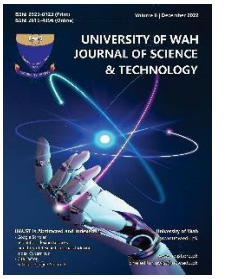
UW Journal of Science and Technology Vol. 7, Issue 1, (2023) 1-10
ISSN: 2523-0123 (Print) 2616-4396 (Online)

University of Wah
Journal of Science and Technology

www.uow.edu.pk



Effect of Structural Modifications on the Electronic Characteristics of Cadmium Oxide

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Abstract

The density function theoretical approach has been utilized for investigating the effect of oxygen deficiency on the electronic and optical characteristics of CdO. For this purpose, Graphical User Inter-phase (GUI) of Quantum Espresso i.e. BURAI 1.3 is used first to estimate the lattice parameters of CdO that are in total agreement with earlier experimental and/or theoretical findings
i.e. calculations show that SCF converges with total energy value of -586.6300 RY. After creating a CdO super cell initially with a [2x1x1] scale, the changed properties of CdO were then evaluated at the supercell level to determine the impact of oxygen deficit on the electronic features of CdO. The results reveal that creating oxygen vacancy at supercellular level significantly affects the electronic characteristics of CdO as the conduction and valance band gap has lesser value after modification in the CdO structure. Furtherance to it, the depicted picture of band structure and state densities confirmed the semi-conducting characteristics of CdO because of presence of direct band gap at 1.30 eV after O-vacancy. Due to the aforementioned structural changes, an increase in conductivity and electron movement is expected. However, it is determined that the lattice constants' findings are reliable, and the behavior of CdO remains nonmagnetic and semiconducting on inducing oxygen vacancies.

Keywords

DFT, CdO, Oxyegn-deficiency, Super cell, Band Structure, Density of States

1. Introduction

Cadmium oxide is an inorganic compound having chemical formula CdO and molecular mass

128.4112g.mol^{-1}. It serves as one of the basic building constitute for other cadmium compounds, and is readily available [1, 2]. It is an order less crystalline solid that occurs naturally as mineral and is commercially made by oxidizing cadmium vapor [3]. It also exists in the form of tablets, pellets, bits, powder, sputtering targets, powder, and nano-powder. It dissolves in weak acids, dissolves slowly in ammonium salts, and is insoluble in alkalis [4]. Like sodium chloride, it crystallizes in a cubic rock salt lattice with octahedral cation and anion centers.

Figure 1: Cadmium Oxide Powder

CdO is an inorganic n-type semiconductor transparent metal oxide having the 2.18 eV value of band gap at ambient temperature (298 K) [4]. Its chemical characteristics include melting and boiling temperatures, which are for sublimation 1,559 °C (2,838 °F; 1,832 K) and for the amorphous form has value of 900–1,000 °C (1,170-1,270 K). It has hexagonal quartzite structure which preferred the crystal direction of its plane is [002].

Due to the abovementioned physical, chemical, and band gap characteristics, the CdO is one of the strongest contenders in the family of transparent conductive oxides for thermo electric energy applications [5], electroplating baths, tuning band gaps [6-8] for optoelectronic devices , pigments etc [9]. The properties more specifically the band gaps (direct and indirect), density of states of transparent metal oxides can be tuned while introducing the charge deficits at the cellular level as it is well accepted fact this enhances semiconductor device's electronic properties. Numerous theoretical and practical researches have been carried out over the last 20 years by scientists to study these properties of CdO. For theoretical approximations standard density functional theory (DFT) may be utilized to precisely describe the structural properties of CdO using the local density approximation (LDA) and generalized gradient approximation (GGA) approaches. Although results are somewhat reliable as far as semiconductor behavior of CdO is concerned but no attempt is made, to best of our knowledge, to study the effect of charge deficit on the electronic characteristics of CdO.

As a result, the main aim of this study is to create charge deficits at the super cellular level examining the effect of modification on the electronic and band gap features of CdO. Quantum espresso based DFT calculations (which are frequently used for computationally modeling the quantum mechanics that is used to look into the electrical structure of many-body systems like atoms, molecules, and condensed phases) have been utilized for the

theoretical analysis to gain insight into the electrical and optical characteristics of unmodified CdO [10]. On the basis of the predicted band gaps, analyzes for the updated electronic properties on creating oxygen deficit are obtained and analyzed. Finally, numerous beneficial findings will be made, providing theoretical information for the design and utilization of CdO in optoelectronic materials [9].

2. Computational Detail

In the current study, the Graphical User Interphase (GUI) of Quantum Espresso,*BURAI 13*, has been used to carry out the first principles Density Function Theory (DFT) based computations. The calculation of electronics and band gaps structural properties of oxygen deficit CdO has been performed and compared with the properties of CdO. The cubic crystal structure generated by the Burai from the CIF file downloaded from https://www.materialssquare.com/ [11, 12] given below in ***Figure 2***.

Adding to information, the CIF (Crystallographic Information File) format is a standard file format used for representing crystallographic information. It contains data about the atomic positions, unit cell dimensions, symmetry operations, and other parameters necessary to describe the crystal structure of a material. For CdO, it is Halite, structured and crystallizes in the cubic $Fm\bar{3}m$ space group. Cd^{2+} is bonded to six equivalent O^{2-} atoms to form a mixture of corner and edge-sharing CdO_6 octahedra. The corner-sharing octahedra are not tilted. All Cd–O bond lengths are 2.36 Å. O^{2-} is bonded to six equivalent Cd^{2+} atoms to form a mixture of corner and edge-sharing CdO octahedra. The corner-sharing octahedra are not tilted.

We employ first principle calculation DFT for improved electronic properties and better determination of energy band gap values [13]. At normal temperature, CdO with the Fm-3m space group crystallizes in the CdO structure. The original structure is cubic lattice and consists of K-points (5×5×5). Fermi-Dirac smearing is the occupation type that is utilized here.

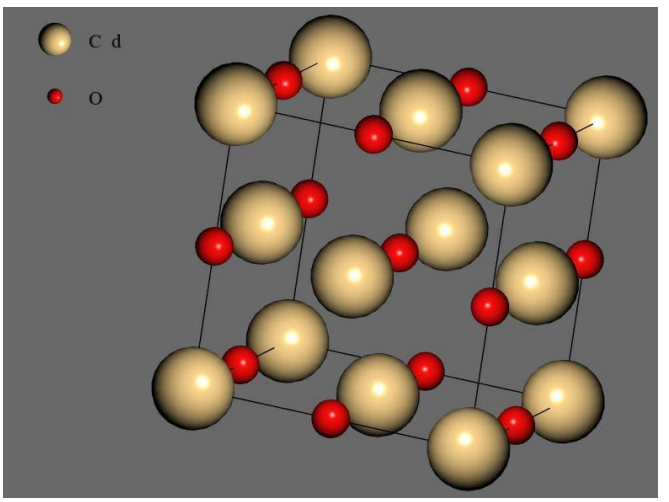

Figure 2: Crystal Structure of CdO, Fm-3m space group. Atoms of cadmium and oxygen are represented by the golden and red balls, respectively.

The CdO has the valence-electron configurations $\mathbf{4d^{10}5s^2}$ and $\mathbf{2s^22p^4}$. The ab-initio calculations were performed with pseudo potential with the following computational parameters

- **A cutoff energy** of **600 eV** was used during the all calculations after testing its convergence for various volumes of total energy[14]
- The **k-point** set's Brillouin-zone sampling mesh parameters were set **(5×5×5)**
- The implementation of the maximum force of 0.01 eV/, **the maxima stress of 0.02GPa,** and also displacement of 10^{-4} is also guaranteed by this set of parameters.
- The lattice constant has a value of 4.6948 and the total volume of the lattice parameters is 27.3673.
- These are the characteristics of the crystal structure of pure CdO.

To figure out the effect of oxygen deficiency, supercell of CdO have scalling of (2×2×1) has been made. The structural characteristics such SCF, Band Gap and DOS of oxygen deficit CdO and pure CdO were calculated and compared for better understanding of the alterations within the structure[13, 14].

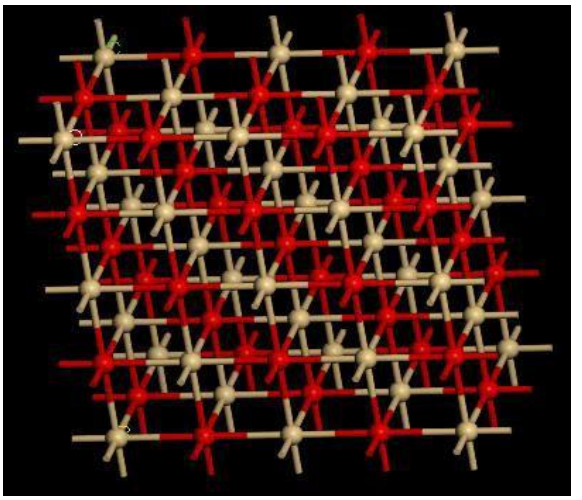

Figure 3: Supercell of CdO having sacle (2x2x1)

The behavior of CdO as far as its semiconducting nature and nonmagnetic performance were investigated and discussed. This study is extremely important because it was reported in the literature that the development of the metallic cadmium phase, which takes place during synthesis at temperatures above 300°C, is favored by the existence of oxygen vacancies.

3. Results and Discussion

3.1 Analysis of Results

Electronic properties refer to the properties of a material that are related to its electronic structure and behavior. Here, we are going to discuss the two main electronic properties that are **Band Gap** & **Density of States (DOS)**.The electronic properties of a substance can be find by analyzing the distribution of energy levels in the valence and conduction bands of its electrons. An accurate description of these electronic properties requires an understanding of how the individual orbitals contribute to the overall electronic structure of the material. Tetragonal phase CdO is used in the current study's calculations while using the Burai version 1.3, which uses the Quantum Espresso that is based on DFT calculation while using ultra soft and norm conserving form of pseudo-potentials. The characteristics of simple CdO were examined first before moving on to oxygen

deficits calculations at the super cellular level. The CdO monolayer adopting the hexagonal structure, was considered during calculations. The optimized lattice parameters for the CdO unit cell are a = b = c = 4.78 and the bond length between Cd-O is 2.38 A, which agrees well with previously published work.

3.2 Electronic properties of Simple CdO Crystal Structure

❖ **Self-Consistent Field (SCF)**

In the context of computational chemistry or quantum chemistry, "SCF stands for Self-Consistent Field". It is an iterative method used to solve the electronic structure problem of molecules or materials. The SCF method involves an initial guess of the electronic wavefunction, which is used to calculate the electron density and the electronic energy. The calculated energy is then compared to the previous iteration, and if it hasn't converged (reached a stable value), the wave function is updated based on the new density. This process is repeated until the electronic energy converges to a desired level of accuracy.

Convergence is important in the SCF calculation because it ensures that the electronic structure is accurately represented. When the SCF process converges, it means that the electronic wavefunction and density have reached a stable state, and the calculated energy represents a good approximation to the true electronic energy of the system. Achieving convergence guarantees that the calculated properties and observables, such as bond lengths, band energies, and spectroscopic properties, are reliable, otherwise, the calculated properties may be unreliable.

Self-Consistent Field SCF calculations for simple CdO structure are presented in ***Figure 4***.The y-axis represents energy in RY units, and the x-axis represents iteration factor. With -585.600RY energy level, the values of total energy start to decrease from 1.0 to 2.0 iteration scale. The curve subsequently undergoes a second jump, this time from 2.0 to 3.0 iteration factors, with energy equal to -589.85RY.

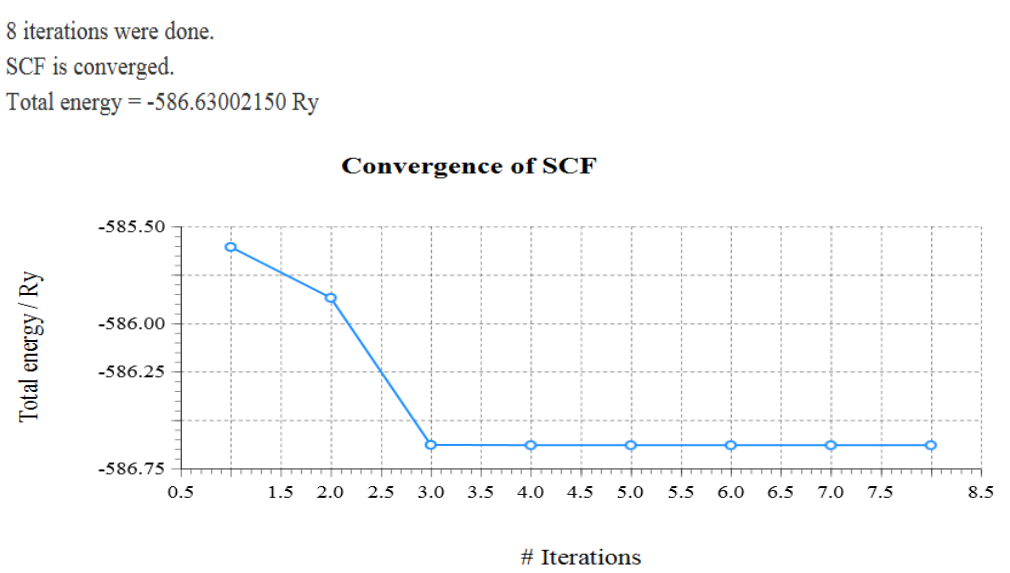

Figure 4: SCF Calculations of Simple CdO Crystal Structure

As a result, following these values, the values are steady and do not change. Convergence has

been achieved in 8 iteration. So, 8 iteration were done and SCF is converged with total energy -585.6300RY.

❖ **Energy Band Structure**

Figure 5 exhibits the electronic band structure for CdO structure. In general, the bandgap energy of the material is determined by the VBM and CBM values. The energy distribution of electrons in valance and conduction bands can be used to predict the properties of solid electronic materials. The basic gap is indicated by the grey area. Zero energy point is chosen to be the maximum of the valence band.

Because the bottom of conduction band in the diffuse pattern has a much larger bandwidth i.e 5.52eV than the upper side of valence band (1.38 eV), CdO may be used as a transparent conducting material. Above the point where the conduction band minimum occurs, there is a negative indirect band gap of approximately -0.5eV. It is obvious the indirect bandgap, with energy of -0.55 eV, appears at the site.

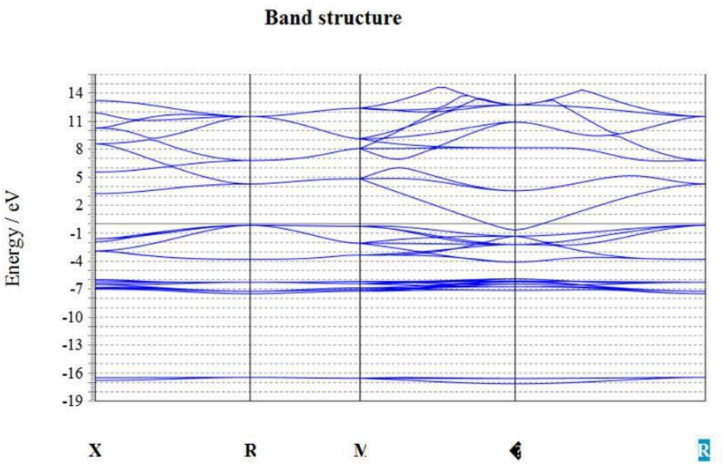

Figure 5: CdO's energy band structure estimated using the DFT model

❖ **Density of States (DOS)**

The DOS curves typically show two main regions: the valence band and the conduction band. The valence band represents the energy levels that are occupied by electrons in their ground state, while the conduction band represents the energy levels that can be accessed by electrons when they are excited to higher energy states. The DOS in the valence band is relatively high and extends over a broad energy range, while the DOS in the conduction band is lower and more sharply peaked. O 2s states predominately make up the energy bands between -7.5 and -6 eV, Based on an evaluation of the density of states (DOS). Because to its high localization feature, the energy bands at roughly -7.5eV, which are made up of Cd 4d states, exhibit a dramatic rise. And it is discovered that there is some mingling between the Cd sp states and the O 2p states. CdO thus seems to have certain covalent characteristics. In the upper valence bands, there are two peaks at roughly -4.5 eV and -0.86 eV. The lowest one is mostly caused by Cd 5s and 4d states hybridising with O 2p states. The O 2s and 2p exhibit just a weak hybridization with the Cd 5s and 4p that

make up the majority of the conduction bands. Together, the Cd 4p and O 2p, which control the kind of charge carrier and the characteristics of electric conduction for CdO, account for a large portion of the energy state density curve around the Fermi level. In this band gap, there are no peaks in the energy range of 0 to 2.5 eV.

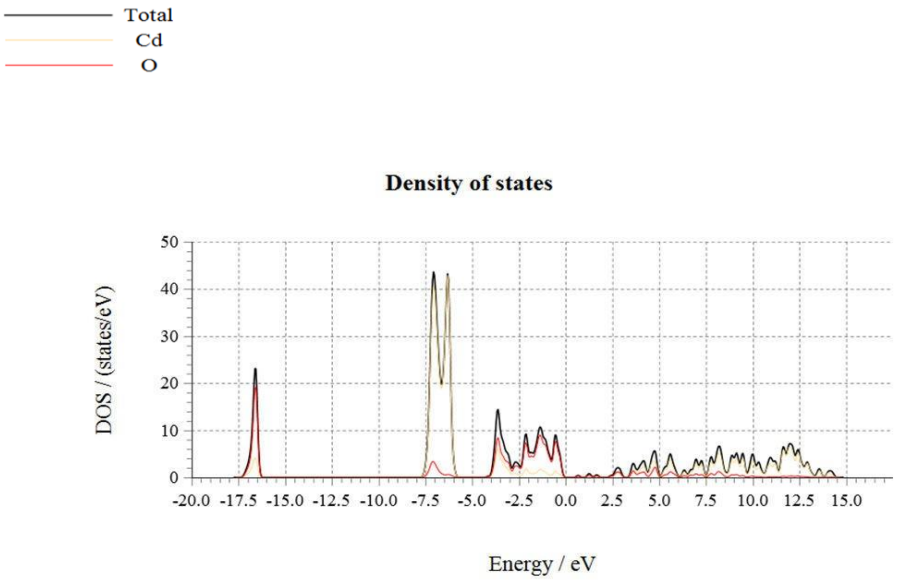

Figure 6: Density of States of Simple CdO Crystal Structure

CdO thus seems to have certain covalent characteristics. In the upper valence bands, there are two peaks at roughly -3.56 eV and -0.26 eV. The states of Cd & O which control the kind of charge carrier and the characteristics of electric conduction for CdO, account for a large portion of the energy state density curve around the Fermi level.

3.3 Electronic properties of CdO crystal at Supercell Level While Creating Oxygen Deficiency

Currently, a supercell of cadmium oxide with a scaling of 2x2x1 is present. Here, super cellular level is created so that we can use this cell to advance toward the project's goal. Our goal is to research how to change the structural makeup of CdO and improve its qualities while introducing oxygen charge deficits. So I intentionally left one oxygen atom out of the CdO supercell that can be seen in ***Figure 7***.

We currently have updated SCF and DOS calculations for this cell. In order to better comprehend the electrical structure of oxygen deficient crystal structure of CdO, we have carried out a theoretical examination using density function analysis (DFT).We now have the modified SCF and DOS calculations for this unit cell as shown in ***Figure 8*** & ***Figure 9***.

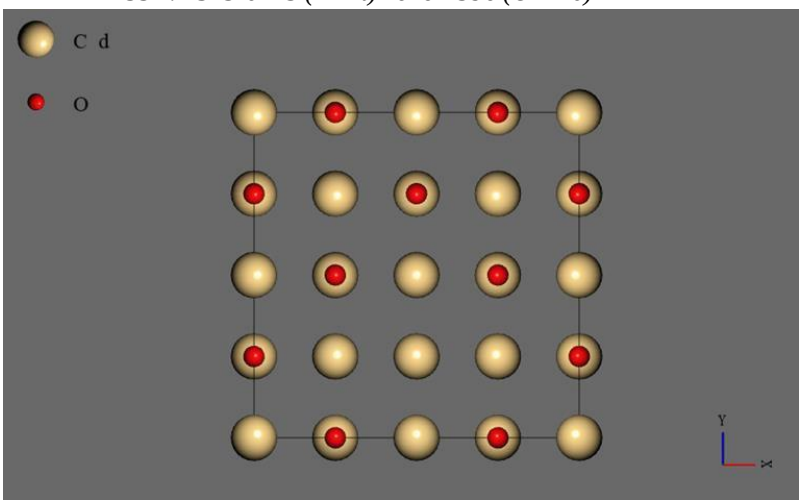

Figure 7: CdO's Supercell with one oxygen atom missing

❖ **Self-Consistent Field (SCF)**

Now we have modified calculated values of Self-Consistent Field *SCF* for ***oxygen deficient CdO*** cell as shown in ***Figure 8***. We have energy in RY units on the y-axis and iteration factor on the x-axis. With a -2314.5987RY energy level, the values of total energy start to decrease from 1.0 to 2.0 iteration scale. The curve subsequently undergoes a second jump, this time from 2.0 to 3.0 iteration factors, with energy equal to -2301.1RY. There is another iteration factor of 4 at value of energy -2301.7RY. As a result, following these values, the obtained values are steady and do not change. Convergence has been achieved in 8 iteration. So, 8 iteration were done and SCF converged with total energy -585.6300RY.

12 iterations were done.
SCF is converged.
Total energy = -2314.59875906 Ry

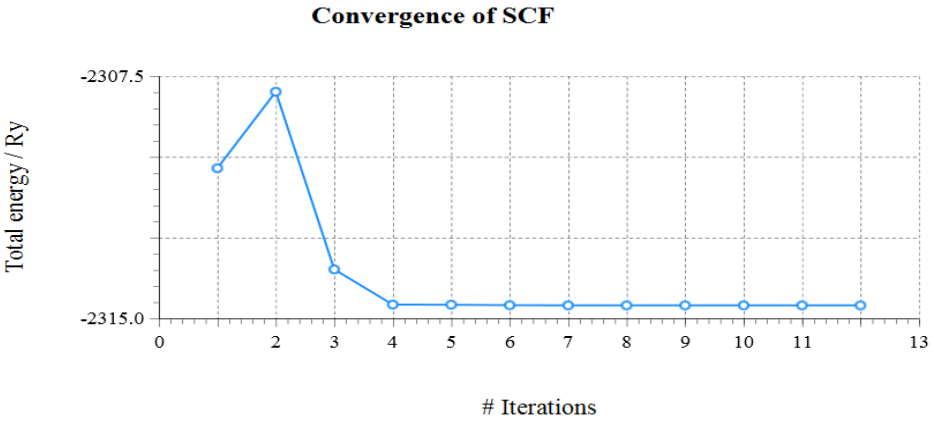

Figure 8: SCF Calculations of Oxygen Deficient CdO Crystal Structure at Super cellular Level

❖ **Density of States (DOS)**

The Fermi level is assumed to be 0 eV in DOS calculations. According to the results of the density of states DOS, it was discovered that O 2s states predominately make up the energy bands between -19 eV and -17 eV. Due to the high localization feature of the Cd 4d states, the energy bands at -8.5 eV have a pronounced peak. Here also represent that unlike simple CdO structure, there are small peaks across the fermi level. This result indicates that creation of O-vacancy increase conductivity and electron mobility by setting low band gap values.

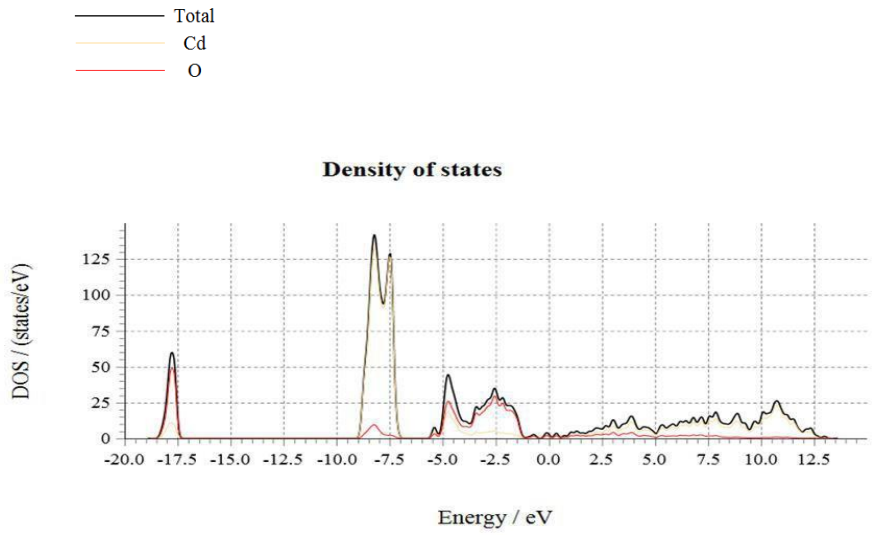

***Figure 9*: Density o*f States of Oxygen Deficient CdO at Supercell Level Calculation**

4. Conclusion

In conclusion, using fist principles the electronics and band gap structural characteristics of CdO has been calculated. The calculations were performed with ***BURAI1.3 which is the Graphical User Interface (GUI) of Quantum Espresso which is based on plane wave self-consisted*** **DFT** calculations.

The electrical structures showed that the 2p state of oxygen and 4p states of cadmium, which determine the upside of conduction band and lower part of valance band, respectively. These structural results were also calculated for the oxygen-deficient CdO super cell and it was found that oxygen deficiency does have affects total density of states (DOS) and SCF calculations. The calculations reveal that there is less energy band value after creation of O-vacancy. DOS also represents that in O-deficient supercell of CdO, we have greater value of transitions across fermi level. This indicates that greater transition values enhance the conductivity and electron mobility after O-deficiency in the CdO. However, the semiconductor nature and nonmagnetic behavior of CdO because of oxygen deficiencies at super cellular level were found to be remained unaffected. This investigation is necessary for using CdO in optoelectronics applications because during the development of metallic Cd Phase at elevated temperature i.e. at or above 300°C, existence of oxygen deficiency is highly probable.

Acknowledgements
Authors are thankful to UET, Taxila for providing the platform to complete this work

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