2O materials

II.1. Introduction

In the rapidly evolving domain of microelectronics, the focus has always been on refining materials that could potentially transform how we interact with technology. The concerted effort to better understand these materials has led to a keen interest in semiconductors such as Cupric Oxide (CuO) and Cuprous Oxide (Cu_2O). Despite many similarities, these materials exhibit intriguing differences in their physical properties, inviting potential applications in the field of microelectronics.

This chapter aims to delve into an in-depth exploration of the physical properties of CuO and Cu_2O materials. These materials that have emerged as remarkably promising candidates for microelectronic applications due to their versatile natures. We will journey through their fundamental characteristics, understanding their structure, stability, electronic, optical, mechanical, and thermal properties, and investigate their role in microelectronics.

In doing so, our objective is to shed light on the importance and potential of these materials. Furthermore, by comparing and contrasting CuO and Cu_2O materials. We will provide valuable insights into their distinct features and applications, equipping readers with the necessary knowledge to evaluate their future prospects in microelectronics. By examining state of the art technological advances and recent findings, we set the stage for contemplating new trajectories in microelectronics.

The study of CuO and Cu_2O's physical properties will serve as a roadmap for future developments, bridging the comprehension gap and charting a fresh course for technological progression in microelectronics.

II.2. Basics of material science

II.2.1. Presentation of CuO and Cu_2O compounds

a) CuO - Copper(II) Oxide

CuO, or copper(II) oxide, is an inorganic compound with the chemical formula CuO. It is also known as cupric oxide and is a black, powdery solid that occurs in nature as the mineral tenorite. It is a basic oxide, meaning it can react with acids to form copper(II) salts.

- ***Molecular weight***: 79.545 g/mol
- ***Density***: 6.31 g/cm^3

- ***Melting point***: 1,200 to 1,300 °C (decomposes)
- ***Solubility***: Insoluble in water and alcohol; soluble in ammonium chloride and potassium cyanide solution when heated.
- ***Crystal structure***: Monoclinic

Copper(II) oxide is used in various applications:

- As a pigment in ceramics to produce blue, red, and green (and sometimes black) colors.
- In the production of copper salts, which can be used for applications in agriculture as pesticides, fungicides, and feed additives.
- CuO compound can be used as a precursor in the synthesis of many copper-containing substances.
- It serves as a catalyst in different chemical reactions, like the hydrogenation of certain organic compounds.
- In the field of semiconductors, CuO has prospective use, for example, in the form of thin-film transistors.
- For purifying hydrogen gas by removing traces of sulfur compounds.

Copper(II) oxide is also a subject of interest in environmental and materials science:

- It has been researched for use in batteries, like lithium-ion cells.
- It's effective as a photovoltaic material for the degradation of organic pollutants.
- CuO nanoparticles have been explored for antimicrobial applications due to their high surface area and chemical activity.

b) Cu_2O - Copper(I) Oxide

Cu_2O, or copper(I) oxide, is an inorganic compound with the chemical formula Cu_2O. It is also commonly referred to as cuprous oxide and appears as a red to brown solid with a lower oxidation state of copper than copper(II) oxide. It occurs in nature as the mineral cuprite.

- ***Molecular weight***: 143.09 g/mol
- ***Density***: 6.0 g/cm^3
- ***Melting point***: 1,232 °C
- ***Solubility***: Insoluble in water and dilute acids; soluble in NH4OH and in concentrated NH4Cl solution.

- ***Crystal structure***: Cubic

Copper(I) oxide is used in many applications:

- Cu_2O compound is used as a pigment in various types of glass and ceramic glazes.
- It has applications in the electronic industry, mainly in solar cells, due to its semiconductor properties.
- It is used in antifouling paints for ship hulls to prevent organisms from attaching and forming a biofilm.
- Like CuO, cuprous oxide also serves as a catalyst in specific chemical processes.
- Copper(I) oxide is investigated as a potential non-toxic replacement for lead-based materials in various applications.

In materials science, Cu_2O material has drawn attention:

- Its p-type semiconductor characteristics make it interesting for solar energy conversion.
- It exhibits photovoltaic properties useful in the breakdown of organic compounds.
- Cu_2O is a potential material for gas sensors due to its capacity to react with gases like hydrogen.

Both CuO and Cu_2O materials have complex electronic structures (see Figure II.1) and exhibit interesting magnetic and electrical properties at the nanoscale. Research into both substances is ongoing, with new applications - especially in green technologies and nanotechnology - being explored continually.

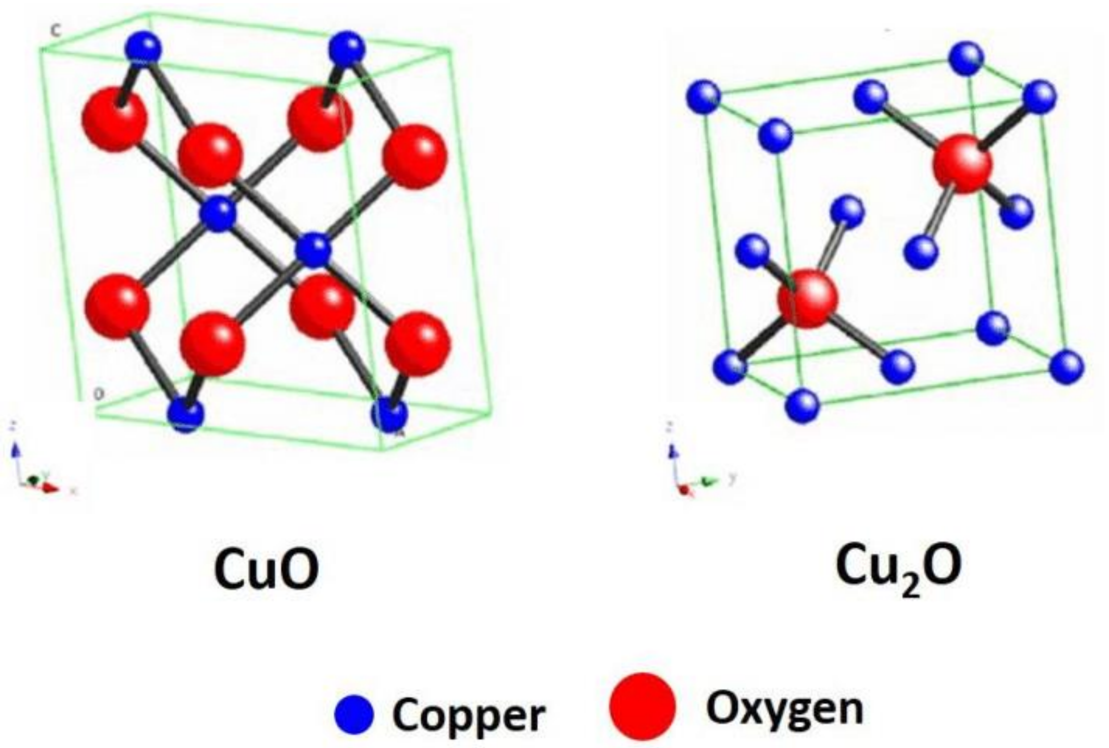


Figure II.1: Unit cell structure of cupric (CuO) and cuprous (Cu_2O) oxide [1].

II.2.2 Chemical and physical properties of CuO and Cu₂O materials

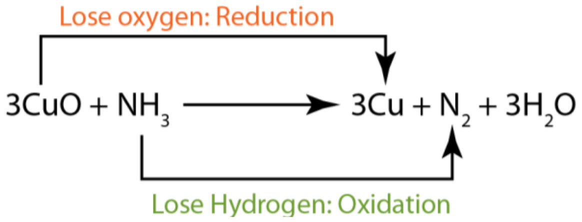
a) CuO - Copper(II) Oxide [2]

❖ ***Chemical Properties***

- **Oxidation State**: In CuO, copper is in a +2 oxidation state.
- **Reactivity with Acids**: CuO reacts with acids to form corresponding copper(II) salts. For example, with hydrochloric acid, it forms copper(II) chloride:

$$CuO\ (s) + HCl\ (aq) \longrightarrow CuCl_2\ (s) + H_2O\ (l)$$

- **Reactivity with Hydrogen**: CuO reacts with hydrogen gas at high temperatures to form copper metal and water in a reduction reaction:



- **Thermal Stability**: Copper(II) oxide decomposes into copper(I) oxide (Cu_2O) and oxygen when heated above 1026°C in a process known as disproportionation.

❖ ***Physical Properties*** **[3]**

- **Appearance**: CuO is a black to a brownish-black powdery solid.
- **Solubility**: It is insoluble in water and organic solvents but becomes soluble in ammonium chloride and potassium cyanide solutions under heating.
- **Density**: The density of CuO is approximately 6.31 g/cm^3.
- **Melting Point**: CuO does not have a true melting point because it starts to decompose when heated intensely at temperatures around 1200°C to 1300°C.
- **Crystal Structure**: It crystallizes in a monoclinic structure.

b) Cu_2O - Copper(I) Oxide

❖ ***Chemical Properties*** **[4]**

- **Oxidation State**: Copper in Cu_2O is in a +1 oxidation state.
- **Reduction and Oxidation**: Cu_2O can be further reduced to copper metal and can also be oxidized to CuO. It acts as a reducing agent and can reduce strong oxidizers, such as hydrogen peroxide.
- **Reactivity with Acids**: Copper(I) oxide reacts less readily with acids compared to CuO, forming copper(I) salts with stronger acids.

❖ ***Physical Properties*** **[5]**

- **Appearance**: Cu_2O generally has a red or reddish-brown color and is also a powdery or crystalline solid.
- **Solubility**: It is insoluble in water and most acids but soluble in solutions of ammonia or ammonium chloride due to the formation of complex ions.
- **Density**: The density is slightly lower than that of CuO, with a value close to 6.0 g/cm^3.
- **Melting Point**: Cu_2O has a melting point of about 1232°C.
- **Crystal Structure**: It has a cubic crystal structure, more specifically a cubic face-centered lattice known as the cuprite structure.

Both CuO and Cu_2O are semiconductors with differing band gaps. CuO is a p-type semiconductor with a band gap of about 1.2 eV, whereas Cu_2O has a band gap of approximately 2 eV, which also makes it a p-type semiconductor. These electronic properties underscore their importance in solar energy and photovoltaic.

It's also relevant to point out that both oxides exhibit toxicity to aquatic life and can be harmful if inhaled or ingested. They should be managed with care to mitigate occupational exposure and environmental release.

II.3 In-depth Analysis of CuO

Copper(II) oxide (CuO) is an interesting compound due to its prominent role in various industrial processes, including catalysis and the production of superconducting materials. Here we will explore the structure and stability of CuO in detail:

II.3.1. Structure and Stability

- **Structure of CuO [6]**

CuO has a monoclinic crystal structure (see Figure II.2). It belongs to the C2/c space group, with lattice constants a = 4.6837 Å, b = 3.4226 Å, and c = 5.1288 Å, with a monoclinic angle (beta) of approximately 99.54°.

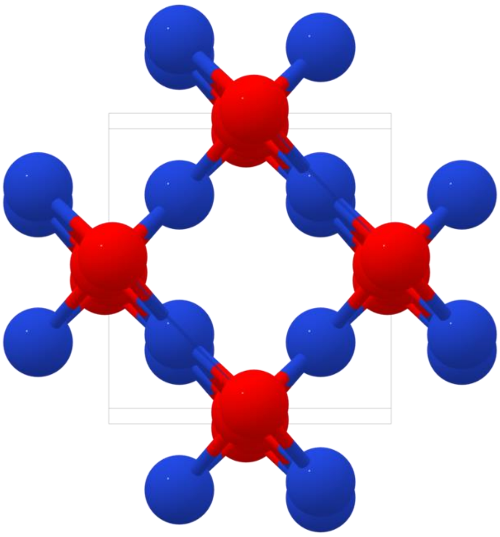


Figure II.2: CuO structure as crystallizes in the monoclinic C2/c space group.

Each Cu atom is coordinated by four oxygen atoms in a square planar arrangement. This complex structural arrangement gives rise to strong antiferromagnetic ordering below the Néel temperature, a characteristic of the material's magnetic properties.

- **Stability of CuO [7]**

Stability of CuO can be considered in terms of thermal and chemical stability:

a) Thermal Stability

CuO is thermally stable under normal conditions. It starts to decompose into copper(I) oxide (Cu_2O) and oxygen at temperatures above 1026°C through a disproportionation reaction. However, this high thermal stability makes it suitable for high-temperature processes.

b) Chemical Stability

Chemically, CuO is considered to be a stable oxide. It is insoluble in water and resistant to corrosion. When heated, it behaves as a stoichiometric compound, maintaining its composition without significant loss of oxygen. The compound's stability makes it a good catalyst in organic synthesis reactions where stable and robust materials are required.

These properties are utilized in various functionalities like the fabrication of ceramics, acting as a pigment in glasses, and the manufacturing of other copper salts.

II.3.2. Electronic and optical properties of CuO material

Copper(II) oxide (CuO) exhibits intriguing electronic and optical characteristics owing to its semi-conducting nature and its interaction with electromagnetic radiation across various energy ranges.

❖ Electronic Properties

CuO is a p-type semiconductor that possesses a narrow band gap, typically reported to be in the range of 1.2 to 2.0 eV depending on the measurement technique and sample purity.

The valence band maximum is primarily composed of O 2p orbitals (see Figure II .3), while the conduction band minimum is dominated by Cu 3d states. This leads to strong electron correlation effects, which are responsible for the material's characteristic Mott insulator behavior.

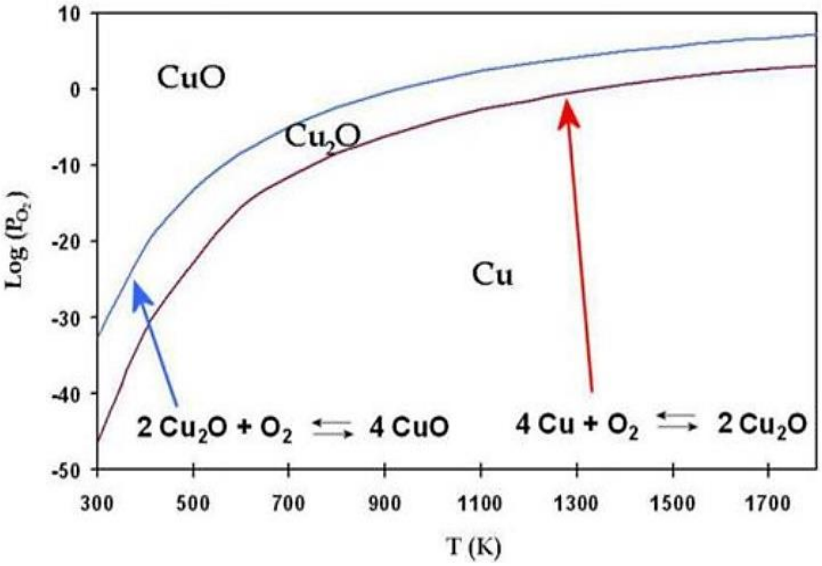


Figure II.3: Phase diagram of copper oxides calculated by the method of the equilibrium state density functional (DFT).

Due to its electronic structure, CuO features strong electron-electron and electron-phonon interactions (see figure II .4), giving rise to various physical phenomena such as high-temperature superconductivity in CuO-containing compounds and the formation of charge density waves within the crystal lattice.

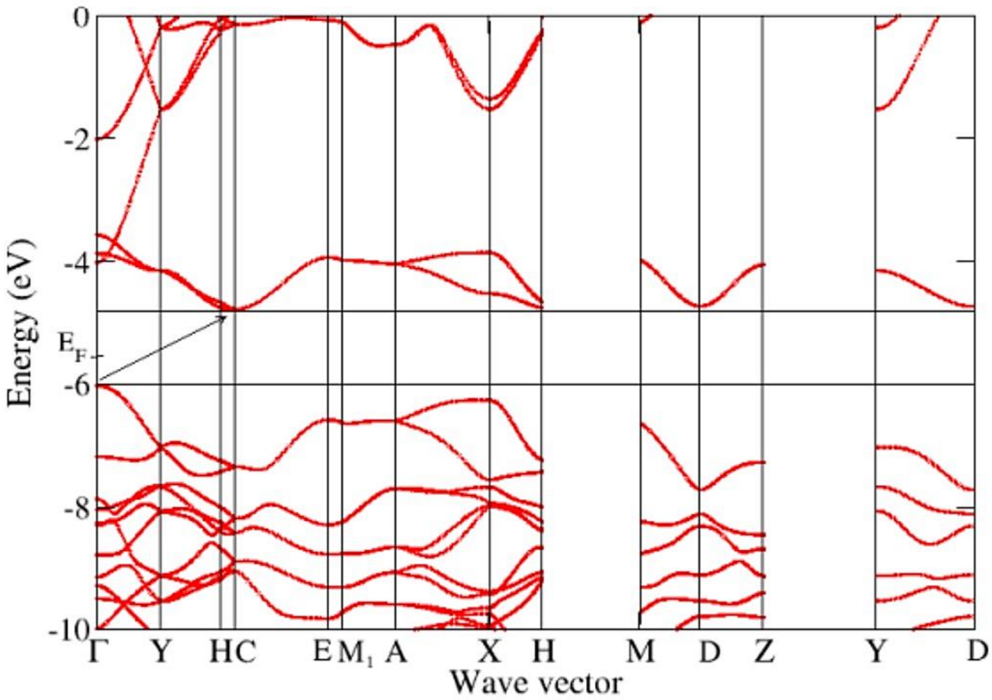


Figure II.4: Electronic band structure and density of states of CuO material.

- ***Optical Properties* [8]**

Optically, CuO demonstrates significant absorption in the visible spectrum, which is why it is often a black to brownish-black powder. The material's absorption properties are chiefly exploited in the form of solar energy applications where CuO can be used as an absorbent layer in photovoltaic cells.

Moreover, CuO thin films have displayed notable photoconductive properties. Exposing CuO to light can change its electrical conductivity, a trait that is advantageous for optoelectronic devices. The wide range of photon-induced effects in CuO makes it a flexible material for sensors and other devices that respond to light.

The refractive index of bulk CuO is equal to 2.63. For thin CuO films, the refractive index varies from 1.5 to 3.5 depending on the deposition conditions [9].

The extent of these electronic and optical properties is heavily dependent on the methods used to synthesize CuO, with properties being influenced by factors such as particle size, morphology, and the presence of crystallographic defects.

II.3.3. Mechanical and Thermal Properties of CuO material

When discussing materials such as Copper(II) oxide (CuO), it is essential to consider their mechanical and thermal properties, as these crucial parameters determine their suitability for various applications.

- ***Mechanical Properties*[10]**

Copper oxide as a ceramic material exhibits high hardness and moderate fracture toughness. Its elastic modulus, a measure of its stiffness, and its hardness can be influenced by the material's grain size and defect density. Higher defect densities can lead to a decrease in the effective hardness. Despite its hardness, CuO exhibits brittleness, a common trait among ceramic materials.

- ***Thermal Properties* [11]**

CuO is characterized by its exceptional thermal stability. It starts decomposing only at temperatures above 1026°C (see Figure II.6), dissociating into Cu_2O and O2. Furthermore, the material exhibits a rather high thermal conductivity for a ceramic, which, combined with its thermal stability, makes it well suited for use in high-temperature applications.

On the other hand, CuO is high heat capacity makes this material an excellent choice for thermal energy storage systems. The heat capacity of a material refers to its ability to store thermal energy (see Figure II .5), with higher values allowing the material to store more energy for the same temperature change.

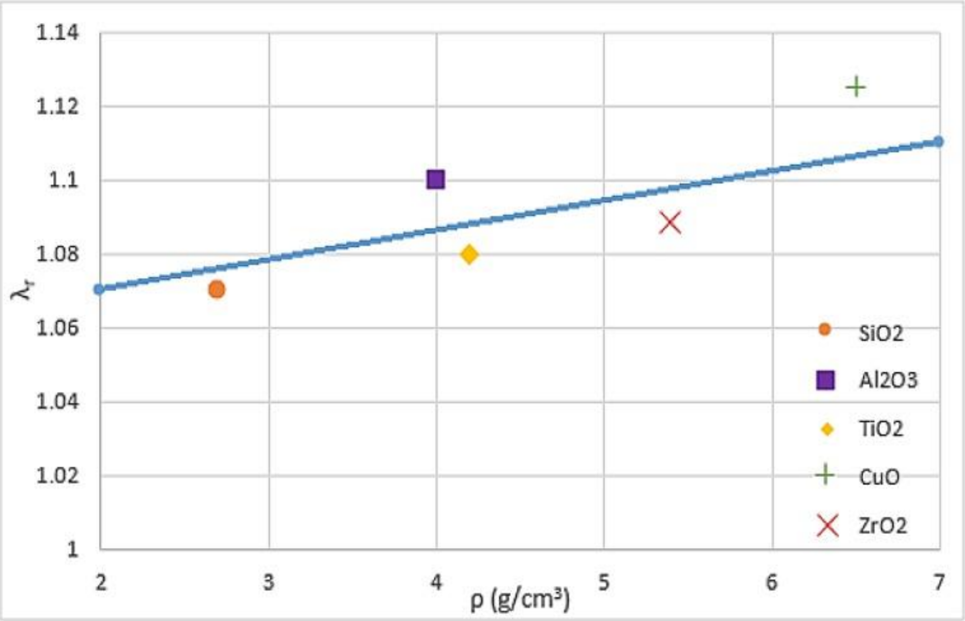


Figure II.5: Relative thermal conductivity coefficient versus density.

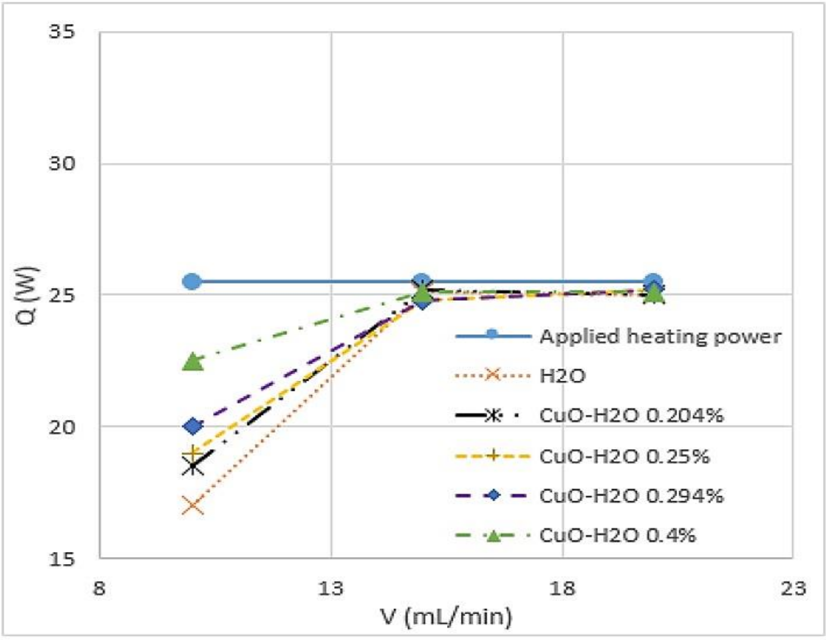


Figure II.6: Heat transfer rate (Q) of CuO.

II.3.4. Applications of CuO material in Microelectronics

Copper(II) oxide (CuO) has gained considerable attention in the field of microelectronics due to its unique set of properties, such as its semiconducting behavior, the availability of a range of oxidation states, and compatibility with established micro fabrication processes.

Following are some notable applications of CuO in microelectronics:

- **Gas Sensors** : CuO has been extensively used in the fabrication of gas sensors due to its high reactivity with gases like hydrogen and carbon monoxide. Its change in resistance when exposed to these gases allows for the detection and measurement of gas concentration, which is important in safety systems and environmental monitoring [12].
- **Photovoltaic Cells** : Due to its favorable band gap for absorbing sunlight, CuO is investigated for use in solar cells. It is often used as an active layer or a hole-transporting layer in thin-film solar cells because of its ability to absorb a wide spectrum of visible light [13].
- **Thin-Film Transistors (TFTs):** The semiconducting nature of CuO is explored for use in TFTs, which are components of liquid crystal displays (LCDs), organic light-emitting diode (OLED) displays, and in radio-frequency identification (RFID) tags. TFTs with CuO active layers are appreciated for potential low-cost and low-temperature processing [14].
- **Memory Storage**: CuO thin films are evaluated for non-volatile resistive random access memory (ReRAM) applications due to their ability to exhibit resistive switching behavior, which is crucial for the development of next-generation memory devices.
- **Energy Harvesting**: The unique electronic properties of CuO are also exploited in piezoelectric devices for energy harvesting. These devices convert mechanical strain into electrical energy and can be used in various applications, including self-powered Nano devices.
- **Catalysis in Micro reactors**: Copper oxide, owing to its excellent catalytic properties, is utilized in micro reactors for facilitating chemical reactions at the micro-scale. This is beneficial in micro fabrication processes that require precise chemical modification of surfaces or materials.

- **Interconnects**: CuO can be used in the formation of conductive interconnects in integrated circuits. While pure Cu is typically used, CuO forms on the surface and must be managed carefully during manufacturing since it affects the reliability and performance of the microelectronic device.
- **LED and Transducers**: It is also investigated for application in light-emitting diodes (LEDs) and transducers due to its optoelectronic properties which can be tailored for specific wavelengths.

These are just snapshots of what CuO can do in the field of microelectronics. There is ongoing research to fully realize the potential of CuO and overcome challenges such as improving the material's stability and compatibility with current silicon-based microelectronics technology.

II.4. In-depth Analysis of Cu_2O material

II.4.1. Structure and stability

Copper(I) oxide (Cu_2O) is a fascinating p-type semiconductor with a cubic crystal structure. It is known for its use in various applications due to its low-cost synthesis and unique properties [15].

❖ ***Structure***

Cu_2O crystallizes in a cubic lattice with a space group of Pn3m. The structure can be seen as a simple cubic array of anions with half of the cubic sites occupied by captions (see Figure II .7).

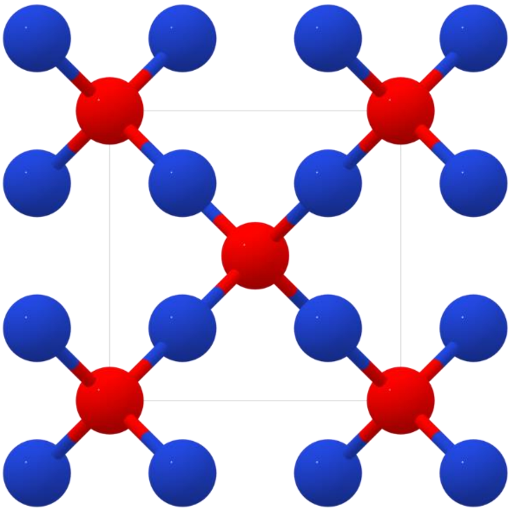


Figure II.7: Illustration of Cu_2O Cubic structure.

This arrangement forms a crystal lattice where each copper atom is at the center of a tetrahedron, with oxygen atoms at the vertices. The unit cell contains two molecules of Cu_2O.

- ***Stability***

Cu_2O is relatively stable under ambient conditions but deteriorates in moist air by oxidizing to Copper(II) oxide (CuO). It is stable up to temperatures of approximately 1230°C, beyond which it starts to decompose into copper metal and oxygen gas. When exposed to light, Cu_2O can exhibit photo corrosion, leading to degradation of the material and affecting its structural integrity [16].

In the context of thermodynamic stability, Cu_2O is stable over a wide range of oxygen partial pressures and temperatures, which contributes to its prevalence as a naturally occurring mineral known as cuprite.

II.4.2. Electronic and optical properties

Copper(I) oxide (Cu_2O) is valued for its distinctive electronic and optical properties, making it a significant material in various electronic and optoelectronic applications.

- ***Electronic properties***

Cu_2O is a p-type semiconductor with a direct band gap, which equips it for use in semiconductor devices. It has a band gap of approximately 2.0 to 2.2 eV, which makes it absorb visible light.

This property is leveraged in applications like photovoltaic cells. The high hole mobility in Cu_2O also contributes to its utility in electronics, where efficient charge transport is necessary.

- ***Optical properties* [17]**

The optical properties of Cu_2O arise from its band structure, giving rise to absorption in the visible region. This absorption is associated with the creation of exciting, which are bound states of an electron and a hole.

Cu_2O exhibits a strong excited binding energy, which allows for the formation of exciting even at room temperature, contributing to its high optical absorption coefficient.

These exciting are also responsible for the photoluminescence seen in Cu2O, which can be harnessed in applications like light-emitting diodes (LEDs).

Additionally, due to the band gap of Cu_2O falling in the red region of the visible spectrum, it is used for creating red-colored glass and ceramics (see Figure II.8).

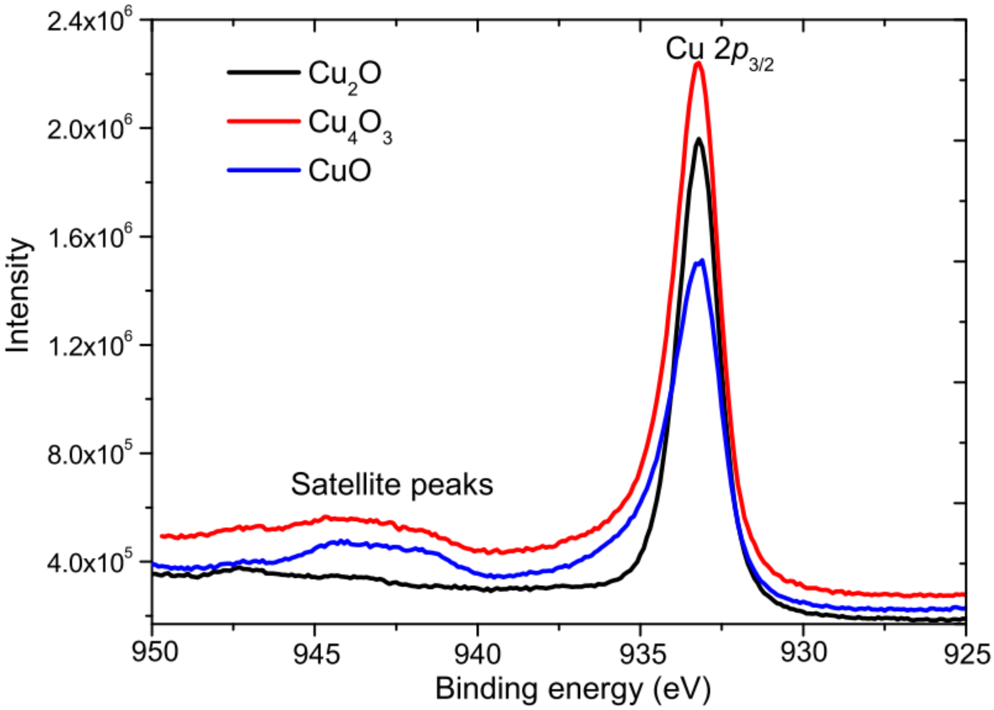


Figure II.8: Cu 2p3/2 core-level XPS spectra of Cu_2O, Cu4O3, and CuO thin films.

II.4.3. Mechanical and thermal properties of Cu_2O material

❖ ***Mechanical properties*** **[18]**

- Cu_2O has a Mohs hardness of about 3.5 to 4, indicating that it is relatively soft and, therefore, not suitable for applications that require high wear resistance.
- The material has a moderate Young's modulus, reflecting a reasonable degree of stiffness and rigidity for a semiconductor.
- It also exhibits a Poisson’s ratio that is typical for ceramic materials, which is an indication of its ductility under stress.

❖ ***Thermal properties*** **[19]**

- The melting point of Cu_2O is around 1235°C (2255°F), allowing it to withstand high temperatures but also limits its applications in environments exceeding this temperature.
- Cu_2O has relatively low thermal conductivity, consistent with typical semiconductors, which might necessitate thermal management in electronics applications.

- The specific heat capacity of Cu_2O is in the range consistent with semiconducting oxides, reflecting its ability to absorb heat energy.
- The material experiences thermal expansion, and its coefficient of thermal expansion is essential in applications where it may undergo significant changes in temperature.
- As a semiconductor, the band gap of Cu_2O can be affected by temperature, impacting its electronic and optical properties under varying thermal conditions.

II.4.4. Applications in microelectronics

- **Photovoltaic Devices**: Cu_2O is used as a p-type semiconductor layer in photovoltaic cells due to its suitable band gap for solar absorption.
- **Photocathodes for Water Splitting**: The material's band structure is also favorable for photovoltaic reactions in photo electrochemical cells for hydrogen production.
- **Gas Sensors**: Cu_2O is sensitivity to gases such as CO makes it a viable candidate for use in chemical and gas sensor applications [20].
- **Transparent Conductive Oxide (TCO) Layers**: With adequate doping, Cu_2O can serve as a TCO, useful in display technologies and solar cells.
- **Energy Storage**: Cu_2O is investigated in battery technologies, particularly in lithium-ion batteries as an electrode material.
- **Memory Storage Devices**: There are emerging applications of Cu_2O in resistive switching memory devices due to its electrical conductivity properties.
- **Field-Emitter Arrays**: The material's electron emission properties when under an electric field make it suitable for use in field-emitter arrays.

II.5. Comparison between CuO and Cu_2O materials

Table II.1: Comparison between CuO and Cu_2O materials.

Materials	**Cu_2O**	**CuO**
Structure	Cubic	Monoclinic
Spatial Groups	Pn-3m	C2/c
Mesh parameters (°A)	a = b = c = 4.26 °A $\alpha = \beta = \gamma = 90°$	a = 4.46 °A b= 3.42 °A c= 5.13 °A $\alpha = \gamma = 90°$ $\beta = 99.57°$
Density (g/cm^3)	6.09	6.51
Volume of a cell ($10°pm^3$)	77.31	81.12
Z	2	2
Cu-O bond length (°A)	1.849	1.96
O-O separation (°A)	3.68	2.62
Cu-Cu separation (°A)	3.012	2.90

II.6. Conclusion

The in-depth analysis of CuO reveals its robust structure and stability, which underpins its mechanical and thermal endurance. The detailed examination of its electronic and optical properties highlights its potential in advancing microelectronics, indicating how these properties can be harnessed for technological innovation.

Similarly, the comprehensive study of Cu_2O echoes the structure of the discussion on CuO, mapping a close, nuanced comparison of their structures, stability, and thermal and mechanical attributes. The compilation underscores how the slight differences in electronic configuration between CuO and Cu_2O result in significantly different electronic and optical behaviors, thus differentiating their applications in the field of microelectronics.

The comparison section adeptly synthesizes the properties of both compounds, contrasting their merits and explaining the implications of using one over the other in specific applications. It is evident that while both oxides share some similarities due to their copper content, their distinct features make them suitable for diverse applications, reflecting the interplay between structure at the atomic level and macroscopic functionality.

In essence, the journey through the chapters encapsulates not only the foundational knowledge of the materials in question but also provides insights into the scientific and technological implications of their properties. This narrative accentuates the significance of material science in innovating and optimizing materials like CuO and Cu_2O for specialized roles in technology, especially within the microelectronics industry. As the quest for smaller, faster, and more efficient electronic devices continues, understanding and manipulating the properties of such materials remain pivotal. This comprehensive literature primes the scientific community for future explorations, aiming to exploit the full potential of CuO and Cu_2O in emerging technologies.

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Chapter III

Results and discussions

Chapter III

Results and discussions

III.1 Introduction

In this chapter, we will investigate the structural, electronic, and optical properties of CuO and Cu_2O compounds using the CASTEP computational software. Our study divided into two main parts. The first part is concerned the structural, electronic, and optical properties of CuO material and the second one is about the structural, electronic, and optical properties of Cu_2O material. A good comparison between two materials in the last section of this section.

CASTEP program is a powerful computational tool used in physical materials science and chemistry for simulating the properties of organic and inorganic materials at the atomic level. It stands for "Cambridge Serial Total Energy Package" and is developed by researchers at the University of Cambridge [1].

At its core, CASTEP utilizes density functional theory (DFT), a quantum mechanical method, to describe the electronic structure of materials. This allows researchers to investigate a wide range of properties, including but not limited to, crystal structures, electronic densities, band structures, and energies [2].

One of the key features of CASTEP program is its ability to model complex materials accurately. It can handle various types of systems, from simple molecules to large and intricate crystal structures. Additionally, CASTEP incorporates advanced algorithms for efficient and accurate calculations, making it suitable for both research and industrial applications

Both CuO and Cu_2O materials have attracted significant interest in various fields due to their unique properties, including their electrical conductivity, catalytic activity, and optical properties. Researchers study these materials for applications in electronics, renewable energy, catalysis, and more. Their properties can be further explored through computational methods like density functional theory (DFT), which can provide insights into their structural, electronic, and optical properties, as well as their potential applications [3].

III.2 Overview of the CASTEP program

CASTEP is a versatile software for simulating material properties from first principles, relying on Density Functional Theory (DFT). It predicts a wide range of properties, from structural to electronic, optical, and magnetic, without empirical input. Utilizing pseudopotentials and plane wave basis sets, it calculates electronic structures and performs structural optimization.

It can predict electronic properties like band structures and density of states, optical properties such as dielectric constants and absorption spectra, and magnetic properties like moments and ordering. CASTEP finds applications in materials science, condensed matter physics, and chemistry for fundamental research and practical applications. The program interface includes a toolbar for operations, an input panel for setting parameters, an output panel for displaying results, and a visualization panel for interpreting data.

III.3 Computational details

In this exploration of CuO and Cu_2O's structural properties, we have leveraged the CASTEP software, a quantum mechanics-based computational tool. Acting as a virtual microscope, CASTEP allows us to dissect the arrangement of atoms within their cubic crystal lattices (all edges equal length, 90° angles), as reflected by the shared $P\bar{n}3m$ space group (defining atomic positions).

To accurately represent their electronic structures within CASTEP, we employ a (8 × 8 × 8) k-point sampling scheme and a 750-eV plane-wave cutoff, balancing accuracy and computational efficiency for both materials. Finally, we utilize the well-established Perdew-Burke-Ernzerhof (PBE) functional within the Generalized Gradient Approximation (GGA) class of DFT methods. This consistent selection of space group, k-point sampling, plane-wave cutoff, and functional (PBE-GGA) establishes a robust CASTEP framework for analyzing the structural properties of both CuO and Cu_2O materials, ensuring reliable and comparable results for these closely related materials.

III.4 Structural, electronic and optical properties of CuO material

III.4.1 Structural properties (Geometry optimization)

Geometry optimization plays a crucial role in CASTEP simulations as it allows researchers to find the stable and energetically favorable atomic configurations of materials. To attain optimal convergence for both computed structures and energies, we must calculate total energy as a function of K-points and cut-off energy.

III.4.1.1 Total energy as a function of (k-points) and (cut-off Energy)

In the context of geometry optimization in materials science and computational physics, "k-points" refer to the points in reciprocal space that are sampled during calculations using periodic boundary conditions. These "k-points" are a key aspect of the Brillouin zone sampling technique, which is used to accurately describe the electronic structure of materials.

In geometry optimization within CASTEP program, the "cut-off" refers to the maximum distance beyond which interactions between atoms are considered negligible and not included in the calculation. This parameter helps to control the computational cost of the optimization by limiting the range of interactions that need to be considered during the calculation.

The compounds exhibited Pn̄3m space groups. Figure III.1 shows the total energy with different values of k-points, mesh and utilizing cut-off energy as 750 eV. Following the computations, we determined that employing a (8 × 8 × 8) Brillouin zone k-point is suitable of our calculation.

Figure III.2 shows the total energy with different values of cut-off energies for CuO material, which resulted in stability and suitability for our analysis.

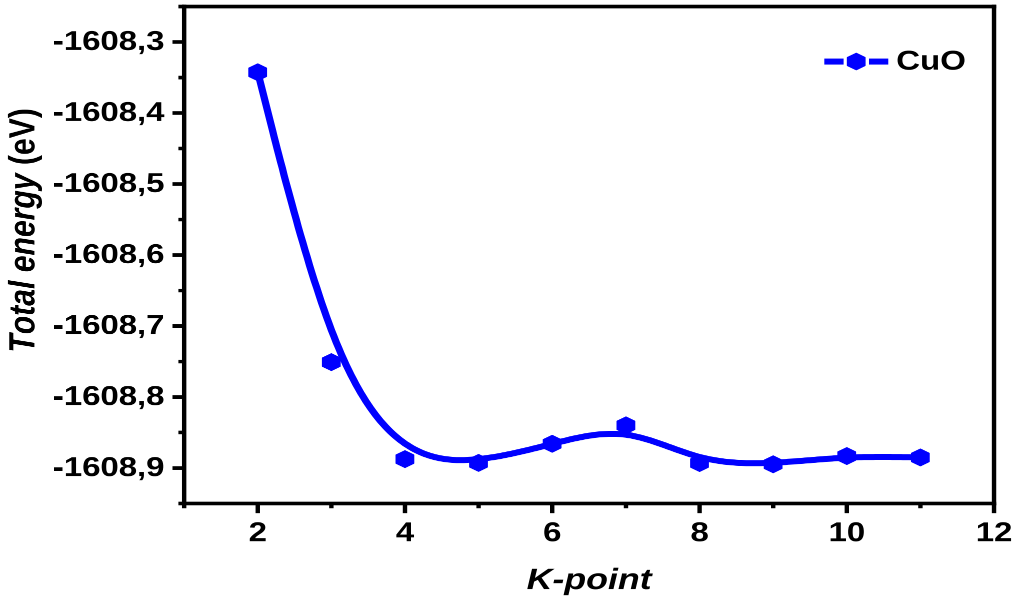


Figure III.1: Total energy versus K-points for CuO material.

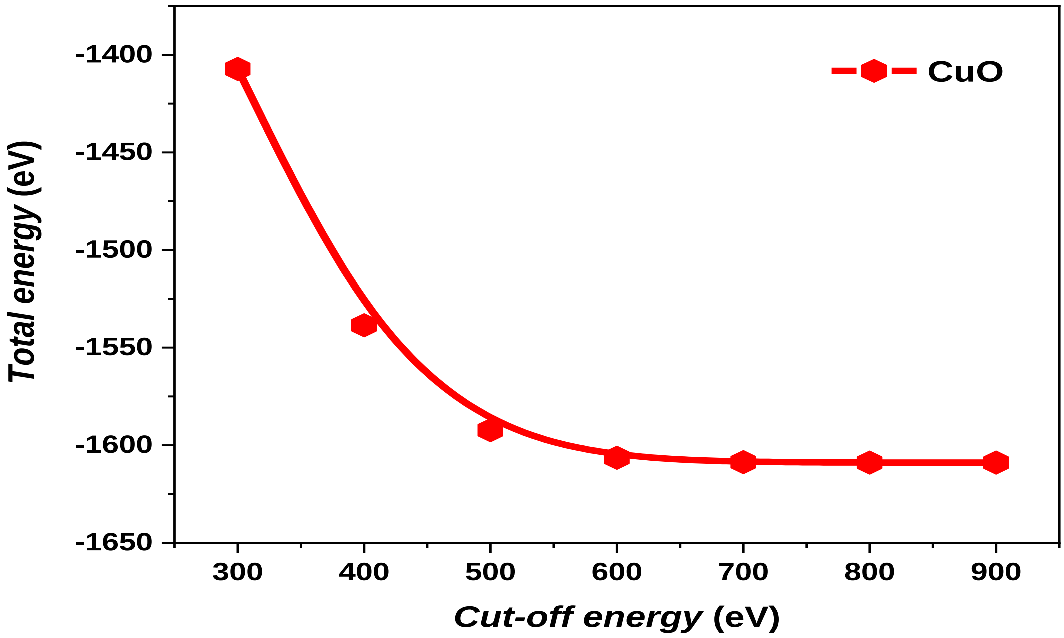


Figure III.2: Total energy versus cut-off energy for CuO material.

III.4.1.2 Total energy as a function of volume (Å^3)

This type of plot is typically called an "energy versus volume curve" (see Figure III.3) it's an important tool in materials science for understanding the structural and energetic properties of materials. The energy versus volume curve shows the relationship between the total energy of the system (such as the total electronic energy) and the volume of the crystalline unit cell.

For the CuO material, we can generate an energy versus volume curve by changing the volume of the CuO unit cell and calculating the total energy for each volume. The energy versus volume curve typically exhibits a distinct peak representing the optimal unit cell volume for the system, where the total energy is at its minimum level.

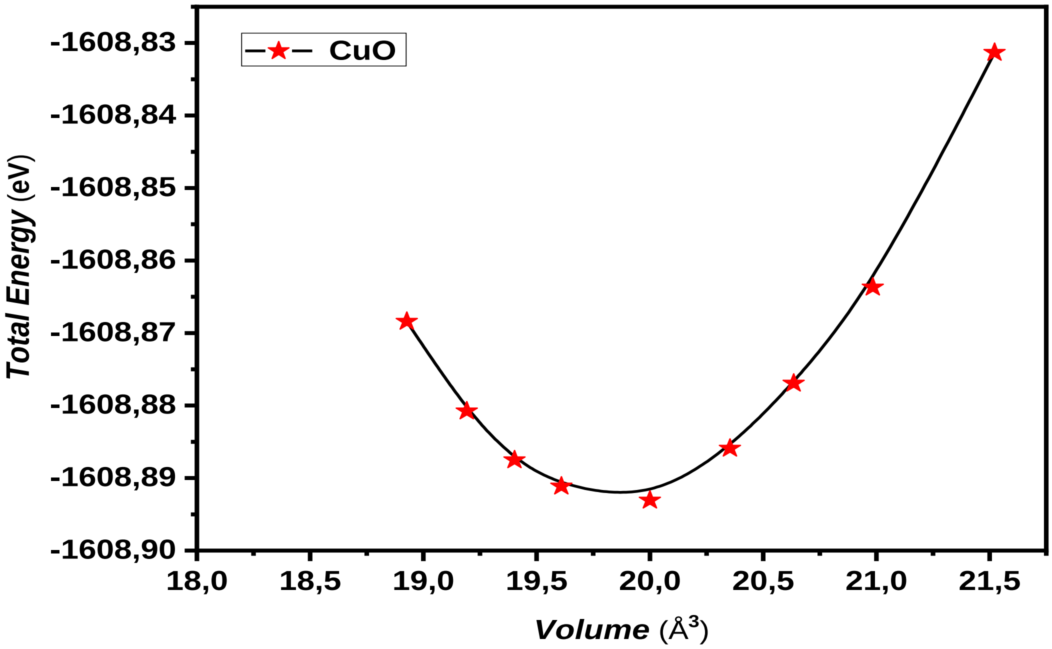


Figure III.3: Total energy versus volume for CuO material.

III.4.1.3 Lattice parameters calculation of CuO material using CASTEP

For Local Density Approximation (GGA) method, we employed the Perdew-Burke-Ernzerhof (PBE) approach and we use a cubic crystal structure. Primitive lattice representation of face-centered cubic (FCC) and the arrangement of atoms in CuO compounds was schown in Figure III.4. The lattice constant, the volume and the bulk modulus calculated are indicated in Table III.1.

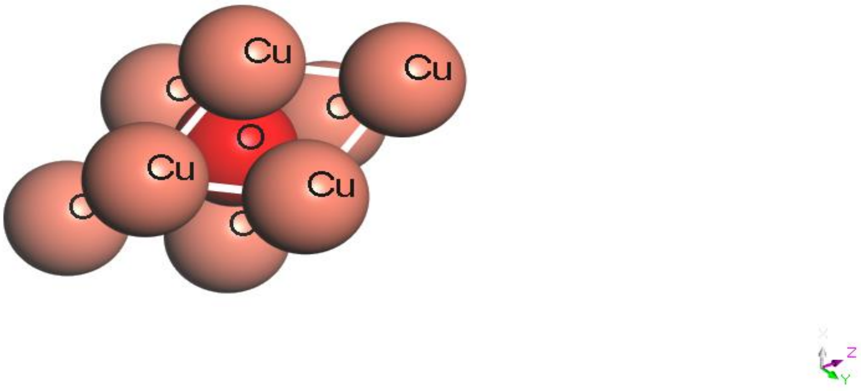


Figure III.4: Arrangement of atoms in CuO compound: crystal structure.

Table III.1: Lattice constant, volume, bulk modulus calculated of CuO compound.

Compound	**a=b=c (Å)**	**α=β=ɣ (C°)**	**Volume (Å^3)**	**Bulk Modulus (GPA)**
CuO	3.04712	90.0000	20.0057	158.21355

III.4.2 Electronic properties

III.4.2.1 Band gap energy

Electronic properties, particularly the energy gap, play a pivotal role in comprehending bonding characteristics, electronic conductivity, optical responses, and stability. Notably, the energy gap's influence extends to optical attributes governing the material's photovoltaic traits. Investigating the band structure yields insights into the compound's nature, it will be a conductor, semiconductor or insulator.

As shown in Figure III.5, we found that this compound is not a semiconductor, because the band gap value calculated was approximately 0 eV for CuO material, at ambient temperature (300K). Experimental results confirmed that there is an indirect band gap of up to 1.5 eV, but these results occurred due to temperature changes and improvements to the calculations.

III.4.2.2 Total and partial densities of states (TDOS and PDOS)

The density of states (DOS) refers to the distribution of electronic states in a material with respect to their energy levels. It provides valuable information about the electronic structure of the material, including the number of available electronic states at different energy levels.

TDOS represents also the total number of electronic states available at different energy levels in a material. It provides an overall picture of the electronic structure of the material, showing the distribution of electronic states across the entire energy spectrum. Figure III.6 represents the Total Density of States (TDOS) for CuO compound.

PDOS, on the other hand, breaks down the total density of states into contributions from individual atoms or atomic orbitals in the material. It provides information about the electronic states associated with specific atomic species or orbital types, allowing for a more detailed analysis of the material's electronic structure.0 Figure III.7 represents the partial density of states (PDOS) spectra, calculated for CuO compound.

As indicated in Figure III.6, The TDOS results showed that there was a BV region that exceeded the Fermi level. In Figure III.7, the BV region are dominated by Cu-d and O-p states. The second region BC is dominated by O-d states.

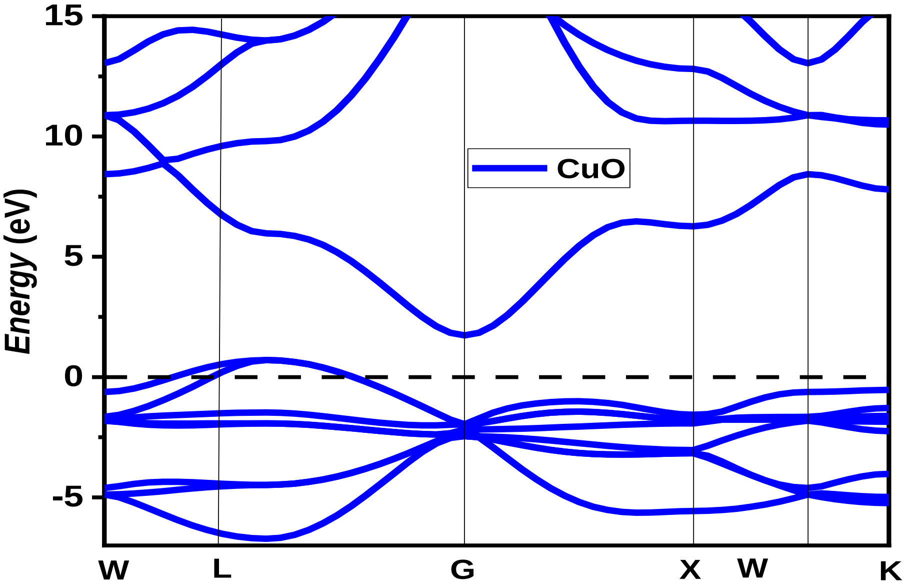


Figure III.5: Calculated band structure for CuO alloy.

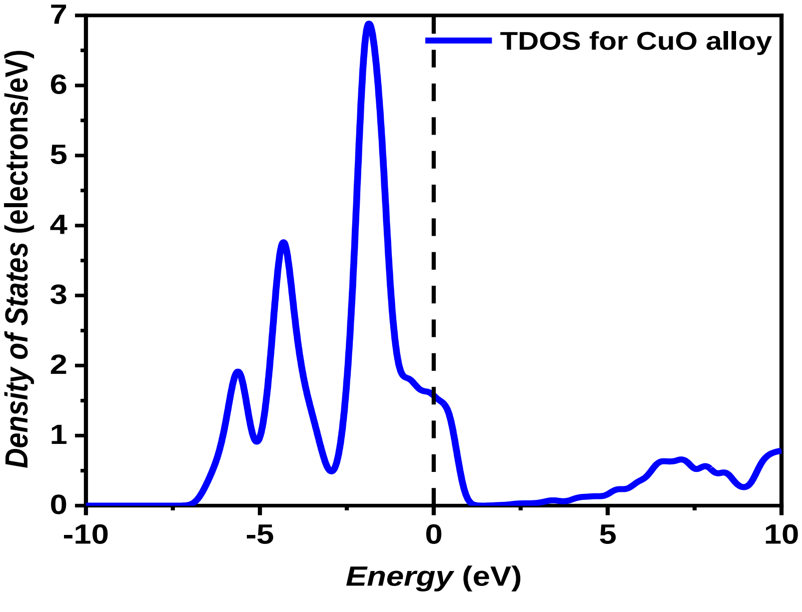


Figure III.6: Total Density of States for CuO compound.

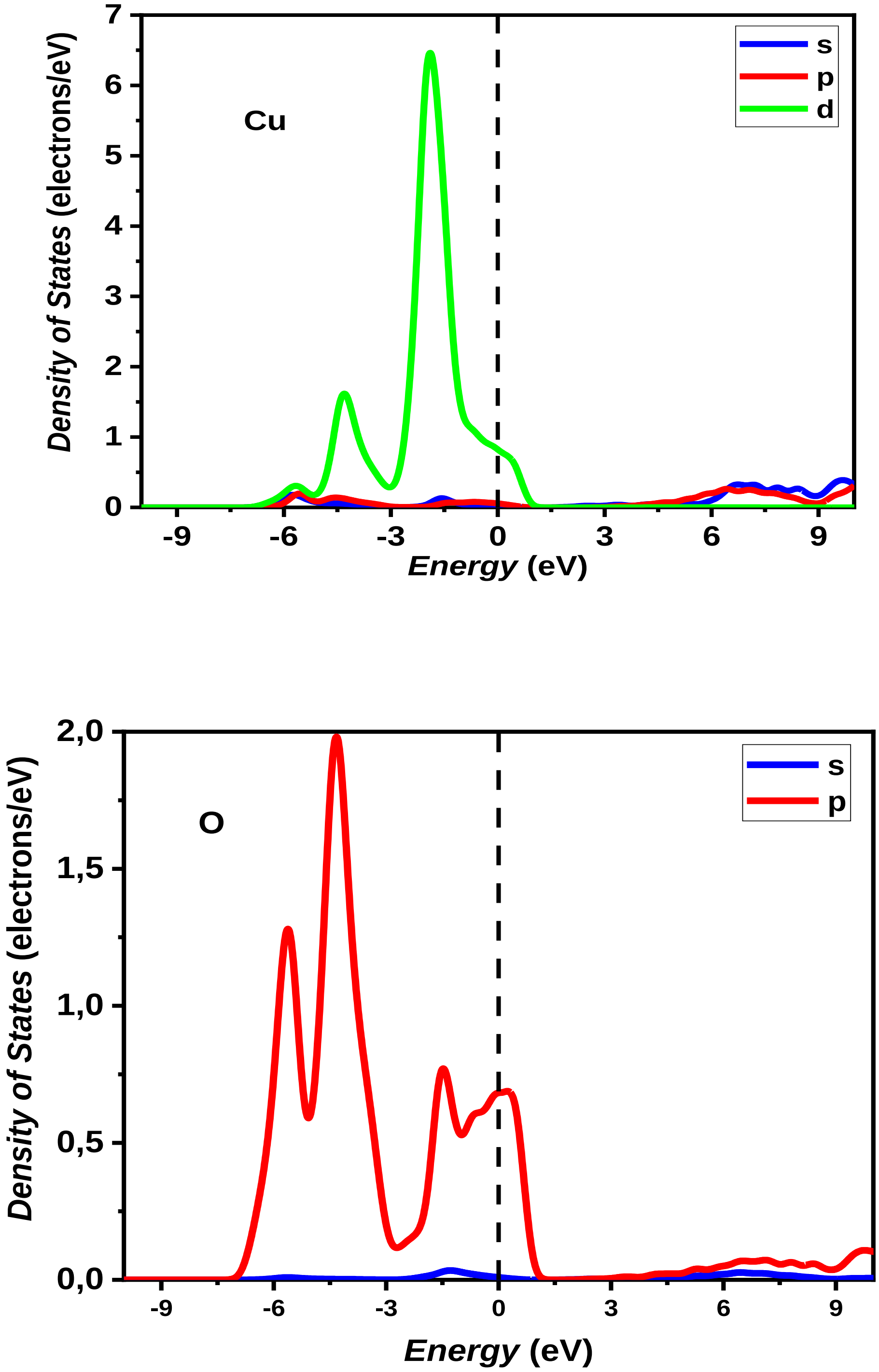


Figure III.7: PDOS spectra calculated for CuO compound.

III.4.3 Optical properties

The optical properties of CuO, including absorption, refractive index, and reflectivity spectrum, are important for understanding how the material interacts with light. Here's a brief overview of each:

III.4.3.1 Absorption spectrum

The absorption spectrum of CuO material describes how the material absorbs light at different wavelengths. It provides information about the energy levels of electrons in the material and the transitions between them. By measuring the absorption spectrum, one can identify the energy of electronic transitions and determine factors such as band gaps and exciton energies. Figure III.8 presents the absorption spectra calculated for CuO material.

CASTEP simulations have shown that CuO have been found to exhibit high absorption in the ultraviolet regions, with values reaching up to 350000 × 10^4 cm^{-1} (Figure III.8). By understanding the absorption properties of CuO compounds, researchers can design materials with specific absorption properties for various optoelectronic applications.

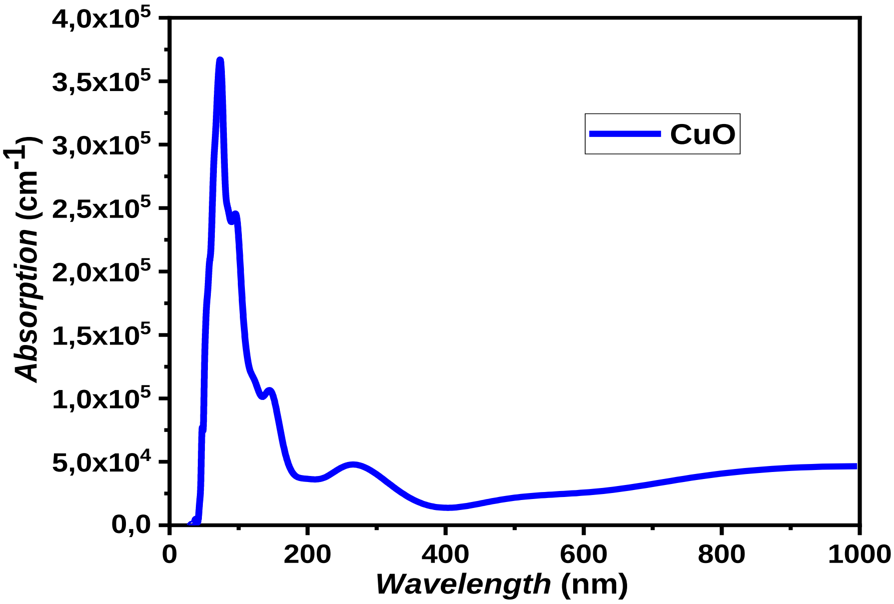


Figure III.8: Absorption spectra calculated for CuO material.

III.4.3.2 Refractive Index

The refractive index of CuO material indicates how much light is bent, or refracted, as it passes through the material. It is defined as the ratio of the speed of light in a vacuum to the speed of light in the material. The refractive index is related to the material's electronic and structural properties and affects phenomena such as reflection and transmission of light at interfaces. Figure III.9 presents the Refractive index n and K calculated for CuO material.

As indicated in Figure III.9, CuO material has high refractive indices in the ultraviolet regions, respectively, with values reaching up to 5.

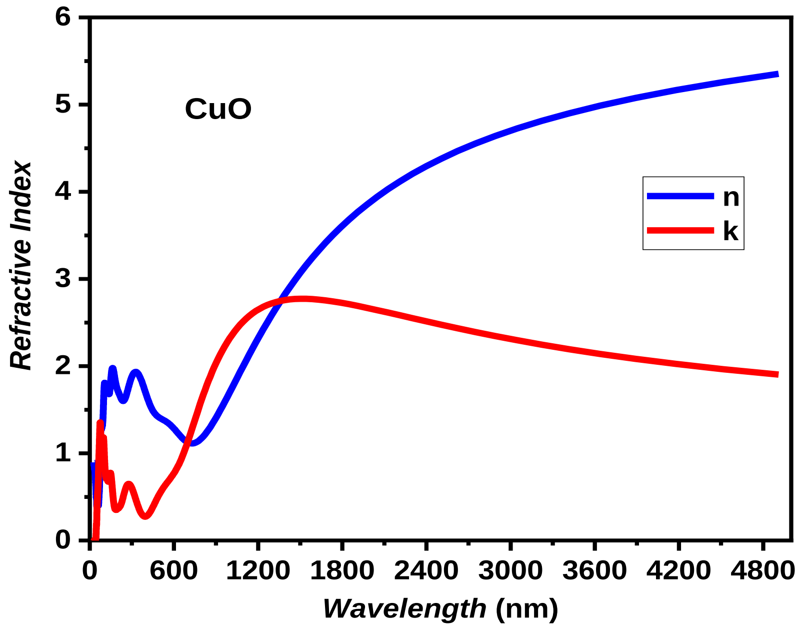


Figure III.9: Refractive index n and K calculated for CuO material.

III.4.3.3 Reflectivity spectrum

The reflectivity spectrum of CuO material describes how much light is reflected from the surface of the material at different wavelengths. It is influenced by factors such as the material's composition, surface roughness, and the angle of incidence of light. The reflectivity spectrum can provide insights into the optical properties of CuO material and its potential applications in areas such as photovoltaics, optical coatings, and sensors. Figure III.10 presents the Reflectivity (R) spectra calculated for CuO material.

Copper oxide CuO material exhibits a strong reflective nature, particularly in the ultraviolet range of the light spectrum. In fact, its reflectivity can reach up to 40%. This knowledge of CuO reflective properties empowers researchers to develop materials with tailored optical characteristics, making them suitable for a wide range of applications in optoelectronics (Figure III.10).

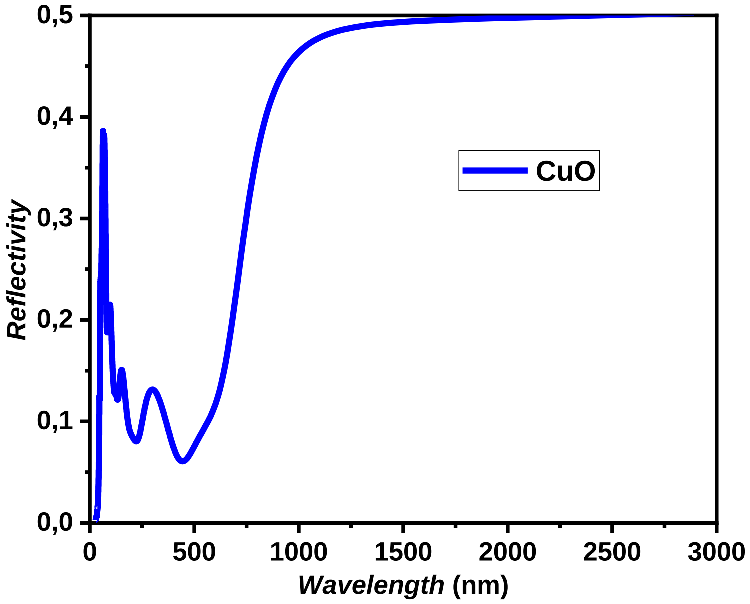


Figure III.10: Reflectivity (R) spectra calculated for CuO material.

III.5 Structural, electronic and optical properties of Cu_2O material

III.5.1 Structural properties (Geometry optimization)

Cu_2O material, also known as cuprous oxide, is a compound composed of copper (Cu) and oxygen (O). It has a cubic crystal structure, specifically a simple cubic structure, with each copper atom surrounded by four oxygen atoms arranged in a tetrahedral configuration.

III.5.1.1 Total energy as a function of (k-points) and (cut-off Energy)

The compounds exhibited $Pn\bar{3}m1$ space groups. Following the computations, we determined that employing an (8 × 8 × 8) Brillouin zone k-point. Figure III.11 shows the total energy with different values of k-points, mesh and utilizing cut-off energy as 800 eV.

Figure III.12 shows the total energy with different values of cut-off energies for Cu_2O material, which resulted in stability and suitability for our analysis.

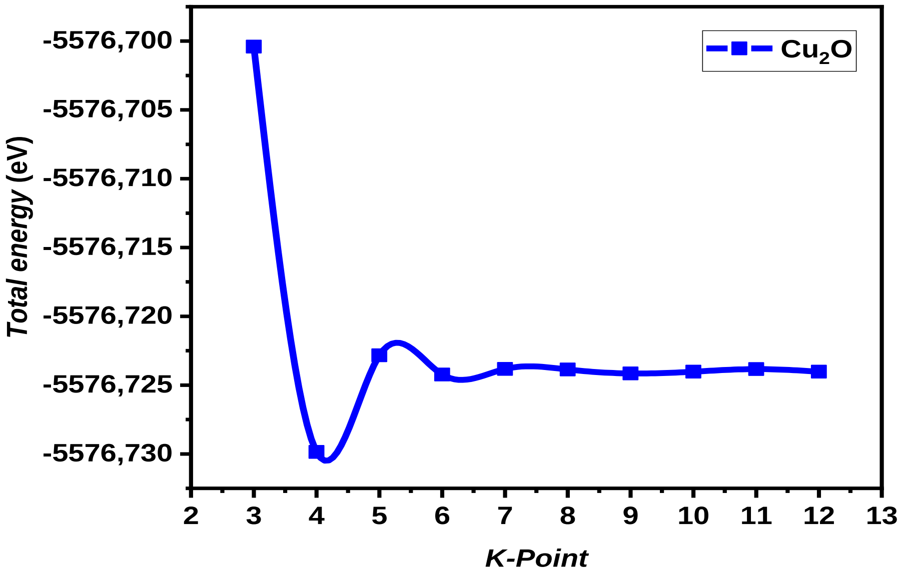


Figure III.11: Total energy versus K-points for Cu2O material.

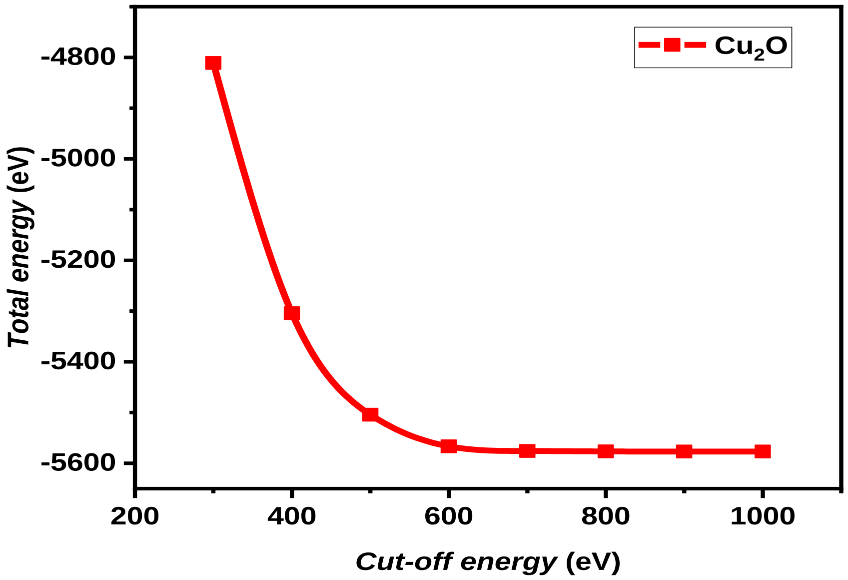


Figure III.12: Total energy versus cut-off energy for Cu_2O material.

III.5.1.2 Total energy as a function of volume (Å^3)

The curve in the Figure III.13 shows the total energy of Cu_2O material as a function of its volume. The curve has a minimum point, which is the equilibrium volume of this material. The equilibrium volume is the volume at which the substance is most stable. At the equilibrium volume, the forces that are acting on the substance are balanced.

If the volume of the substance is less than the equilibrium volume, the substance will expand. This is because the forces that are pushing the atoms apart are stronger than the forces that are pulling them together.

If the volume of the substance is greater than the equilibrium volume, the substance will contract. This is because the forces that are pulling the atoms together are stronger than the forces that are pushing them apart.

The curve in the image can be used to understand the properties of materials. For example, it can be used to predict the bulk modulus of a material, which is a measure of how much the volume of the material changes when it is subjected to a pressure.

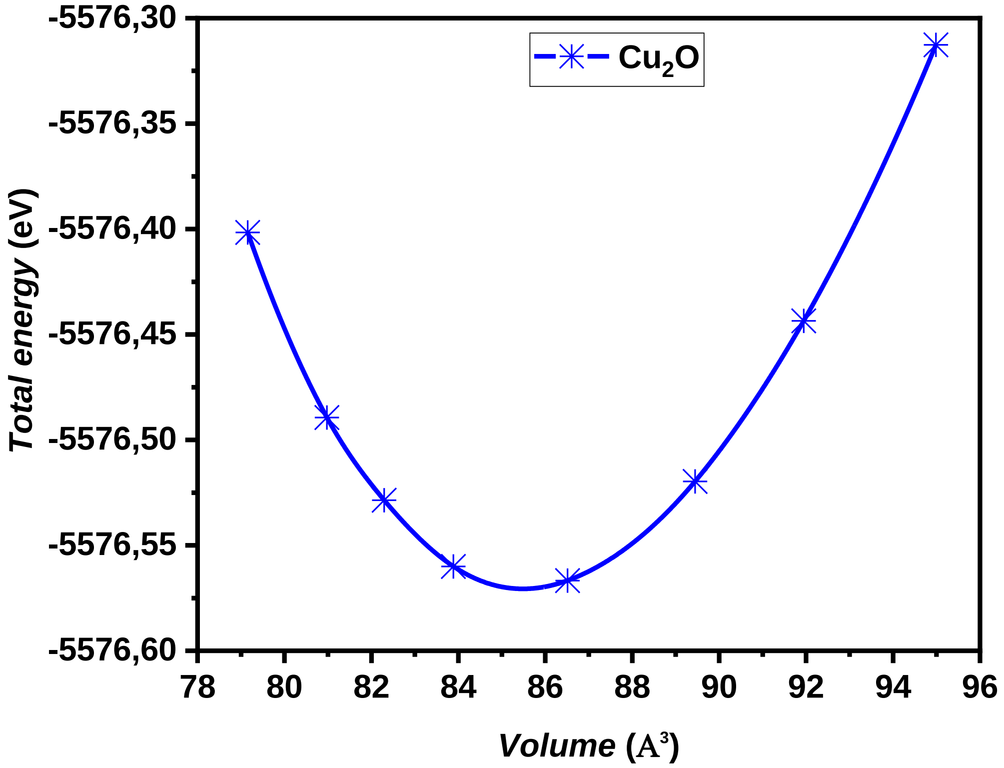


Figure III.13: Total energy versus volume.

III.5.1.3 Lattice parameters calculation of Cu_2O using CASTEP

Figure III.14 presents the arrangement of atoms for Cu_2O compound: crystal structure. The lattice parameter refers to the length of the edges of the cubic unit cell. Table III.2 gives the lattice constant, volume, and bulk modulus calculated of Cu_2O compound. This parameter typically falls in the range of 4.26 to 4.32 angstroms.

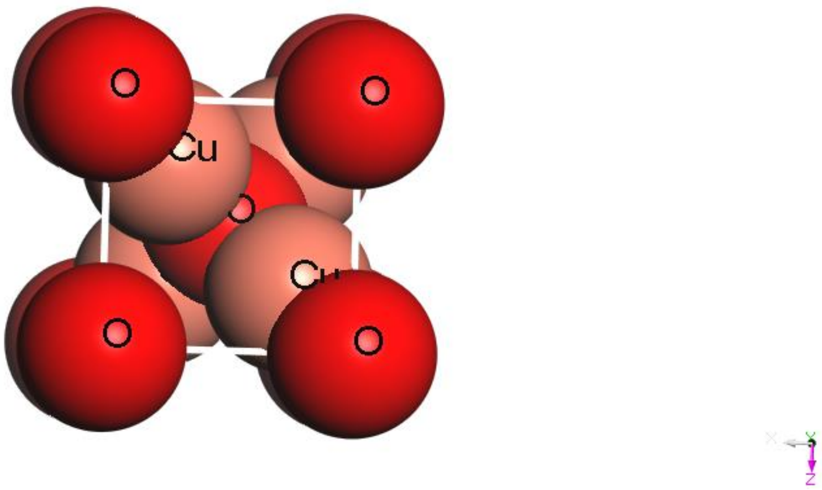


Figure III.14: Arrangement of atoms in Cu_2O compounds: crystal structure.

Table III.2: Lattice constant, volume, bulk modulus calculated of Cu_2O compound.

Compound	**a=b=c (Å)**	**α=β=γ(C°)**	**Volume (Å³)**	**Bulk Modulus (Gpa)**
Cu_2O	4.42273	90.0000	86.510711	899.10913

III.5.2 Electronic properties

III.5.2.1 Band gap energy

Figure III.15 shows that the Cu_2O material is a semiconductor with a small band gap of about 0.212 eV. This means that it takes very little energy to excite an electron from the valence band to the conduction band. As a result, Cu_2O has several interesting properties and potential applications:

- **High electrical conductivity**: With more electrons free to move in the conduction band, Cu_2O can conduct electricity more effectively than materials with larger band gaps.
- **Light absorption:** The small band gap allows Cu_2O to absorb infrared light. This makes it useful in infrared detectors and space PV modules.
- **Direct Band Gap:** Cu_2O is a direct band gap material, making it a potential material for high efficient solar cells.

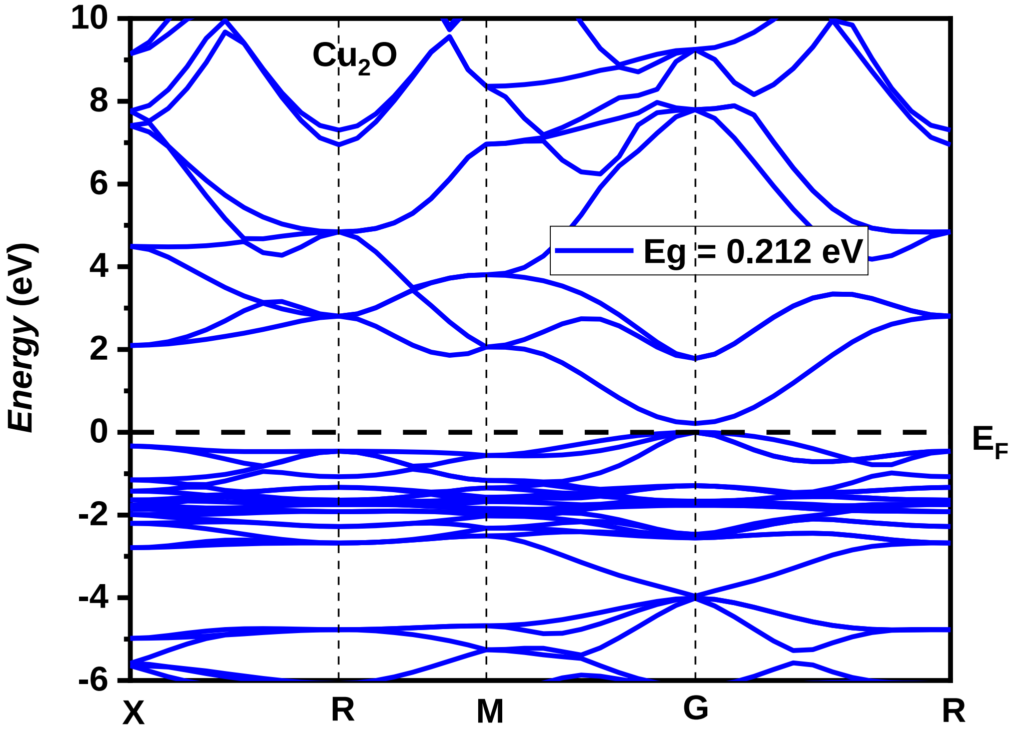


Figure III.15: Calculated band structure for Cu_2O alloy.

III.5.2.2 Total and partial densities of states (TDOS and PDOS)

The TDOS represents the total number of electronic states available at different energy levels in Cu_2O. As depicted in Figure III.16, the TDOS provides an overall picture of Cu_2O's electronic structure by showcasing the distribution of electronic states across the entire energy spectrum.

Unlike the TDOS, the partial density of states (PDOS) breaks down the total number of states into contributions from individual atoms or atomic orbitals within Cu_2O material. This provides information about the electronic states associated with specific atomic species or orbital types in Cu_2O material. Figure III.17 showcases a more detailed analysis of Cu_2O's electronic structure using PDOS.

As shown in Figure III.16, the DOS results indicate the presence of a valence band (BV) region do not exceeding the Fermi level. By analyzing Figure III.17, we can further understand that Cu-d and O-p states dominate the BV region in Cu_2O.

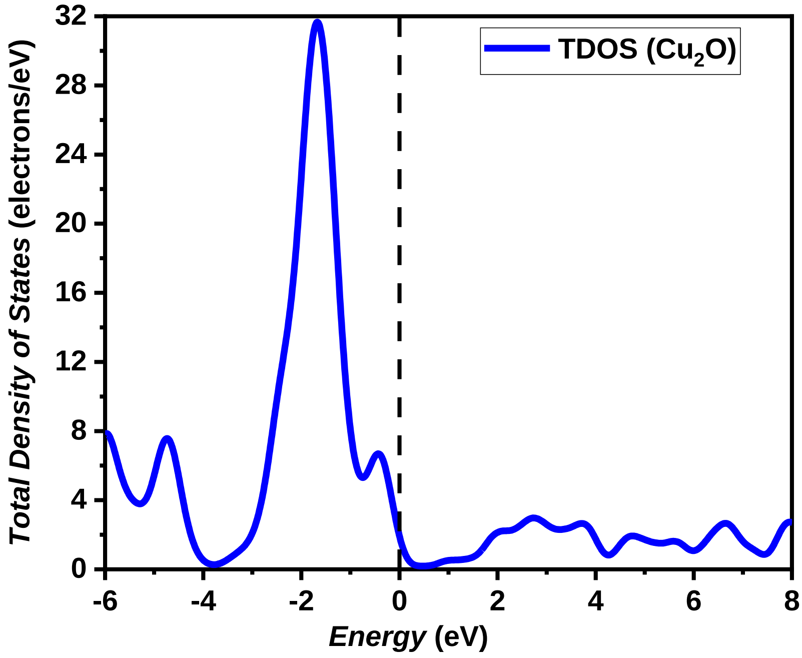
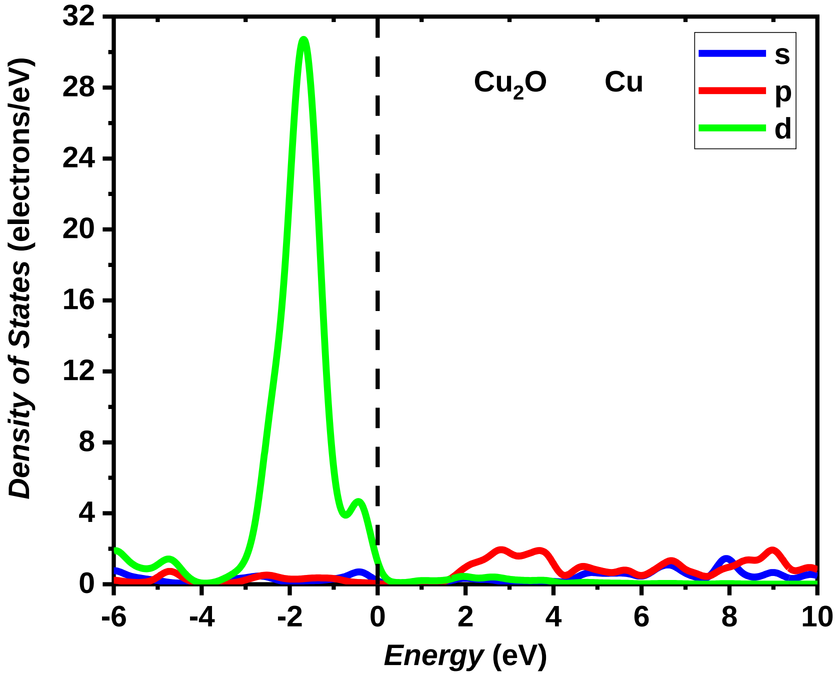


Figure III.16: Total density of states for Cu$_2$O compound.



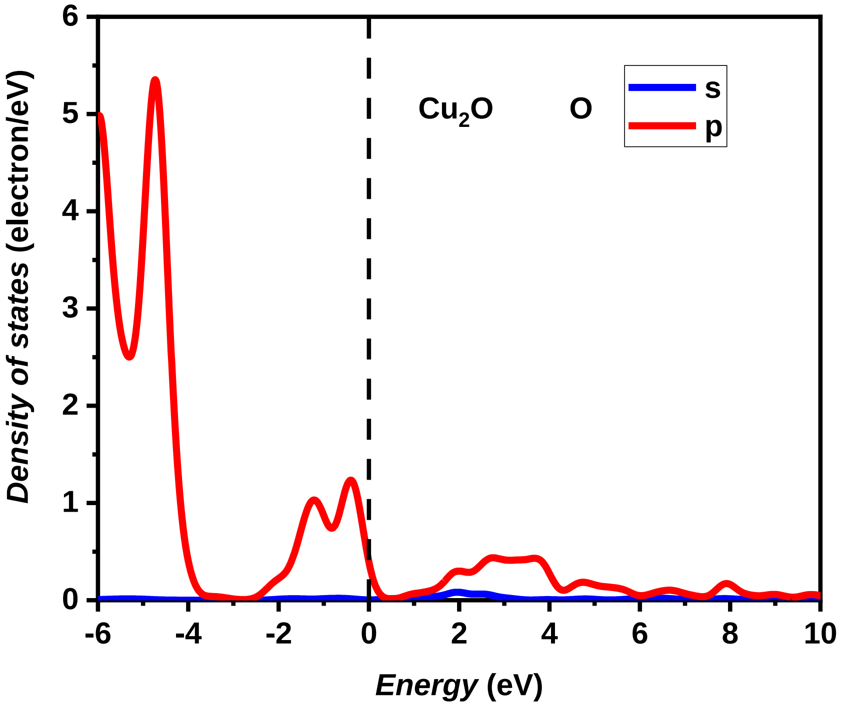


Figure III.17: PDOS spectra calculated for Cu_2O compound.

III.5.3 Optical properties

We will calculate the optical properties of Cu_2O material, such as the absorption, refractive index and reflectivity spectrum.

III.5.3.1 Absorption spectrum

The graph shows the absorption coefficient (y-axis) of Cu_2O material, across a range of wavelengths (x-axis). The absorption coefficient indicates how strongly light is absorbed by the material at a specific wavelength. A higher value indicates stronger absorption. The wavelength is measured in nanometers (nm) and ranges from 0 to 1500 nm. The absorption coefficient is measured in inverse centimeters (cm^{-1}) and ranges from 0 to 200000 cm^{-1}.

The absorption coefficient of Cu_2O material is relatively low throughout most of the wavelength range. There seems to be a sharp increase in absorption coefficient around 200 nm. This indicates that Cu_2O material strongly absorbs light at wavelengths around 200 nm. For instance, Cu_2O's strong absorption around 200 nm suggests it might be useful in ultraviolet (UV) filtering applications. Figure III.18 presents the absorption spectra calculated for Cu_2O material.

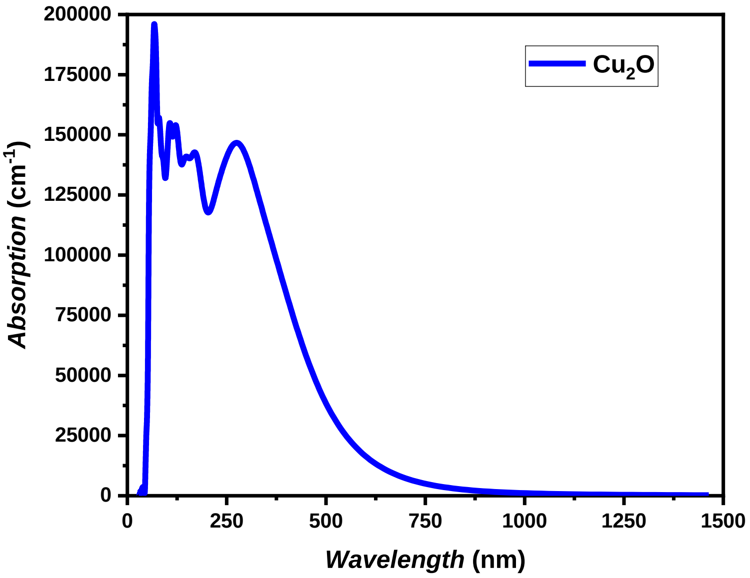


Figure III.18: Absorption spectra calculated for Cu_2O material.

III.5.3.2 Refractive Index

Figure III.19 shows the refractive index (n) and extinction coefficient (k) spectra of Cu_2O material. The refractive index (n) is a measure of how much light is bent as it travels through a material, while the extinction coefficient (k) is a measure of how much light is absorbed by the material. The blue curve represents the refractive index (n) of Cu_2O material. It shows that the refractive index of Cu_2O decreases with increasing wavelength. This means that light bends less as the wavelength of light increases. The red curve represents the extinction coefficient (k) of Cu_2O material.

It shows that the extinction coefficient of Cu_2O increases with decreasing wavelength. This means that Cu_2O material absorbs more light at shorter wavelengths. The refractive index of Cu_2O material is relatively high in the visible range of light (400-700 nm). This means that Cu_2O material is a good reflector of visible light. The extinction coefficient of Cu_2O material is relatively low in the visible range of light. This means that Cu_2O material is relatively transparent to visible light. The extinction coefficient of Cu_2O material increases sharply in the ultraviolet (UV) range of light (below 400 nm). This means that Cu_2O material strongly absorbs UV light.

The optical properties of Cu_2O material make it a promising material for a variety of applications, including:

- **UV filters:** Cu_2O material can be used to block harmful UV radiation from reaching the skin.
- **Solar cells:** Cu_2O material can be used to absorb sunlight and convert it into electricity.
- **Sensors:** Cu_2O material can be used to detect changes in the environment, such as the presence of gases or chemicals.

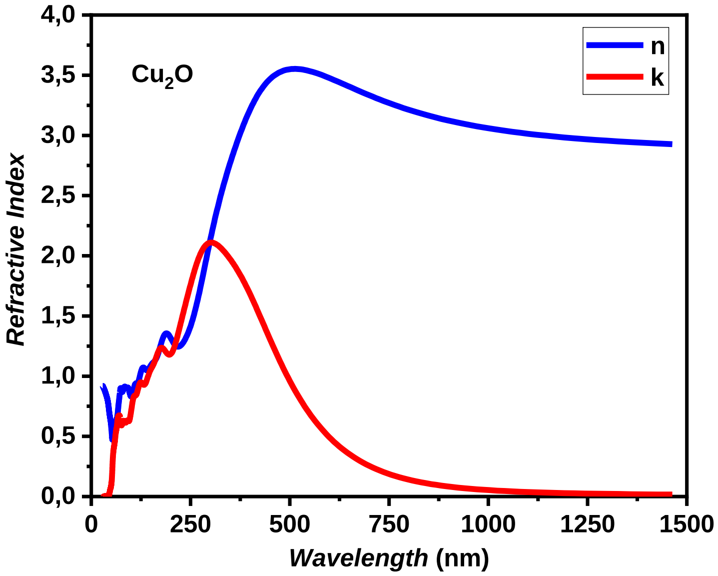


Figure III.19: Refractive index n and K calculated for Cu_2O material.

III.5.3.3 Reflectivity spectrum

Figure III.20 appears the reflection of light at different wavelengths for a material. Y-axis: The vertical axis represents the reflectivity of the light. This indicates how much of the incident light is reflected back by the material at a specific wavelength.

The reflectivity of the material is particularly high in the ultraviolet (UV) range of light (below 400 nm). This means that the material reflects a large amount of UV light. The reflectivity of the material is relatively low in the visible range of light (400-700 nm). This means that the material reflects a relatively small amount of visible light. The reflectivity of the material increases again in the infrared (IR) range of light (above 700 nm). This means that the material reflects a moderate amount of IR light.

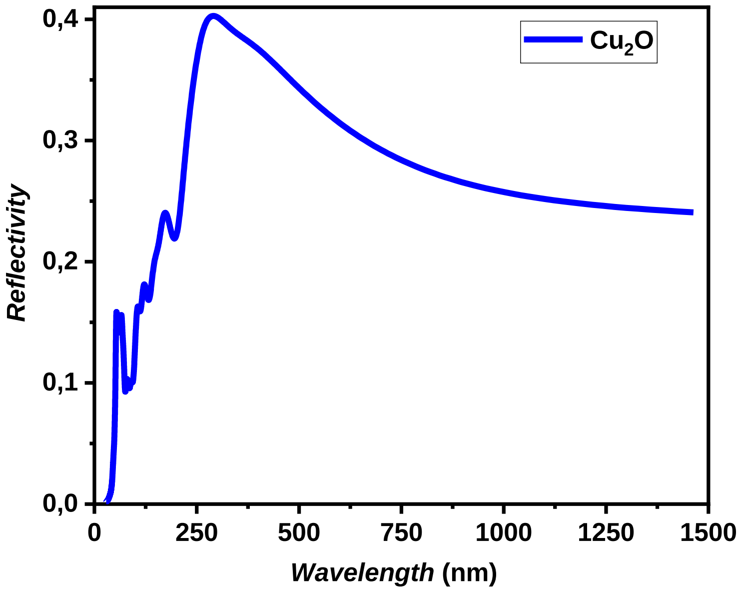


Figure III.20: Reflectivity (R) spectra calculated for Cu_2O material.

III.6 Comparison between CuO and Cu_2O materials and potential applications

This study aims to provide a comprehensive understanding of the structural, electronic, and optical properties of CuO and Cu_2O materials using the CASTEP computational software. The results obtained were compared with theoretical and experimental data, and the potential applications of these compounds were discussed.

Copper(I) oxide (CuO) and copper (II) oxide (Cu_2O) materials are both compounds that can exhibit cubic crystal structures. However, they differ significantly in their physical and electronic properties.

a) Structural Properties

CuO:

- Lattice Parameters: a=b=c=3.04712 Å
- Angles: α=β=γ=90°
- Volume: 20.0057 $Å^3$
- Bulk Modulus: 158.21355 GPa

Cu_2O:

- Lattice Parameters: a=b=c=4.42273 Å
- Angles: α=β=γ=90∘
- Volume: 86.510711 Å³
- Bulk Modulus: 899.10913 GPa

b) Electronic Properties

CuO:

- Bandgap: 0 eV
    - This indicates that CuO behaves as a metallic conductor in this context, allowing free movement of electrons between energy bands.

Cu_2O:

- Bandgap: Typically, around 0.212 eV
    - Cu2O typically acts as a semiconductor, with a significant bandgap that restricts electron flow between the valence and conduction bands unless sufficient energy is provided.

c) Comparison of Physical Properties

- Lattice Parameters:
    - Cu_2O has significantly larger lattice parameters (4.42273 Å) compared to CuO (3.04712 Å), indicating a more extended crystal structure.
- Unit Cell Volume:
    - Volume of Cu_2O (86.510711 Å³) is much larger than that of CuO (20.0057 Å³).
- Bulk Modulus:
    - The bulk modulus of Cu2O (899.10913 GPa) is substantially higher than that of CuO (158.21355 GPa), indicating that Cu2O is much more resistant to compression.

III.7 Conclusion

Given these properties, CuO and Cu_2O materials exhibit significant differences in their crystal structures, resistance to pressure, and electronic behavior. Cubic CuO material, with a bandgap of 0 eV, behaves as a metallic conductor, making it suitable for applications requiring high electrical conductivity. In contrast, cubic Cu_2O material, with a typical semiconductor bandgap, is useful in electronic applications such as sensors or photovoltaic devices, that rely on its semiconducting properties.

References

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General conclusion

General conclusion

In conclusion, this comprehensive study conducted by CASTEP simulator has made significant strides in elucidating the difference between CuO and Cu_2O properties. By employing computational simulations utilizing the GGA-PBE-DFT methodology, the investigation delved into the difference between CuO and Cu_2O properties on the structural, electronic, and optical properties.

In this work, we conducted a comprehensive study of the structural, electronic, and optical properties of copper (II) oxide (CuO) and copper(I) oxide (Cu_2O) materials, focusing on their cubic structures. The study revealed significant differences in the physical and chemical properties of the two compounds, providing valuable insights into their potential applications in technological and industrial fields.

The investigation showed that CuO material has a bandgap of 0 eV, indicating its excellent metallic conductivity. In contrast, Cu_2O material has a typical semiconductor bandgap, making it effective for various electronic and optical applications.

The structural analysis revealed clear differences in unit cell volume and bulk modulus between the two compounds, impacting their resistance to deformation under pressure. These structural properties are crucial in determining the applications of both CuO and Cu_2O materials in sensors and photovoltaic devices.

Based on the findings from this study, we propose the following recommendations for further research and development:

It is essential to conduct further studies to understand the effects of environmental factors such as temperature, pressure, and humidity on the structural and electronic properties of the compounds. This can help improve their stability and performance in practical applications.

Detailed investigations into the use of CuO as a conductive material in electronics, such as electrical conductors and electrodes in batteries, are recommended. Focus should be on exploring ways to enhance charge transport efficiency and improve the performance of electronic devices.

Both CuO and Cu_2O materials could play significant roles in developing renewable energy technologies, such as solar cells and photovoltaic devices. Studies on improving energy conversion efficiency using these compounds are suggested.

It is advised to explore the use of CuO and Cu_2O materials in electrical and optical sensor devices. Their unique properties could provide improvements in sensitivity and accuracy for detection and monitoring devices.

Research into new compounds based on similar or modified crystal structures may yield enhanced or novel properties, opening up new avenues for technological and industrial applications.

This study highlighted the significant potential of CuO and Cu_2O materials in various applications due to their unique structural, electronic, and optical properties. The findings provide a general framework for understanding the behavior of these compounds in different practical applications. With ongoing advancements in material technology, these compounds are expected to play a crucial role in enhancing performance and efficiency across a wide range of industrial and technological applications.

ملخـــــــص :

يهدف هذا العمل إلى دراسة الخصائص الهيكلية والإلكترونية والبصرية لمواد CuO وCu_2O بتقريب GGA-PBE باستخدام كود CASTEP . تم استخدام النمذجة الحاسوبية لدراسة الترتيب الذري والتركيب الإلكتروني لهذه المواد. كما تم دراسة الخصائص البصرية لهذه المواد باستخدام الحسابات الكمومية. توفر النتائج الناتجة رؤى عميقة حول خصائص هذه المواد وتسلط الضوء على فائدة CASTEP في دراسة الخصائص الفيزيائية. تتوافق النتائج التي تم الحصول عليها مع القيم النظرية والتجريبية المذكورة في الأدبيات. تشير خصائص المواد CuO وCu_2O إلى أن هذه المواد لديها إمكانات كبيرة لاستخدامها في الأجهزة الكهروضوئية.

الكلمات المفتاحية : مركب CuO, Cu_2O , برنامج CASTEP , الخصائص الهيكلية و الإلكترونية و البصرية .

Abstract :

This study aims to investigate the structural, electronic, and optical properties of CuO and Cu_2O materials with GGA-PBE approximations using the CASTEP code. Computer modeling was employed to study the atomic arrangement and electronic structure of these materials. The optical properties of these materials were also investigated using quantum calculations. The resulting findings provide deep insights into the properties of these materials and highlight the utility of CASTEP in studying physical properties. The obtained results are consistent with the theoretical and experimental values cited in the literature. The characterizations of CuO and Cu_2O materials suggest that these materials have a significant potential to be used in photovoltaic devices.

Keywords: Cu_2O, CuO, CASTEP software, structural, electronic and optical properties.

Résume :

Ce travail vise à étudier les propriétés structurelles, électroniques et optiques des matériaux CuO et Cu_2O avec des approximations GGA-PBE à l'aide du code CASTEP. La modélisation informatique a été utilisée pour étudier la disposition atomique et la structure électronique de ces matériaux. Les propriétés optiques de ces matériaux ont également été étudiées à l’aide de calculs quantiques. Les résultats qui en résultent fournissent des informations approfondies sur les propriétés de ces matériaux et mettent en évidence l'utilité de CASTEP dans l'étude des propriétés physiques. Les résultats obtenus sont cohérents avec les valeurs théoriques et expérimentales citées dans la littérature. Les caractérisations des matériaux CuO et Cu_2O suggèrent que ces matériaux ont un potentiel important pour être utilisés dans les dispositifs photovoltaïques.

Mots-clés : Cu_2O, CuO, logiciel CASTEP, Propriétés structurelles, électroniques et optiques.