Chapter 4
Electronic Structure of VO$_2$
Using Compton Spectroscopy
4.1 Introduction

Understanding of electronic structure of a material is role key for all physical and chemical properties in accordance to Condensed Matter Physics. It is well known that there are so many techniques for this like Compton scattering, positron annihilation spectroscopy, X-ray diffraction. Among all these Compton scattering has been acknowledged as a powerful search for the understanding of ground state properties in real as well as reciprocal space because in a material the momentum distribution of electrons that can be measured through the Doppler shift of Compton scattered photons by valence electron.

The most fascinating and studied constituent of the Vanadates family is known to be Vanadium dioxide (VO$_2$). This compound is strongly associated transition metal oxide with a perceptible metal insulator transition at 68°C and has entice not only for scientific discernment but also for the practical applications in thermal sensing and switching [1-2]. Transitions from a metal to an insulator is MIT, which are accompanied by huge resistivity changes and have been widely observed in condensed matter physics. Since a lot of work has been reported relatively large number of solids which have a sudden transition at some temperature from high temperature metallic behavior to low temperature semiconductor behavior and shows a discontinuous change in conductivity [3]. Reversible crystal structural phase transitions [4-5] occur for Vanadium dioxide (VO$_2$) from monoclinic to tetragonal structure (rutile type).

This transition makes a strong variation in the physical properties like magnetic, optical, conductivity etc.[6] of VO$_2$. This materials exhibits semiconducting behavior at lower temperature, allocates some transmission of solar radiations. The behavior switches to metallic beyond a critical transition temperature accompanied by an increase in reflectance and a decrease in solar transmission. There may be two main reasons for the phase transition, firstly it can be due to a strong interaction of electron-electron which represents Mott Physics [7] and secondly because of the structurally-driven phase transition which represents Peierls instability [8] in which the changes of orbital occupation have been observed [9].
Among all MIT materials VO₂ is one of the best known solid and has been studied expansively in the past 50 years due to its energy saving potential [10-15]. Its physical effects can also be utilized for different microelectronic device applications. The electronic configuration of vanadium [Ar] 3d³4s², provide unique 3d-orbital mixing within the chemical bonds and this directly leads to its multivalent character (+2, +3, +4, +5) due to which the V-O phase diagram has many compound phases that can be affected by crystal structure, external redox reaction and habit defects. The compounds of vanadium are stable and exhibits repeatable properties at both meso and nano scale because these compounds have a little isotropic disorder.

Chang et al.. [16] have studied the isotropic Compton profiles of Vanadium oxides (VO, V₂O₃, VO₂, V₆O₁₃ and V₂O₅ with 59.54 keV Gamma-rays. Theoretically the Compton profiles were calculated using the molecular cluster model. The results were found to be inappropriate in describing the experimental results for VO and VO₂. Formation of oxides because of the localization and delocalization of valence electrons was discussed on the basis of the atomic superposition model. The metal-legand covalency was underestimated by the molecular-cluster model for these materials.

The first principle electronic structure calculations for the metallic rutile and the insulating monoclinic phase of Vanadium dioxides were performed by Eyert et al.. [17]. The insulating M2 phase was also investigated for the first time. The results were shown that the metallic conductivity was carried by metal t₂g orbitals for the rutile phase, which falls within the one dimensional d∥ band and the isotropically dispersing e₃d bands. For both the bands hybridization was found to be weak. In M1 phase, an effective separation was reported for both types of bands due to increased p-d overlapping. The results were found to be fitted for VO₂ into the general scenario of instability of the rutile type transition metal dioxides towards anti-ferromagnetic ordering within the characteristic metal chains at the beginning of the d series.
Using the combination of the three-dimensional periodic shell model and the discrete-variational (DV)-Xα cluster method the electronic structure for VO₂ in the metallic phase and insulating phase have been evaluated by Nakatsugawa et al. [18]. The electron-phonon coupling constant was estimated by the shell model which also presented the direct theoretical evidence that in the low temperature phase the dimmers are stable.

The electron energies in [V₂O₁₀]⁻¹² clusters were calculated by the DV-Xα cluster method as well as the value for the intersite repulsive nearest-neighbor d-d Coulombic interaction. The results for electron-phonon interactions were found to split d band into the empty upper and the occupied lower Hubbard band and found a noticeable energy gap between these bands in the insulating phase. The MI transition in VO₂ was well explained by these calculations.

Leroux et al. [19] have reported the intermediate steps of the phase transition between the metastable monoclinic VO₂(B) phase and the stable tetragonal rutile VO₂(R) phase using in situ electron microscopy. The long range order is lost in the complex monoclinic VO₂(B) phase and slowly but surely a first intermediate ill crystallized phase was formed as supported from the diffraction patterns with a significantly reduced symmetry. This was a crystallographic interpretation which based on the static concentration waves theory was proposed.

A completely automatic general electrical single crystal diffractometer was used to collect the data for the structure refinement of VO₂ through counter technique by Longo et al. [20]. Entire description of the data collection as well as the processing was mentioned. The results are found to be in good agreement for the least square refinement with the original parameter determination but the standard deviation which has been achieved was very low.

In addition this group has reported that VO₂ doping with tungsten can lower the MIT temperature. For the identification of structural changes has been employed using infrared spectroscopy as a tool. The above literature review shows that for VO₂ the
investigations are limited to electronic, optical, and structural and phase transition properties etc. while study on EMD have not been reported much.

So in this chapter we will discuss the Compton profile study of VO$_2$ and compare the experimental data with the theoretical Compton profiles computed using DFT-PBE. We have also reported the anisotropy curve and the ionic curve for VO$_2$. All the quantities reported here are in atomic units (a.u.) with $e = h = m = 1$ and $c = 137.036$, giving the unit momentum $1.9929 \times 10^{-24}$ kg m/s, unit energy $27.212$ eV, and unit length $5.2918 \times 10^{-11}$ m.

This chapter is organized in following way: In section 4.1, a brief description of the crystal structure is specified. The salient features of theoretical calculations are presented in section 4.2. Further section 4.3 explains the experimental details. In section 4.4 the results and discussions & finally we are drawing conclusion in section 4.5.

**Crystal Structure**

VO$_2$ exhibits tetragonal rutile structure at high temperature having space group P4$_2$/mn (136) [21-22]. A symmetric structure is presented by this group. VO$_2$ is reported to exist in tetragonal symmetry above $68^\circ$C whereas in ambient condition it exists in simple monoclinic symmetry with P2$_1$/C (14) space group [23-24]. The crystal structure of VO$_2$ is shown in figure 1. The unit cell consists of 4 formula units with 3 atoms per formula unit; accordingly representing 12 atoms in a unit cell i.e. 4 atoms of vanadium and 8 atoms of oxygen. The V atom occupies 4e symmetry position while O atoms are present at two distinct 4e positions and their atomic positions are shown in table 1.
Table 4.1. Crystallographic parameters of vanadium dioxide (VO$_2$)

<table>
<thead>
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<th>Parameters</th>
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Figure 4.1. Crystal structure of VO$_2$. 
4.2 Theoretical Details

4.2.1 DFT-LCAO

Theoretical calculations for VO$_2$ are carried out using CRYSTAL06 [25] code. CRYSTAL06 provides a platform with Gaussian basis employing HF, DFT, and hybrid schemes to identify the electronic structure of periodic systems. Its architecture revolves around all electron *ab-initio* self consistent field (SCF) periodic LCAO procedure [26-27]. According to this method every crystalline orbital $\Psi_i(r, k)$ is a linear arrangement of functions defined in terms of local functions which are Bloch functions $\Psi_u(r, k)$. The correlation scheme $&$ exchange scheme of the Perdew- Burke-Ernzerh of (PBE) [28] and Becke [29] respectively was taken into account. Monoclinic structure with space group $P2_1/c$ (14) [23-24] was considered for carrying out further calculations. Considering the fact that, 170 $\vec{k}$ are present for VO$_2$ in the irreducible Brillouin zone with sufficient tolerances, the self consistent calculations were performed. 75% self-consistency was achieved by considering mixing of successive cycles and within 20 cycles for VO$_2$ self-consistency was achieved. The lattice parameters used in the present calculation for VO$_2$ have values as follows, $a = 5.743$ Å, $b = 4.517$ Å and $c = 5.375$ Å with angle $\beta = 122.61^0$ [23] respectively. In this chapter the atomic positions of V and O in VO$_2$ are considered as (0.242, 0.975, 0.025) and (0.10, 0.21, 0.20), (0.39, 0.69, 0.29) [24]. The crystal structure is shown above in Figure 4.1. After adding the spherical average valence profile to the free atom core contribution, the theoretical profiles are compared with polycrystalline data. The Compton profile anisotropies, electron momentum density and charge transfer from V to O are calculated with the help of this method.

4.2.2 PAW method

The band structure and DOS calculations are performed using PAW method as employed in VASP code [30-32]. The exchange-correlation interaction was treated within DFT-GGA using PBE functional [28]. The basis set of respective constituents i.e. of V and O atoms were treated with plane wave cut off energy of 400eV. Optimization of lattice parameters and the relaxation of atomic positions have been done by the conjugate gradient method. To achieve the convergence in electronic iterations,
tolerance of $10^{-6}$ eV in total energy was used. A 3x3x3 grid of Monkhorst–Pack points was used. The total and projected DOS have been calculated by the linear tetrahedron method with Blöchl corrections [33].

4.2.3 Ionic Model

The different ionic configuration for VO$_2$ can be computed by calculating the theoretical Compton profiles of VO$_2$ using the free atom Compton profile of V and the O atoms which were taken from Bigg’s et al. [34]. The valence profile for various $V^{+x}(O^{-x/2})_2$ ($0 \leq x \leq 2$) configurations were deliberated by transferring $x$ electrons from the $4s$-shell of V to the $2p$-shell of O atom. The total theoretical Compton profile can be evaluated by adding the valence profile for $V^{+x}(O^{-x/2})_2$ configuration to the core contribution. All these profiles then compare with the experimentally measured profile of VO$_2$ after normalizing these theoretical profiles appropriately.

4.3 Experimental technique

The Compton measurements for polycrystalline VO$_2$ with effective density 2.5096g/cm$^3$ has been performed using 5 Ci $^{241}$Am Gamma-ray Compton spectrometer [35]. The high energy gamma-rays of 59.54 keV were scattered by the polycrystalline sample of VO$_2$ at an angle equal to $166^\circ \pm 3.00$. To ease the contribution of air scattering, the chamber was leaved to about 1.3 Pa with rotary oil pump. A high purity germanium detector (Canberra model, GL0110S) was used to analyze the scattered. The spectra were documented with a MCA giving a channel width of 20eV with 4096 channels.

The Compton spectra were measured for around 12.55 hrs to collect 74846 counts at the Compton peak. The raw data were processed for several systematic corrections to deduce the true Compton profile similar to background, instrumental resolution, sample absorption, scattering cross section and multiple scattering using the computer code of Warwick group [36-37]. The theory is then convoluted with instrumental resolution i.e. 0.639 a.u. After the conversion of profile to the momentum scale, a Monte Carlo simulation for the multiple scattering was performed. The contribution of multiple scattering was found to be 11.23% in the momentum region -10 to +10 a.u. At last the
experimental CP was normalized to 18.090 electrons in the range from 0 to +7 a.u. at an interval of 0.1 a.u., being the area of free atom CP in the given range [34]. The 1s electron contribution of vanadium atom is neglected for \( p_z > 8.4 \) a.u. for the experimental calculations.

4.4 Result and Discussions

4.4.1 Compton Profile

Spherically averaged theoretical and experimental CP is shown in figure 4.2. For their qualitative analysis we have also plotted their difference profile in the lower panel of figure 4.2. The theoretical profile is constructed from CP calculated by Bigg’s et al. [34]. From the figure 4.2, experimental CP is observed to be sharper in the momentum range 0-0.8 a.u. This sharper profile in experimental data is associated with the diffuse wave nature of valence electrons wave function, which originates as a result of screening by core contribution. While, DFT-LCAO scheme is alleged to underestimate the nature of chemical bonding in the compound which contributes to charge distribution and thereby result in disagreement between the two profiles.

Apart from this, selection of basis set may also be the reason of present discrepancy between the two CP, as they are the one which govern EMD in computation. Dominant feature of DFT-LCAO profile is observed in momentum range of \( 1.0 < p_z < 3.0 \) a.u., in comparison to the experimental profile. Beyond \( p_z = 3.0 \) a.u. experimental CP overlap with DFT-LCAO profile, showing prominence of core electrons as they remain unaltered during compound formation. Isotropic, unconvoluted CP for DFT-LCAO along with experimental data is shown in table 4.2. At certain selected points experimental error has also been tabulated.
Figure 4.2. The absolute DFT-PBE and experimental Compton profiles of VO$_2$. The upper panel presents the absolute curve and the lower panel shows the difference between experimental and LCAO scheme based Compton profile. Both profiles are convoluted with the Gaussian of 0.6 a.u. FWHM.
Table 4.2. Unconvoluted experimental and theoretical (DFT-PBE and ionic) Compton profiles of VO\textsubscript{2}. All profiles are normalized to 18.090 electrons in the range 0–7 a.u. Experimental errors (±\(\sigma\)) also given away at some points.

<table>
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<tr>
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<th>Experiment</th>
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<td>(V^{+1.0}) O\textsuperscript{0.5}</td>
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4.4.2 Directional Compton Profile

In order to evaluate the directional Compton profile for VO$_2$ theoretically, we have derived directional Compton profiles in framework of electron momentum density around the crystallographic directions [100], [110] and [001] using PBE in DFT scheme. The convoluted difference profiles between [100]-[110], [100]-[001] and [110]-[001] directions are shown in figure 4.3.

The scrutiny of anisotropic profile reveals that the maximum anisotropy occurs at $p_z = 0$ a.u. for [100] direction. Further, [100] direction has largest distribution of anisotropy in low momentum region, from $0.0 \leq p_z \leq 1.3$ a.u. as compared to two profiles indicating maximum occupied states in the corresponding direction. However, from the close inspection of the nature of anisotropy it is found that all difference anisotropic profiles are positive at $p_z = 0$ a.u. This nature of anisotropy is interpreted from the band structure calculation on the basis of available energy states across the Fermi level. On comparing the value of conduction band minima at different k-points of BZ i.e. along Γ, B, A and Z point it is observed that conduction band minima at Γ point is the closest energy band in the vicinity of Fermi energy which in turn construe presence of highest electron momentum density along Γ point. As on moving across Γ-B, Γ-A and Γ-Z branch i.e. along [100], [110] and [001] direction respectively, energy levels are found to be shifted away from Fermi level. Due to shifting of these bands towards higher energy value, availability of electrons get diminishes across the Fermi level and hence electron momentum density gets reduced. Therefore, maximum value of electron momentum density at $p_z = 0.0$ a.u. is attributed along Γ-B branch i.e. along [100] direction. This characteristic of Γ-B branch further can be interpreted for the presence of positive oscillation in [100]-[110] difference profile till $p_z = 1.1$ a.u. Similarly, negative oscillation along $p_z = 2.1$ a.u. could be explain.

Beyond this, anisotropic behavior of free atom profile is visible up to $p_z = 3.7$ a.u. for all the difference profiles further than the isotropic contribution of core atoms starts dominating the electron momentum density and hence anisotropies diminish in this region respectively.
Figure 4.3. Compton profile anisotropies for VO$_2$. Anisotropies are computed following the DFT-PBE scheme. The entire anisotropies are obtained from unconvoluted directional Compton profile.
4.4.3 Charge Transfer

The experimental Compton profiles are compared with various ionic arrangements to approximate the charge transfer in Figure 4.4. The theoretical Compton profile for different ionic configurations of VO₂ was estimated from the free atom profiles of V and O atoms [35]. By transferring x electrons in the range of 0 ≤ x ≤ 2.0 with an interval of 0.5 a.u. from 4s state of V to 2p state of O atom, the valence profile were computed for various V⁺ₓ (O⁻ₓ/2)₂ configurations. To obtain the total profile, the valence profile then added to the core contribution. For numbers of compound, similar approach has been used to determine the charge transfer [38-41].

The difference profile (ΔJ = J\text{Theor} (p_z) − J\text{Exp} (p_z)) has been deduced after convoluting all ionic profiles with a Gaussian function having resolution of 0.639 a.u. FWHM to get a quantitative comparison of experiment and the ionic computation. All ionic values are normalized to 18.090 a.u. electrons in the momentum range 0 to +7 a.u. From the figure 4.4, it is observed that the effect of charge transfer from V to O atoms is apparent within p_z range of 0 to 3.0 a.u. and the largest deviation between experiment and theory and, at J(0), is shown by the configuration x = 0.5 while on the basis of χ² test, best agreement among all the ionic arrangements is found for x=2.0 [V⁺2.0(O⁻1.0)₂] configuration. On the other hand maximum deviation at J(0) is observed for the charge transfer from 3d state of V to 2p state of O atom and the trend for all ionic configuration is seems to be exactly same everywhere.
Figure 4.4. The difference $\Delta J$ between convoluted ionic and experimental Compton profiles of VO$_2$: curve 1—$V^{+0.5}(O^{-0.25})_2$; 2—$V^{+1.0}(O^{-0.5})_2$; 3—$V^{+1.5}(O^{-0.75})_2$; 4—$V^{+2.0}(O^{-1.0})_2$. Experimental errors ($\pm \sigma$) are also given at the points. Every ionic profile is convoluted with the Gaussian of 0.6 a.u. FWHM.

4.4.4 Band Structure and DOS

Band structure of VO$_2$ has contribution from five different bands corresponding to transition metal element V with electronic configuration 3p$^6$ 3d$^3$ 4s$^2$ and O atom with configuration 2s$^2$ 2p$^4$. From partial density of state it is observed that s-state of O-atom, produces low lying energy bands in the energy range of -20 to -18eV. These deep lying s-states of O atoms show entirely different contribution in low energy state.

As observed from partial density of state the s-state of O2 atom dominates while that of O1 atom is suppressed due to existence of non-equivalent structural co-ordinate of O-atom. As these bands lie at far distance from the valence band thus do not effectively contribute in the electronic property of the system. Further, in the energy range of -7.35 to -1.23eV p-state of O1 and O2 atom show nearly equal contribution.
Energy bands in the valence region corresponding to energy range -7.35eV to -1.2eV originate from the hybridization of 2p orbital of O1 and O2 atoms and 3d and 3p orbital of V atom. In the upper valence region i.e. below $E_F$ at Y-point of BZ 3d orbital of V atom gives maximum share in energy band with small contribution from p-state of O1 and O2 atoms. However, in the conduction region at $\Gamma$-point, 3d state of V atom highly dominates. Thus, gives indirect band gap with energy of 0.36 eV.

Figure 4.5. (a). Band structure of VO$_2$ and (b). Partial density of states of VO$_2$
4.5 Conclusion

Using Compton spectroscopy technique, the electronic structure study of polycrystalline VO$_2$ is performed. The experimental data for Compton profiles is compared with the theoretical DFT-PBE based values. The charge transfer for different configuration has been also performed for the compound and the ionic model suggests a better agreement for the configuration $[V^{+2.0}(O^{-1.0})_2]$ with a charge transfer of 2.0 electrons form 4s state of V atoms to 2p state of O atoms. In addition, the directional anisotropies in momentum density range shows the enhanced occupied states along the direction [100] with low momentum region. Due to which the anisotropies along [100]-[110], [100]-[001] and [110]-[001] are positive in nature at $p_z = 0.0$ a.u. for VO$_2$. All anisotropies are found to be diminished beyond $p_z = 3.0$ a.u. as this shows the region of core electrons where the isotropic behavior dominates the valence region.
References


13. B.I. Halperin and T.M. Rice, “The Excitonic State at the Semiconductor-
Rev. 120, 67(1960).
17. V. Eyert, “The metal-insulator transitions of VO₂: A band theoretical approach”,
18. H. Nakatsugawa and E. Iguchi, “Electronic structures in VO₂ using the periodic polarizable point-ion shell model and DV-Xα method”, Phys. Rev. B 55,
2157(1997).
19. C. Leroux, G. nihoul and G.V. Tendeloo, “From VO₂(B) to VO₂(R): Theoretical structures of VO₂ polymorphs and in situ electron microscopy”,
20. R. Long, B. Qu, R. Tan, Y. Sun, X. Tan, W. Ying, B. Pan, Y. Xiong and Y. Xie,
“Identify structural distortion in doped VO₂ with IR spectroscopy”, Phys. Chem.
22. S. Westman, “Note on a Phase Transition in VO₂”, Acta Chem. Scand. 15,
23. G. Andersson, “Studies on Vanadium Oxides. II. The Crystal Structure of
Pascale, B. Civalleri, K. Doll, N.M. Harrison, I.J. Bush, Ph. D’Arco and M.
