Chapter One

Introduction

1.1: Background:

The study of electron charge density distribution (ECD) in different chemical compounds is considered an important part of the modern X-ray structure analysis [1]. For this purpose, experimental methods are well developed and held using high precession and computerized instruments depending on standard measurements. These lead in the last years to study experimentally the properties and characteristics of the crystals that depend on the electron density. Among these properties is the electrostatic potential (ESP) which depends on the total charge density (the sum of electronic and nuclear parts), through Poisson's equation. However there is another way to study the (ESP) depending on diffraction of electrons with energy 20-100 KeV. In this case the exchange of electrons between the beam and the crystal is ignored and the incoming electrons are scattered from the electrostatic potential of the crystal.

1.2: Historical look:

A long time ago the majority of electron diffraction patterns obtained, was mainly qualitative and used for solution of some applied problems, such as the study of crystallization in thin films. One of the first attempts to realize the structure analysis of electron diffraction, was made by Lashkarev and Usiskin in 1933, who investigated the arrangement of hydrogen atoms around nitrogen in NH_4Cl. Pinsker made purposeful efforts to turn electron diffraction into an independent method of structure analysis [2]. The development of electron diffraction involving Fourier synthesis was realized in a series of workers carried out at the end of forties. In particular these works were used in the detection of the positions of light atoms in the presence of heavy ones [3]. Cowely and his coworkers made an important contribution to the theoretical and experimental studies of electron diffraction in 1967. Further, Zvayagin introduced electron diffraction in the wide practice of study of minerals in 1967, Semeltov and Imamov performed the same method in semiconductors in 1981 [2].

1.3: Purpose of the study:

The progress in electron diffraction in combination with other methods, and the development of theoretical and experimental techniques permits the expectation of many new results and remarkable achievements in the study of the crystal structure of matter. Theoretical calculations of the (ESP) are also developed and used for three-dimensional periodic crystals using the Hartree-Fock method [4].

The study of the (ESP) of Cu_2O is one of the main purposes of this work. This compound is chosen because of its importance in superconductivity. Another important property to be studied is the charge density distribution, from which other magnetic, electric and optical properties can be found. These properties specify the chemical bonds in the crystal.

1.4: Description of thesis:

This thesis is composed of four chapters. The first one is the Introduction. The second discusses the theoretical background of this work. The third chapter contains the results of the calculated properties of cuprite. The fourth chapter contains the discussion of the achieved results and comparison with related previous works.

This work is considered as forward step towards a comprehensive study of many properties of crystals using diffraction of electrons and X-rays. These properties include: the magnetic susceptibility, the static polarization constant, the dielectric permeability, and the electrostatic potential distribution depending on the charge density. These properties can be studied experimentally as well as theoretically using Hartree-fock calculations of the structure factors, with reference to the good agreement of experimental and theoretical results obtained by Kitaneh [5], for MgO, MnO and CuI crystals.

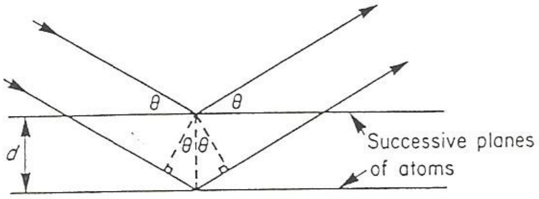

Fig (2.1): Specular reflection of parallel beam from two successive planes of atoms in a crystal [7].

2.2: Methods of diffraction:

There are several techniques to perform diffraction of an incoming beam on a sample. These methods include Laue Method, Rotating Crystal Method and Powder Method [7]. The first two methods are used for crystalline materials, while the third is mainly used for powder samples. In the following, a brief discussion of the powder method

2.2.1: The Powder Method:

The powder method is the most convenient one. The used sample is a finely powdered crystalline material deposited on a holder. The crystalline orientations are random but nearly continuous, and many of them satisfy Bragg's law and hence the diffracted beam emerges from the sample as a series of cones concentric with the incident beam direction, but with different intensities as shown in figure (2.2).

Special computerized detectors measure the intensity I_{hkl} of the diffracted beam. The resultant measurement of the intensity is a number of peaks of different heights. The main interest is in the relative intensity ($I_{hkl} \backslash I_0$) where I_0 is the intensity of the incident beam- it can be considered as the height of the peak or the area under it.

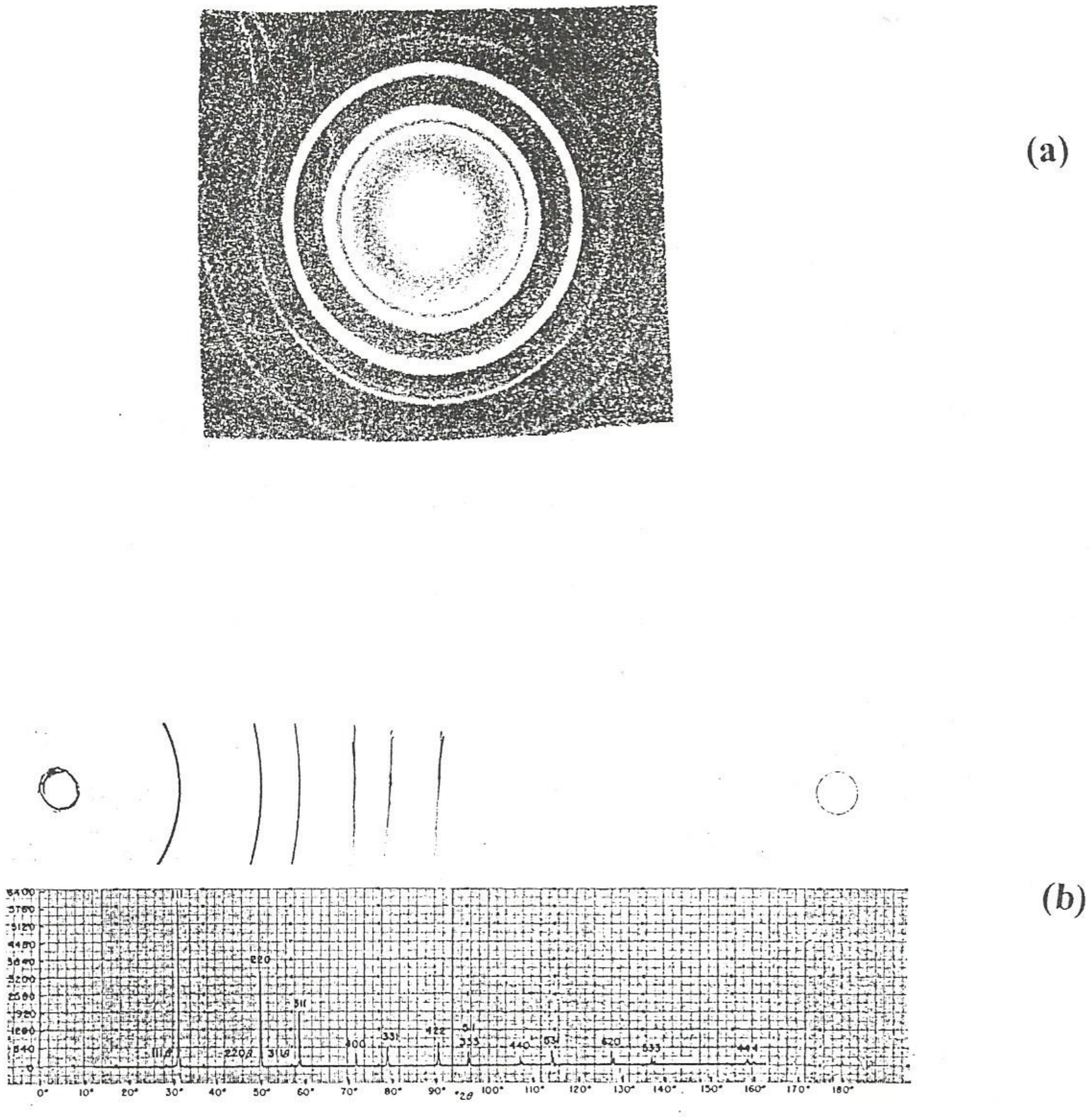

Fig (2.2): (a) Electron diffraction patterns of thin films deposited on cleaved [001] NaCl single crystal surfaces. The method used in this diffraction pattern is the powder method. (b) The upper Figure is a film showing the diffraction pattern, and the lower is a counter recording of the beams diffracted [7].

2.3: Dynamic diffraction of electrons:

Taking the diffracted beam into account, then the relation between the fields of multiwaves -which depends on the angle of diffraction- and the crystal type can be found out. For a dynamic diffraction of electrons some important effects appear such as the effect of extinction leading to weaken some peaks in comparison with the values of those peaks calculated by kinematic theory. The principles of dynamical theory of diffraction are found in the Bethe work [19] who solved Schrodinger equation in its analytical form and a plane wave in Fourier series. The intensity formula in dynamic diffraction for a double wave approximation is:

$$\frac{I_{hkl}}{I_0} = \lambda^2 \left| \frac{\Phi_{hkl}}{\Omega} \right|^2 D(A)L \qquad (2)$$

where,

$$D(A) = \frac{1}{A} \int_0^A J_0(2x)\, dx \qquad (3)$$

I_0 is the intensity of the incident beam

J_0: a zero order Bessel function

Ω: volume of primitive cell

Φ_{hkl}: structure factor

L: a factor calculated for the crystal structure, L: a factor calculated for the crystal structure,

$$L = \frac{t\lambda\ p}{2\,\pi \sin\theta} \tag{4}$$

t: thickness of the sample

p: repetition factor depends on the values of hkl

D(A) can be written as: $D(A) = \frac{I^{d}_{hkl}}{I^{k}_{hkl}}$

The superscripts of d and k stand for dynamic and static respectively.

Analysis of charge distribution in molecules and crystals, with the physical and chemical properties related to it, leads to the important role of studying the electrostatic field, associated with this charge distribution. This field can be described by a vector electromagnetic potential $\vec{A}(\vec{r},t)$, and a scalar potential $\varphi(\vec{r},t)$ [17]. In systems with stationary nuclei, the electronic charge density $\rho(\vec{r})$ can be considered as time-independent, and the resultant field of the total charge density $\sigma(\vec{r})$ is considered electrostatic. The electric field strength $\vec{E}(\vec{r})$ related only to the scalar potential φ, according to the relation:

$$\vec{E} = -\vec{\nabla}\varphi \tag{5}$$

Using Maxwell equation of the form: $\varepsilon_0 \vec{\nabla}.\vec{E}$ directly gives Poisson's equation:

$$-\nabla^2 \varphi(\vec{r}) = \frac{\sigma}{\varepsilon_0} \tag{6}$$

If an infinitesimal small quantity of a potential is added to the original value, then the value of the electric field strength will not change as seen in equation (5). The vector potential $\vec{A}$ and the scalar potential φ are nontrivially determined. This applies to the choice of the vector potential for which $\vec{\nabla}.\vec{A} = 0$, this choice is called Coulomb gauge. The idea is to calculate the strength of the electric field $\vec{E}$ and its derivatives, by choosing a nontrivial potential taking into account the electrically neutral primitive cell of the crystal, such that the dipole moment is equal to zero [8,9].

The electrostatic potential (ESP) can be considered as a quantity which can be measured experimentally by using diffraction of electrons of energy (20-100) KeV. Some electrons are exchanged between the beam and the target results in polarizing the sample, but the quantity of those electrons is very small such that their effect is negligible [9,10]. Poisson's equation also helps in measuring the potential using X-ray diffraction by which the electron charge density ρ is calculated, then the (ESP) is found consequently [12,13].

The total charge density of the multi-electron multi-nucleus systems is written in the form:

$$\sigma(\vec{r}) = \sum_a Z_a \delta_n (\vec{r} - \vec{R}) - \rho_e(\vec{r}) \qquad (7)$$

Substituting eq. (7) in Poisson's eq. (6) gives:

$$\varphi_n(\vec{r}) = \sum_a \frac{Ze}{4\pi\varepsilon_0 \left| \vec{r} - \vec{R}_a \right|} \qquad (8)$$

$\vec{R}_a$: radius of the nucleus

$$\varphi_e(\vec{r}) = -\int \frac{\rho(\vec{r})}{4\pi\varepsilon_0 \left| \vec{r} - \vec{r}' \right|} dr' \qquad (9)$$

The total potential is: $\varphi = \varphi_n + \varphi_e$ (10)

the crystal energy can be written as:

$$E = \sum_{at} (E_{at} + E_{p.e} + \Delta E) \qquad (11)$$

Where the first term is the summation of the energies of the isolated neutral atoms, the second one is the electrostatic interaction between the atoms and the third contains electrostatic effects related to deformation in the charge distribution. This classification of energy differs from the usual quantum mechanical analysis, and it will be constructive if the charge distribution is put in a basic analysis instead of a wave function. The second term of the above equation is considered negative for spherical atoms except atoms in H_2 molecule [23]. Theoretically the procrystal can not be described by the anti-symmetric wave function, and does not support the varial theorem. The forces acting on the nuclei in the procrystals are considered to some extent affecting each other, so the procrystals (promolecules) can be used as energetic models, showing the stability of multielectron and multi-nucleus system. In diatomic molecules and either in crystals of ionic chemical bonds [14] $E_{p.e}$ has a good correlation with bond energy and cohesive energy. Usually to show the effect of the Coulomb parts of cohesive energy, the Madelung energy is used [15], which is an electrostatic energy of all ions, considered as point charges.

The (ESP) is considered as a property of atoms, molecules and crystals. The (ESP) determines their various important physical and chemical properties. So the exact determination of the (ESP) is of invaluble importance in determining those properties.

2.4:Quantum Mechanical Description of Diffraction of Electrons:

To describe the electron diffraction (20-100) KeV, the time-independent Schrodinger equation is used. The electrons in the beam and those in the crystal are described by the multielectron wave function $\Psi(\overrightarrow{r})$. When the beam of electrons with Hamiltonian H_b and energy E_b

penetrates a thin crystal of Hamiltonian H$_c$ and energy E$_c$ then the Schrodinger equation is written in SI units as:

$$\left[\frac{-h^2}{8\pi^2 m}\nabla^2 + \hat{H}_b + \hat{H}_c\right]\Psi = (E_b + E_c)\Psi \tag{12}$$

where the Hamiltonian for a crystal containing N identical atoms, each of Z electrons is written as:

$$\hat{H}_c = -\sum_{i=1}^{ZN}\frac{h^2}{8\pi^2 m}\nabla^2 - \sum_{i=1}^{ZN}\sum_{a=1}^{N}\frac{Ze^2}{4\pi\varepsilon_0\left|\vec{R}_a - \vec{r}_i\right|} + \frac{1}{2}\sum_{i\neq j}^{ZN}\sum^{N}\frac{e^2}{4\pi\varepsilon_0 \vec{r}_{ij}} + \frac{1}{2}\sum_{a\neq b}^{N}\sum^{N}\frac{Z^2 e^2}{4\pi\varepsilon_0 \vec{R}_{ab}} \tag{13}$$

where the distance between electrons is: $\vec{r}_{ij} = \left|\vec{r}_i - \vec{r}_j\right|$

and that between nuclei is: $\vec{R}_{ab} = \left|\vec{R}_a - \vec{R}_b\right|$,

Choosing the electron beam coordinate as r, then the Hamiltonian of the beam is:

$$\hat{H}_b = \sum_j \frac{e^2}{4\pi\varepsilon_0\left|\vec{r} - \vec{r}_j\right|} - \sum_a \frac{Z\,e^2}{4\pi\varepsilon_0\left|\vec{r} - \vec{R}_a\right|} \tag{14}$$

In the case of high energy beam the exchange of energy between the beam and the sample is negligible [11]. The wave function can be written as:

$$\Psi\,(\vec{r},\vec{r}_1,\vec{r}_2,\ldots\ldots\ldots,\vec{r}_n) = \Psi_c\,(\vec{r}_1,\vec{r}_2,\ldots\ldots\ldots,\vec{r}_n)\Psi_b(\vec{r}) \tag{15}$$

where Ψ_c is the antisymmetric linear combination of one electron wave functions satisfying the equation:

$$\hat{H}_c \Psi_c = E_c \Psi_c \tag{16}$$

Whereas the beam wave function satisfies Schrodinger equation of the form:

$$\frac{1}{4\pi^2}\nabla^2\Psi_b + \frac{2m}{h^2}\int(\Psi_c^* \hat{H}_b \Psi_c d\tau)\Psi_b = \frac{2m}{h^2}E_b\Psi_b \tag{17}$$

2.5: Some Physical Properties of Cuprite:

The study of physical properties of any matter opens the way to understand how to make use in different fields of industry, such as optics and superconductivity. The properties to be discussed here are the following:

- The electrostatic potential distribution (ESP)
- The electronic susceptibility (χ_e)
- The polarization constant (α)
- The diamagnetic permeability (ε)

2.5.1: The Electrostatic Potential Distribution:

The importance of the electrostatic potential is shown by obtaining it by diffraction methods and making a comparison between them, in additional to this theoretical calculations for a three dimensional periodic crystal using the Hartree-Fock method. This method can be executed using a special program called PROMETHEUS. A suitable plane, which contains all types of atoms in the crystal, can be chosen to study the (ESP) there. In this study the structure factors of cuprite will be calculated using the following equation:

$\Phi_h = \frac{\lambda}{\sigma} \sum_j f^e(S) \exp(2\pi i \vec{h}.\vec{r}_j)$,in which the electronic atomic factors $f^e(S)$ are used as given in the International Tables for X-ray crystallography [28]. Those $f^e(S)$ will be the inputs of our program PROMETHEUS. The electronic structure factors are then determined, and used as the Fourier coefficients to calculate the (ESP) around the atoms in these crystals. The X-ray structure factors will be also calculated by the same way so as to study the charge density. The (ESP) will be calculated at 0 K. The (ESP) is said to be a physical property because the potential around Oxygen atom for instance, in MgO is different than that around Oxygen in MnO or Cu_2O, and similarly for any atom in any crystal.

If Ψ_c is written as a determinant in terms of one electron wave function $X_j(\vec{r})$, then the (ESP), $\varphi(\vec{r})$ on which the electrons are diffracted, is written as:

$$e\varphi(\vec{r}) = \int \Psi_c^* \hat{H}_b \Psi_c d\tau \tag{18}$$

$$= \sum_j \int \frac{e^2 \left| X_j(\vec{r}) \right|^2}{4\pi \varepsilon_0 \left| \vec{r} - \vec{r}_j \right|} d\vec{r}_j - \sum_a \frac{Ze^2}{4\pi \varepsilon_0 \left| \vec{r} - \vec{R}_a \right|} \tag{19}$$

$$= \int \frac{e^2 \rho(\vec{r'})}{4\pi \varepsilon_0 \left| \vec{r} - r' \right|} d\vec{r}' - \sum_a \frac{Ze^2}{4\pi \varepsilon_0 \left| \vec{r} - \vec{R}_a \right|} \tag{20}$$

The last equation looks like the integral solution of Poisson's equation, where the potential $\varphi(\vec{r})$, is the sum of the electronic and nuclear potentials. The charge density $\rho(\vec{r})$ in the experiments of diffraction of X-rays or electrons can be calculated using the above equations. The distribution of the electrostatic potential in a crystal is a periodic function, which can be expanded in a Fourier series:

$$\varphi(\vec{r}) = \frac{h^2}{2me} \sum_h V_h \exp(-2\pi i \vec{h}\vec{r}) = \frac{1}{\Omega} \sum_h \Phi_h \exp(-2\pi i \vec{h}.\vec{r}) \tag{21}$$

where Ω is the volume of the primitive cell and the sum is over all the vectors $\vec{h}$ of the reciprocal lattice , since the electronic potential must be a real finite quantity; then:

$$\varphi(\vec{r}) = \overset{*}{\varphi}(\vec{r}) \tag{22}$$

This implies that:

$$\Phi_h = \Phi_{-h}^* \tag{23}$$

The solution of equation (16) can be written as a superposition of waves having the periodicity of the crystal lattice (Bloch waves) [16,17]. This leads to the dispersion equation, which determines the relation between the wave vector K_h of the emitted wave and its amplitude Ψ_h:

$$(K^2 + V_0 - K_h^2)\Psi_h + \sum_{\vec{g}} V_{\vec{h}-\vec{g}}\Psi_{\vec{g}} = 0 \tag{24}$$

where,

$$K^2 = \frac{2mE}{h^2} \quad , \quad V_{\vec{h}-\vec{g}} = \frac{4\pi\,\Phi(\vec{\mathrm{h}})}{\Omega}$$

The diffraction of electrons can be described by different approximations, under specified diffraction conditions such as: the thickness of the crystal, direction of the incident beam and so on. These approximations are kinematic, multiwave and the double wave approximation [12]. The kinematic is the most famous among them, giving rise to solve the effect of the first extinction where corrections are to be added to the double wave emission [20], in which the beam wave function is written as a sum of two wave functions: incident or principal wave function Ψ_0, and the additional emitted wave function Ψ' such that:

$$\Psi_b = \Psi_0 + \Psi' \tag{25}$$

where Ψ' is written in an integral form:

$$\Psi'(\vec{r}) = -\frac{1}{4\pi}\int\left[U(\vec{r}_1)\Psi_b(\vec{r}_1)\right]\frac{e^{ik(\vec{r}-\vec{r}_1)}}{\left|\vec{r}-\vec{r}_1\right|}dV_1 \tag{26}$$

$$\Psi_0 = \exp(-i\vec{K}_1.\vec{r}) \tag{27}$$

where dV_1 is the increment of volume,

$$U(\vec{r}) = \frac{8\pi \text{ me}}{h^2}\varphi(\vec{r})$$

It is clear that the additional emitted wave function Ψ', is directly proportional to the coefficients of the Fourier analysis of the (ESP), $\varphi(\vec{\mathrm{r}})$.

The coefficients of the Fourier analysis of the electrostatic potential are the structure factors Φ_h calculated from the measured intensity of the diffracted beam, the value of Φ_h can be also approximated as the sum of the atomic factors in the form:

$$\Phi_h = \frac{\lambda}{\sigma}\sum_j f^e(S)\exp(2\pi\, i\vec{\mathrm{h}}.\vec{r}_j) \tag{28}$$

Here σ is a constant given by: $\sigma = \dfrac{2\pi \text{ me}\lambda}{\mathrm{h}^2}$.

2.5.2: The Diamagnetic Susceptibility:

One of the most important characters of ionic dielectric crystals is the diamagnetic susceptibility χ_d. As an approximation the crystal can be imagined as a composition of spherical particles. The classical formula of Langving can be used here [15]. For the j^{th} ion χ_d can be written as:

$$\chi_d = \frac{\mu_0 e^2}{4m}\int(x_j + y_j)\rho_j(\vec{r})dV \tag{29}$$

where μ_0 : the magnetic permeability for vacuum, e and m are the charge and mass of electron respectively, $\rho_j(\vec{r})$: charge distribution in the atom. Choosing the center of the local coordinate system as the center of the jth atom and putting $\rho_j(\vec{r})$ in the Fourier analytical form, then the diamagnetic susceptibility χ_d can be written as a function of the X-ray structure factor [24] in the form:

$$\chi_d = \frac{\mu_0 e^2}{4m\Omega_j} \sum_{hkl} F(hkl) I_j(hkl) \tag{30}$$

Where: Ω_j: the volume of the jth atom,

$$I_j(hkl) = \int_{\Omega_j} (x_j^2 + y_j^2) \exp[-2\pi\, i(hx + ky + lz)]\, dx dy dz \tag{31}$$

As an approximation, the volume Ω_j can be imagined as a cube with side $\frac{a}{2}$, where a is the length of the primitive cell and the ion is located at the center of the cube of volume Ω_j. Integrating the last equation gives the molecular diamagnetic susceptibility χ_d as a function of the structure factors [25] in the form:

$$\chi_d = -\frac{\mu_0 e^2 N_A a^2}{4m} \left[\frac{N}{96} + \frac{1}{2\pi^2} \sum_{h=2,4,\ldots} (-1)^{h/2} \frac{F(h00)}{h^2} \right] \tag{32}$$

where, N: the number of electrons in the cubic primitive cell, N$_A$: Avogadro's number, and h00 is the index of variable even h whereas the values of k and l are zeros.

It is noticed that just the reflections with even positive values of the reciprocal lattices $\vec{h}$ appear in this formula whereas the other values vanished as a result of the existence of positive values and equal negative quantities for cations and anions. The error in χ_d (as a result of experimental errors in the structure factors) can be calculated as a standard deviation by:

$$\sigma(\chi_d) = \frac{\mu_0 N_A e^2 a^2}{8\pi^2 m}\left[\sum_{h=2,4,..}\sigma^2 \frac{|F(h00)|}{h^4}\right]^{1/2} \qquad (33)$$

2.5.3: Electronic Static Polarization constant and the Dielectric Permeability:

The electronic static polarization constant or simply called molecular polarization, is the proportionality constant between the electric dipole moment P and the local electric field E_{loc},

where $P = \alpha\, \varepsilon_0 E_{loc}$ (34)

E_{loc} is the local electric field associated with the dipole moment, α: molecular polarization, which can be written as:

$$\alpha_{\beta\beta}(\omega) = 2e^2 \sum_{n\neq m} \frac{h\omega_{n,m}\left|\langle\Psi_n|X|\Psi_m\rangle\right|^2}{h^2(\omega_{nm}^2 - \omega^2)} \qquad (35)$$

Where,

β = x,y,z. Ψ_n: electronic wave function, ω_{nm} : frequency related to the electronic energy and ω : frequency of the electromagnetic wave [24].

If $\omega << \omega_{nm}$, then the above equation can be written in the form:

$$\sum_{n\neq m}\frac{h\omega_{n,m}\left|\langle\Psi_n|X|\Psi_m\rangle\right|^2}{h\omega_{nm}} \tag{36}$$

Using the Thomas-Kohn summation [25], so we have:

$$\frac{2m}{h}\sum_{n\neq m}\omega_{nm}\left|\langle\Psi_n|X|\Psi_m\rangle\right|^2 = K \tag{37}$$

where K is the number of electrons in the atom.

In the situation of low wave frequency, the electronic static polarization for ionic crystals of type NaCl, can be written as:

$$\alpha_j = \frac{4me^2}{h^2KV^2}\left[\sum_{hkl}F(hkl)I_j(hkl)\right]^2 \tag{38}$$

where I_j is determined from equation (33) and *F(hkl)* is the X-ray structure factor. For a cube of sides $\frac{a}{2}$, and the molecule is imagined to be at the center of this cube, electronic polarization constant is written as:

$$\alpha = \frac{4me^2a^4}{h^2K'}\left[\frac{N}{96} + \sum_{h=2,4,..}(-1)^{h/2}\frac{F(h00)}{2\pi^2h^2}\right]^2 \tag{39}$$

where,

K' : the number of electrons in one molecule,

N: the number of electrons in the primitive cell.

The Clausias–Mosatti equation also allows the calculation of α and the low frequency dielectric constant $\varepsilon(0)$ for the interested crystals [29], this equation has the following form:

$$\frac{\varepsilon(0)-1}{\varepsilon(0)+2}=\frac{4\pi}{3}N\alpha \qquad (40)$$

Where N is the number of molecules /unit volume [24,27].

3.1.2: Calculation of X-rays Structure Factors:

The X-rays structure factors were calculated using the same previously mentioned program, by introducing the X-rays atomic factors, i.e. the factors formed by diffraction of X-rays on atoms, and the crystal parameters mentioned in the previous section for the same values of $\frac{\sin\theta}{\lambda}$. The values of the structure factors are shown in appendix B.

3.2 Calculation of The Electrostatic Potential Distribution in The Crystal:

The electrostatic potential distribution (ESP) is one of the most important properties of crystals since it describes the distribution of the charge around atoms in the crystal. This gives an idea about the type of the chemical bond between the atoms. Fourier analysis is used to calculate the potential because the crystal is cubic and the distribution of the charge and potential is periodic, where the structure factors are the coefficients of the Fourier analysis.

The results of the calculated values of the (ESP) are plotted as contour lines joining the equipotential points in the plane [110]. That plane shows the atoms of both species: Cu and O. The values of the (ESP) at different points were inserted in a program called SURFER, the given results are shown in figure (3.1) which shows the ionicity of the chemical bond between copper and oxygen, that is clear from the drift of negative potential from Cu to O. Figure (3.2) shows clearly the potential along the line joining the two atoms Cu and O. The maximum static potential at the nuclei positions is calculated to be (4174.8) Volts for Oxygen, and (4665.2) Volts for Copper. Those values are considered as specific properties of the O and Cu atoms in the cuprite crystal. The values of the potentials for the same atoms in other crystals have different values [5].

An interesting phenomenon to note here is the drift in potential in the Cu-Cu direction, this drift in the potential means that the bond on the Cu-Cu line is partially covalent bond in the Cu_2O structure as seen in Figure (3.3). Figure (3.4) shows that there is an electron in the midway between the Oxygen atoms, which confirms the existence of the covalent bond in Cu_2O, and that the ionicity is not fully doubled (± 2) but it can be approximated to be (± 1.5).

3.3 Calculation of Some Physical Properties of The Cu_2O Crystal:

In order to extend the analysis of the data obtained by X-ray diffraction, other properties can be calculated. The study of the physical properties on some crystals such as MgO [5] shows a good agreement between the theoretical and experimental results opened the way to study other crystals such as cuprite. In the present work the following properties are discussed:

- The Diamagnetic Susceptibility.
- The Electronic Static Polarization Constant.
- The Dielectric Permeability.

3.3.1: Calculation of The Diamagnetic Susceptibility χ_d:

The diamagnetic susceptibility is one of the most important properties of ionic dielectric crystals. It gives an idea about the magnetic characteristics of the crystal. The relation giving χ_d is derived for cubic crystals using X-ray structure factors was given in equation (32) of chapter 2. The value of χ_d for cuprite is given in table (3.3).

3.3.2: Calculation of The Electronic Static Polarization Constant α:

The electronic static polarization constant α is another important property of the crystal. It determines the optical property for the specific crystal. For cubic crystals α has a specific value as it is shown from equation (39) of chapter 2. The α value for cuprite crystal is given in table (3.3).

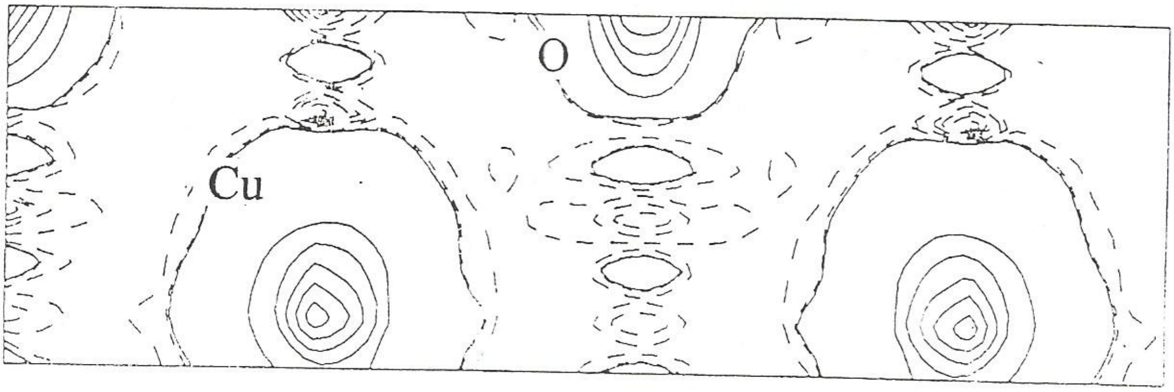

Fig. (3.1): The electrostatic potential distribution (ESP) in the [110] plane of cuprite. The solid line is the positive potentials with an interval of 15 volts between each two successive lines. The dotted lines show the zero potentials, and the dashed lines show the negative ones with an interval of 0.6 volts.

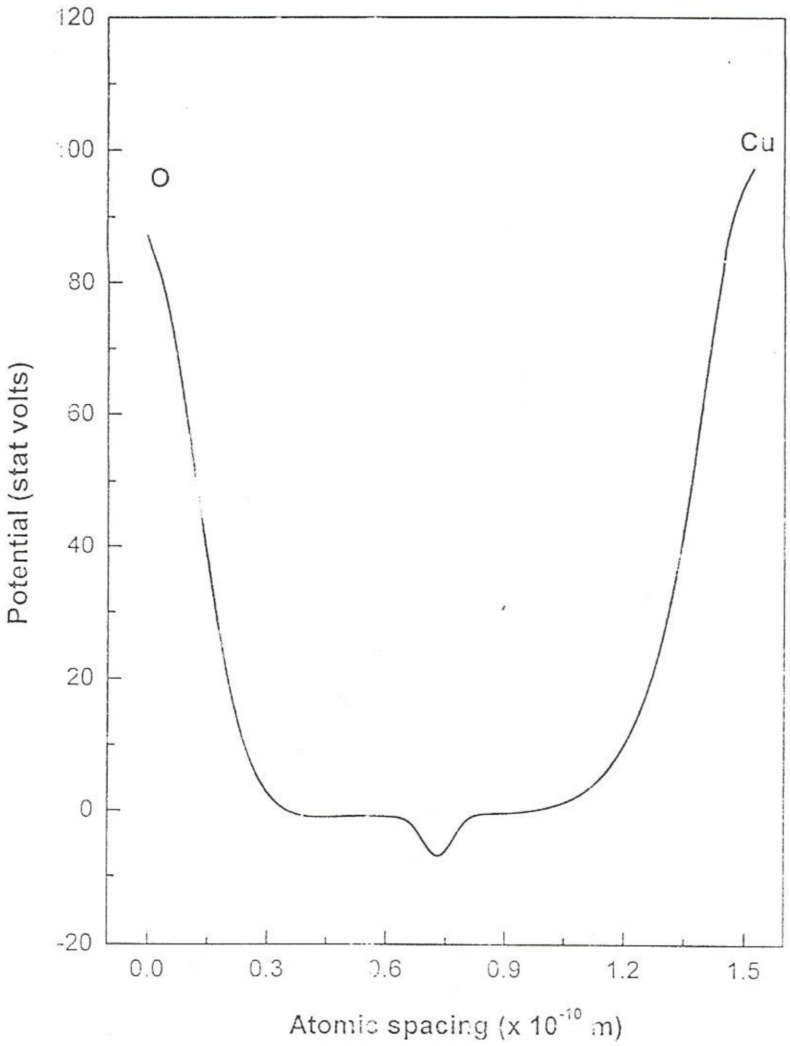

Fig. (3.2): Shows the potential along the line joining the two atoms Cu and O in cuprite.

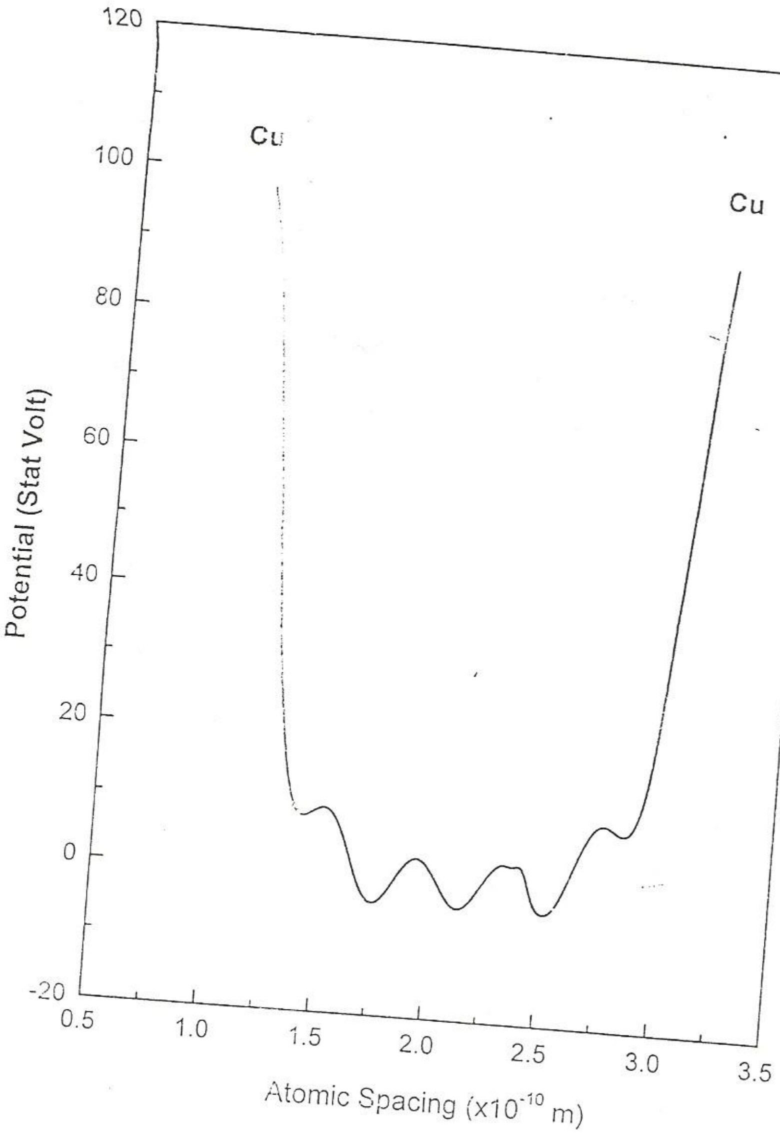

Fig. (3.3): Shows the (ESP) along the line joining the Cu atoms in the Cu_2O crystal.

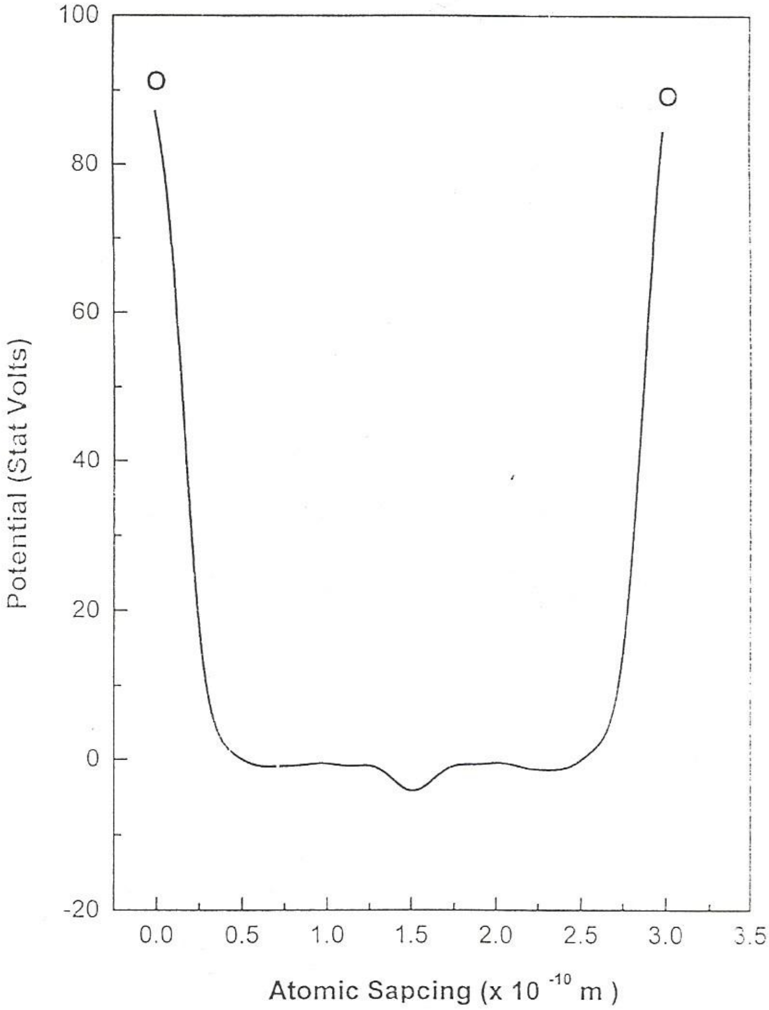

Fig. (3.4): Shows the (ESP) along the line joining the O atoms in the Cu_2O crystal.

3.3.3: Calculation of the Dielectric Permeability $\varepsilon(0)$:

The dielectric permeability determines the electrical properties of the crystal. It can be calculated using equation (40) of chapter 2. Its value for cuprite crystals is given in table (3.3).

3.4: Calculation of The Charge Density:

Using the program PROMETHEUS, the calculation of X-ray structure factors was held as mentioned in 3.1.2. The charge density distribution is then found and mapped as contour lines as seen in figure 3.4.

Property	value
χ_d	$2.0358904 * 10^{-10} (m^3/mole)$
α	$2.074184 * 10^{-9} (m^3)$
ε	-2 (e. V)

Table (3.3):Values of the studied properties for cuprite

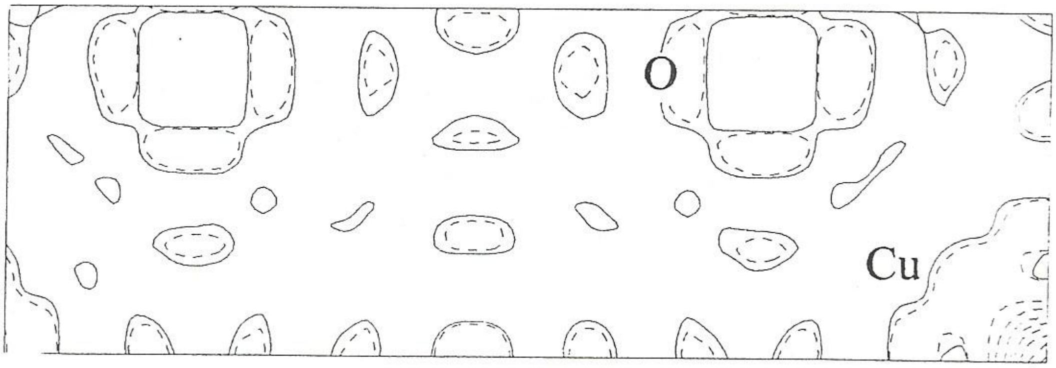

Fig (3.5): Charge density distribution in cuprite in the [110] plane. The solid line is the negative charge density with an interval of 15 between each two successive lines. The dashed lines show the negative ones with an interval of 0.1.

Chapter Four

Discussion

The static potentials at the nuclei positions in cuprite are found to be 4174.8 Volts for Oxygen, and 4665.2 Volts for Copper at zero Kelvin. These values are considered specific properties of the atoms in cuprite crystal. It is found that the values are different for the same atoms in different crystals [5], for example the potential at the O atom in MgO is different from that of the O atom in Cu_2O, also the potential of the Cu atom in CuS is different from that in Cu_2O [5]. The physical properties are also calculated and their values are believed to be convincing. The value of the diamagnetic susceptibility χ_d is $2.036*10^{-10}m^3$/mole, and for The electronic static polarization constant α is $2.074*10^{-9}m^3$, and the dielectric permeability $\varepsilon(0)$ is –2 eV Unfortunately, the calculated parameters were not found in any handbook, so comparison with other researchers' results was not possible.

The electrostatic potential distribution (ESP) seen in figure (3.1) indicates that there is an electron coming out from each Cu atom, one of them arrives completely to the O atom and the other travels only half of the distance between the two copper atoms . It can be concluded that 1.5 electron travel from Cu atoms to O atom i.e. the bond between Cu and O is not completely double iȯnic (± 2) but it can be approximated to be (± 1.5 e). Despite, all the chemistry textbooks always confirms that the bond between the copper atoms in cuprite is metallic; but as it is obviously seen, the existence of one of the two electrons in the distance between the two copper atoms means that there is a partially covalent bond between them. Figure (3.2) illustrates that the potential due to Cu is greater than that due to O, but there is a higher negative potential due to O shown at the left side of the figure, this shows that there is an electron comes from Cu towards O atom. Figure (3.3) shows the drift in the Cu-Cu direction, which confirms the covalent bond between the copper atoms. Figure (3.4) shows the extra negativity in the middle of the line joining O atoms. This negativity is due to the electron from copper in the mid-way between O and Cu, i.e. there is a contribution of a covalent bond between them.

Zue and coworkers [30], studied the bonds in cuprite by developing a method at Arizona University bombarding cuprite crystals with both electron and X-ray beams. As the returning beams interacted with one another, they created a diffraction pattern telling of what they had just hit, which the researchers used to generate a useful image. They got charge density maps of nonionic bonds in cuprite reveal a dumbbell, with a doughnut and three petals around its middle as seen in figure (4.5). The significance of this image is that it clearly shows deviation from ionic bonding, especially the covalent metallic bonding. They found experimentally that about 0.22 electrons have been moved into this bond [30]. In fact this supports this work on the type of bonds in the cuprite crystal. Zue et al (1999) said that:" Covalent bonding appear between copper and oxygen and copper and copper". "The evidence of covalent bonding between metals is likely to make them rewrite the chemistry textbooks,"Spence commented."Chemistry has always assumed that these are only possible between copper and oxygen in this material" [29]. This study is a step on the way of studying properties of other crystals. It is worth suggesting producing a handbook, which is comprehensive of the properties of such crystals.

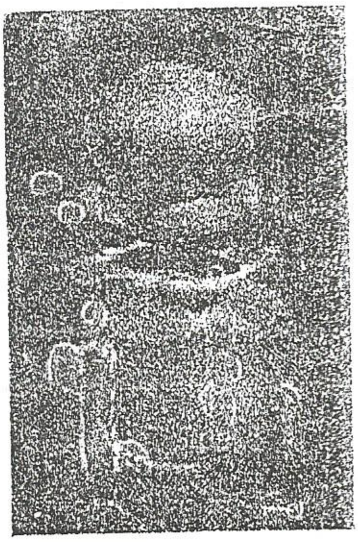

Fig (4.5): The bonds in cuprite

[31]