Chapter 1

Introduction
1. Introduction

Material science is not only serving the industrial purposes but has also become critical for solving problems for the physical sciences, such as testing condensed matter and solid state theories. Materials science paying attention towards the study of materials such as how the structure at the atomic level can be related to various microscopic and macroscopic properties, like the electronic band gap in a semiconductor or the heat capacity of a substance. Basically all of the properties of a material are caused by or mostly affected due to its electronic structure. To understand the function of a material it is thus necessary to understand its electronic structure.

1.1 Materials used

Transition Metal Oxides

The compounds of oxygen atom which are bounded to transition metals are called transition metal oxides. These materials are technologically very important and have many applications. They are commonly used for their catalytic activities. In electrochemical processes these materials are used as electrode materials and also used to make conductors in films. In the chemical industry, catalysts which are employing in a large number of processes to convert hydrocarbons into other chemicals contain TMO’s as the functional components. TMO’s are also used as pigments in plastics and paints. Catalytic properties of these compounds are altered due to the coordination of metal cation and oxygen anion. Due to this reason the catalytic properties are influenced because of structural defects presents in transition metal oxides. Response to electromagnetic radiation of these compounds is one of the most researched properties that makes them useful catalysts for isotope exchange specialized surface, redox reaction and a variety of other uses currently being studied [1]. There is a large impact of defect sites on the stability of the surface.

For the last several years the extraordinary properties of TMO makes them worthy of special attention. Ever since ancient time, some of the properties of TMO like magnetism and colors of naturally occurring minerals and gemstones were known. At the core of the unusual properties of TMO, the unique nature of outer $d$-electrons can be seen clearly.
1.1.1 Copper Oxide (II)

Copper (II) oxide (CuO) is very important among different semiconducting metal oxides. It is a p-type transition metal oxide semiconductor. It has been studied as a unique and attractive mono-oxide material for both practical applications and fundamental investigations. CuO exhibits an inventive scope of applications like selective gas sensing devices, photovoltaic devices, heterogeneous catalysts, field emission devices, solar cells, magnetic storage media and Li-ion electrode materials. It also possesses complex magnetic phases. These materials are used to form the basis for several high T_c-semiconductors and materials with high magneto resistance.

1.1.2 Vanadium (IV) Oxide

From Vanadates family, vanadium oxide (VO_2) is the one which has been studied by the researchers so frequently because of its exceptional and imperative properties. It is an inorganic compound and visible as dark blue solid. VO_2 has a distorted rutile structure at room temperature or below 68^0 and the distance between V-V atoms is very short which indicates metal-metal bonding. Further the structure becomes undistorted rutile and the metal-metal bonds are broken above 68^0. As the bonding electrons are released when bonds are broken there is an increase in electrical conductivity and magnetic susceptibility [2-3]. The occurrence of metal-insulator phase transition at very low temperature makes this material unique and technologically useful. VO_2 used for many applications such as storage for data, cameras and used as optical shutters and modulators for missile guidance systems.

1.1.3 Manganese (IV) Oxide

Manganese (IV) oxide with formula MnO_2 is an inorganic compound. MnO_2 basically used for the growth of dry cell batteries such as the zinc carbon battery and the alkaline battery [4]. MnO_2 is also used as a reagent in organic synthesis. This compound also crystallizes in the rutile crystal structure (β-MnO_2) having three coordinate oxide and octahedral Meta centers [4]. Naturally MnO_2 is non-stoichiometric, being lacking in
oxygen. The knowledge of not long primed MnO$_2$ in organic synthesis is appropriate to the complex solid state chemistry of this compound.

1.2 Review of Literature

1.2.1 At international level

There has been rapid growth of interest in the Compton scattering over the last four decades for the study of electron momentum density distribution. Many research groups in USA, Finland, Japan, France, Australia, and Poland have been working in this field. These groups have used X-rays and gamma rays for their measurements but since the last decade, synchrotron radiation is used at ESRF, APS, Spring-8 labs. These groups have been working on some technologically important metals, transition metal alloys and compounds [5].

A systematic study of momentum density has been undertaken for MgO from directional Compton profile by Fluteaux et al. [6]. The anisotropies were found in fair agreement with HF calculations. Excellent agreement was found between theoretical and experimental anisotropies. Rérat and Lichanot [7] have calculated average and directional Compton profiles for BeO and BN in order to enumerate the electron correlation cause which depends largely on the nature of chemical bonding. Calculations have been done both at the self-consistent field and configuration interaction levels. Ching and Harmon [8] have studied the electronic structure using LCAO method and the calculated charge density found to be in good agreement with results obtained from x-ray diffraction pattern which gives the lake of a distinct bond charge.

Umrigar and Ellis et al. [9] have calculated the energy levels, momentum density and Compton profiles of the ructile phase of NbO$_2$ in a self-consistent molecular cluster model. The results related to nearby neighbor (NbO$_6$) and second neighbor (Nb$_3$O$_6$) cluster were compared to investigate the metal-metal bonding and the convergence of the cluster approach. The bonding densities between Nb-O and O-O were presented by spherical harmonic expansions. Their influence on the Compton profile was also
discussed. Manninen et al. [10] have reported charge transfer and $d$-band occupancy in FeAl, CoAl and NiAl. These people have also studied the electronic properties of FeAl, CoAl and NiAl using Compton scattering technique. The results have been interpreted using FLAPW method which depicted that the anisotropies at low momentum were heavily influenced by the particular shape of the Fermi surface [11]. The pure constituents Cu and Ni as well as the electron momentum distribution of these alloys are reported using gamma-ray Compton scattering technique by Manninen et al. [12]. The results have been discussed in terms of rigid band and superposition model.

The natural orbital functional theory and pairing correlation effects in electron momentum density have been reported by Barbiellini [13]. Within momentum space, occupation numbers of natural orbitals confine the physics of strong electron correlation. Chang et al. [14] have studied the isotropic Compton profiles of vanadium oxides (VO, $V_2O_3$, VO$_2$, $V_6O_{13}$ and $V_2O_5$) using 59.54 keV gamma-rays. Compton profiles were calculated using the molecular-cluster model and found to be inappropriate in describing the experimental results of VO and VO$_2$. The discussion of the localization and delocalization of valence electrons while forming oxides was done on the basis of the atomic superposition model. The molecular-cluster model appears to underestimate the metal ligand covalency.

The ground state momentum density and Compton profile of TiCl$_4$ have been reported by Seth et al. [15] using discrete variational method. The molecular-orbital (MO) wave functions were obtained using the HFS. Results obtained for MO wave functions were compared with atomic superposition models based on HF and HFS atomic eigen functions. Changes in spherical average momentum density and the Compton profile owing to chemical bonding were observed. The study of symmetry and magnitude of the anisotropy was done.

The behavior of vacancies in close proximity to edge dislocations were measured using Doppler broadenings of positron annihilation on Ni and Fe distorted at high speed and low speed by Koichi et al. [16]. They have also evaluated the formation and migration energies and positron annihilation lifetime of vacancies related with edge dislocations. The experimental results were clarified with calculations based on a rate theory. Ghosh et
al. [17] have presented the results based on calculations of the Doppler broadening of the positron-electron annihilation radiation and positron lifetimes within a large number of elemental defect free materials. For these calculations a simple scheme depends upon the method of superimposed atoms have been used. Measured values of the Doppler broadening were compared with experimental data for a number of elemental materials and a qualitative agreement was attained.

Masanori et al. [18] have studied defects in silicon and iron using positron annihilation spectroscopy. The Compton profiles of polycrystalline FeTi and FeTi hybrids in the β-phase have been reported by Lässer et al. [19] using 320 keV incident energy. RFA was used to analyze the experimental data and the best agreement was obtained for a configuration Fe (3d^6 4s^2)-Ti (3d^24s^2) between theory and experiment. Zukowski et al. [20] have studied the Compton profiles using 412 keV γ-rays and concluded that the replacement of Co by Ni results to charge transfer from 4s to 3d band to investigate the electron momentum density in Co_{70-x}Ni_{x}Fe_{5}B_{10} (x=0,10,40 and 55). Bauer et al. [21] has reported the isotropic difference Compton profiles, using 412 keV incident energy, for Fe_{0.5}Ni_{0.5}. The data were interpreted using RFA calculations and the difference for the configuration Fe(3d^64s^2)Ti(3d^24s^2) was found significant.

Manninen and Inkinen [22] have reported the Compton profile study for polycrystalline hexagonal boron nitride using X-rays. The measured data from this experiment were improbably to have great physical significance owing to well known limitations of the X-ray data. Blass et al. [23] have studied the directional Compton profiles of FeAl on the ground of Fermi surface topology by FLAPW method. Experimental Compton profiles of Al and Al-rich Al-Li alloys have reported by Mastsumoto et al. [24]. The experimental data were compared with KKR-CPA theory. It was concluded that Li-impurities when placed in the Al-matrix might be including some very interesting changes in correlations in the electronic system in their vicinity in the alloys. Stutz et al. [25] have reported the electron momentum densities of Li_{100-x}Mg_{x} (X varies from 0 to 40). The experimental evaluation such as valence CP’s, their second derivatives and the associated directional anisotropies have been compared with the KKR-CPA computations. Discrepancies
between the calculations and measurements were partly traced back to an inadequate behavior of correlation effects within the local spin density (LSD).

Marangolo et al. [26] have studied the momentum density in powder samples of K$_4$C$_{60}$ and C$_{60}$ using 19.9 keV incident photon energy. Isaacs et al. [27] have reported the Compton scattering evidence of the hydrogen bond for covalency in ice. This interpretation has been supported by a very good quantitative agreement between data and a fully quantum mechanical bonding model for ice I$_h$. Three dimensional electron momentum distributions (3D-EMD) of β-PdH$_{0.58}$ have been presented using Compton scattering technique with 115 keV incident energy radiations by Mizuaski et al. [28]. The band structure calculations were done by the LDA-FLAPW method and then compared with the experimental data. Sternemann et al. [29] have studied high resolution Compton scattering spectra of ice, methane hydrate and methane using incidental photon energy of 56.4 keV. The data were compared with the theoretical calculation using DFT using model atomic clusters.

The studies related to different properties such as electronic, structural, optical and magnetic for materials have been investigated by lot of researchers. Okoye [30] have studied the electronic energy band structure with some optical and structural properties, of SnTe and GeTe, using the FP-LAPW method within LDA and GGA schemes. The effects of spin-orbit interactions have also considered. The variations of the band gaps with temperature as well as the dielectric functions have also been discussed. Dantas et al. [31].

The study of electronic and structural properties of CuO has been reported by Himmetoglu et al. [32]. This study shows important deviations from the tendency abide by other transition metal mono-oxides. The insulating ground state for the cubic phase of CuO has made uncovered using an extended Hubbard based corrective functional. This was expected but was not found in the literature. The study of tetragonal distortions of the unit cell was mentioned along with the equilibrium structure.

Cockayne et al. [33] have reported the calculations based on DFT+U to examine α-MnO$_2$ whose structure contains a framework of corner and edge sharing MnO$_6$ octahedra with
tunnels in between. Further, K+ ions were placed among tunnels which stabilized α-MnO2 with respect to the rutile structure β-MnO2 phase. This technique was in good agreement with the experiment. The figured magnetic structure had anti-ferromagnetic Mn-Mn interactions linking corner sharing octahedral. The results showed that pure α-MnO2 was a semiconductor with an indirect band gap of 1.3 eV. To explore the effects of crystal defects on the microwave dielectric reaction and the correlative electromagnetic properties of α-MnO2 using first principles calculations using DFT code have been carried out by Duan et al. [34]. The feasible position of crystal defects in electromagnetic performance was studied using DOS and the bond length between the manganese and oxygen. Ni doping increased the spin-polarization of MnO2 demonstrated by the spin electronic DOS, which specified that the Ni doped MnO2 possesses certain magnetic characteristics helpful for magnetic loss. The appearance of a new defect mode contributes to the relaxation polarization phenomenon. This phenomenon enhances the dielectric loss ability. Further, this group found that the bond strength and covalency of Mn-O bonds were weakened due to the change of the bond length and pseudo gap width which raises the dielectric loss of MnO2.

The stability and electronic structure of rutile β-MnO2 surfaces were studied by David et al. [35] using DFT. A wulff construction was made from relaxed surface energies which indicate a rod like equilibrium morphology that is extended along the c-axis and is consistent with the large number of nanowire type structure that was obtainable experimentally. The reported formation energies of Mn reduction and O vacancy defects at key surfaces specified simplistic formation at surfaces, expressed in the equilibrium morphology. The formation energies were found to be lower than for comparable structures such as TiO2.

Harasa et al. [36] have reviewed the electronic properties of the VO2 (0 1 1) surface. In particular, the nature of surface V-O bonding was discussed. Further, the electronic states of the structurally different surface oxygen sites were described and correlated with their catalytic properties. The ab-initio DFT method was used to perform the calculations. Outcome of the study confirmed the bonding in VO2 as a mixture of ionic and covalent character.
Robert et al. [37] has reviewed the structural properties of vanadium oxides. This paper examined the unique structure and properties of the most two common oxides of vanadium (VO$_2$ and V$_2$O$_5$) which have entered into micro-fabricated devices. Sodium vanadium bronzes and vanadium oxide nanotubes, two emerging new materials were also discussed for their potential use in new microelectronic devices. Dridi et al. [38] have presented the first principle calculation to investigate the effect of vacancies on the structural and electronic properties in sub stoichiometric TiC$_x$ and TiN$_x$. Using a full-potential linear augmented plane wave method, they have studied the effect of vacancies on equilibrium volumes, bulk moduli, electronic band structures and density of states. The results concluded that calculated lattice parameters for both materials were smaller than that of ideal stoichiometric TiC and TiN and for TiC the results were compared to a full-potential calculation with relaxed 16-atom super cells.

Elesin et al. [39] have reported the electronic and magnetic properties of copper oxide sheets using a modified mean field approximation within the framework of the Emery model. Also the density of states and its change on doping, the dependence of Fermi energy on the type of doping and the carrier concentration along with the dependence of the sub lattice magnetization and of the magnetic form factor on the level of p-type and n-type doping were presented respectively. The one particle spectra and the electronic band structure of a CuO$_2$-plane have been reported by Zolfl et al. [40] within the three band Hubbard model.

1.2.2 National Level

Compton profile study by Vyas et al. [41] have been reported on AlN (III-V semiconductor compound). The measurements were compared with various ionic configuration Al$^{+x}$N$^{-x}$ (x from 0 to 3 in step of 0.25) and observed the charge transfer of 2.875 e$^-$ from Al to N. Electronic structure and momentum density distribution of TiO$_2$ studied by Sharma et al. [42]. Sharma et al. [43] studied Compton profile of ZnTe. The measurements were compared with ionic configuration of Zn$^{+x}$Te$^{-x}$ (taking x from 0 to 2 in step of 0.5). It was observed that Zn$^{+2}$ Te$^{-2}$ configuration is in good agreement with experiment.
Vyas et al. [44] have reported the Compton profile study of ZnSe. The experimental data was also compared with local and non-local pseudo potential methods. The agreement was found better with local empirical pseudo potential calculation compared to non-local method. Dutta et al. [45] studied the defects dynamics in annealed ZnO by positron annihilation spectroscopy (PAS), x-ray-diffraction (XRD) analysis, thermogravimetric analysis (TGA), and resistivity measurements.

Sanyal et al. [46] have studied defects studies in ZnO by positron annihilation spectroscopy. Found results indicated that a considerable amount of oxygen vacancy has been created in ZnO due to annealing at about 500\textdegree C and above. The results have also deduced that the Zn vacancy created during the ball milling process could be easily removed by annealing the sample at about 500\textdegree C and above. The defect characterization has also been correlated with the magnetic properties of ZnO. Sharma et al. [47] studied Compton profile & charge transfer in intermetallic Ti-Al system. The spherically averaged theoretical values have been compared with the experimental measurements made using 59.54 keV gamma-rays from Am\textsuperscript{241} source. The calculations have been in overall good agreement with previous measurements in all cases. The reported results have been also compared with the superposition of LCAO profiles of elemental solids. Effect of titanium 3d electrons has been clearly visible in the Ti rich alloy within the intermediate range of momentum.

Sharma et al. [48] studied the EMD in TiCu. Comparison of the obtained results was done with results based on LCAO and SPR-KKR methods. The spherically averaged theoretical Compton profiles were reported to be in good conformity with the measurement. The better agreement was measured by the SPR-KKR method. The density of states has also been evaluated from SPR-KKR method to examine the bonding mechanism in the alloy. Deb et al. [49] reported Compton profile of cuprous oxide using LCGO method. The directional Compton profile and their anisotropic effect were reported. The spherical average Compton profile has also been evaluated and compared with the experimental results. Further, calculation for the density of states of this compound was also presented.
Ahuja et al. [50] studied hexagonal BN using gamma rays. The results were discussed in terms of various ionic models, self-consistent Hartree-Fock and LCAO calculation. The LCAO calculation was in relatively superior agreement with the present measurement. The study of Cu$_2$O and Ag$_2$O was carried out by Bandopadhyay et al. [51] employing $^{241}$Am source. Among the valence Compton profiles of these two compounds an interesting comparison has been made which scaled to lattice momentum by normalizing them to equal electron density for outer valence electrons, and this comparison showed some difference between the bonding characters of Cu$_2$O and Ag$_2$O. Joshi et al. [52] have studied the electronic and structural properties of MgB$_2$ by the linear combination of atomic orbitals method. The Compton profiles at 15, 55, and 293 K were measured by allowing for only the thermal expansion of the lattice keeping all other computational parameters identical. The obtained Compton profiles have been compared with the experimental data reported using synchrotron radiation. The calculated profiles under the PW-GGA scheme, found well in accordance with the measurements. The best agreement at the level of first and second order derivatives of Compton profiles has been reported with the B3LYP hybrid function.

A self consistent all electron calculation was carried out for vanadium carbide and vanadium nitride using the LCGO method by Deb et al. [53]. Obtained results were presented and discussed in light of existing theoretical and experimental data for partial density of states, total density of states, charge analysis, and Compton profile. From the comparison of the two compounds a pronounced change in the non-metal $p$ and vanadium $d$ interaction is found, and is discussed in connection with the binding mechanism and directional anisotropies. Vyas et al. [54] have studied the electronic structure and other properties of Al$_2$O$_3$ using Compton profile technique. Results have been computed on the basis of the ab-initio LCAO method embodied in the CRYSTAL code. The HF and hybrid schemes were also applied to the compound. The results showed fine agreement with the measurements. The agreement with experiment is found far better with the hybrid B3LYP scheme. Ionic model interpretation for a number of configurations of (Al$^{+x}$)$_2$(O$^{-2x/3}$)$_3$ (2.75 $\leq$ x $\leq$ 3) to investigate the charge transfer from Al to O atom was also performed utilizing free atom profiles.
Reddy et al. [55] have studied the structural, electrical and optical behaviour of rf magnetron sputtered cuprous oxide films. Tahir et al. [56] have reported Cu, CuO and Cu$_2$O compounds for their electronics and optical properties by x-ray photoelectron spectroscopy (XPS) and reflection electron energy-loss spectroscopy (REELS). The reported details were in good agreement with previous results. REELS spectra were corrected for multiple inelastically scattered electrons to investigate the effective inelastic scattering cross section. The experimental inelastic electron scattering cross section was compared with a simulated cross section measured within the semi-classical dielectric response model to determine the dielectric functions and optical properties. Electron momentum density distribution in SnS by means of Compton profiles has investigated by Sharma et al. [57]. The measurement on polycrystalline sample of SnS has been performed by employing 59.54 keV gamma-rays emanating from an Am$^{241}$ radioisotope. They have performed calculations on the basis of DFT based ab-initio LCAO method embodied in the CRYSTAL program.

The electronic structure and ground state properties of the IV-VI semiconductor, SnTe have been investigated by Sharma et al. [58] using the LCAO method. They have used the calculated Compton profiles to discuss the electronic properties of SnTe. They also examined the nature of bonding and the results showed that SnTe is more ionic as compared to GeTe.

Number of properties for Be-doped CdS, CdSe and CdTe compounds with the dopant concentration $x$ in the range $0 \leq x \leq 1$, have been presented by Noor et al. [59]. They have used FP-LAPW plus local orbitals method within DFT. They have studied the charge density maps, density of states curves and dielectric function. The study of first principle calculations of the structural and electronic properties of rutile phase TiO$_2$, VO$_2$, RuO$_2$, IrO$_2$ and SnO$_2$ using density functional theory (DFT) and full-potential linearized augmented plane waves (FP-LAPW) methods have been performed by Hamad et al. [60] respectively. The exchange correlations functions were described using the generalized gradient approximation (GGA) and the local density approximation (LDA). They have calculated the structural parameters of the all materials, which were established to be in excellent agreement with the previous calculations. They have also showed that TiO$_2$
exhibits maximum cohesive energy and RuO$_2$ exhibits the minimum, exactly opposite to the trend of pure bulk metals.

It is clearly expounded from the above review of literature that a lot of experimental work which have been reported on transition metals systems, however, investigations have not yet been reported on theoretical background. Thus, to explore the physical properties of TMO’s for technological applications, CuO, VO$_2$ and MnO$_2$ are chosen. These materials have rutile structure which is created by filling half of the octahedral sites with cations of the hcp oxygen anion array. The electronic, optical and structural studies of these compounds have a definite importance due to their technological applications. Compton measurements of these materials are useful as compared to other techniques.
References


