ELECTRIC STUDIES OF VANADIUM OXIDE (V_6O_{13}) THIN FILMS

By

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 V_6O_{13} is one of the intermediate phase compounds between the vanadium-oxides VO_2 and V_2O_5 . In bulk, this material undergoes a structural transition at approximately 150K, and a magnetic transition from paramagnetic to antiferromagnetic at 55K. While optical experiments have shown that V_6O_{13} is a metal at room temperature, and that a band gap appears at the structural transition temperature, electrical measurements in single crystals and polycrystalline samples have given contradictory results. In this experiment V_6O_{13} thin films fabricated by the Pulsed Laser Deposition technique were studied. Resistivity measurements were made on the samples using the four-point-probe technique in the temperature interval from 30 to 280K. It was confirmed that V_6O_{13} thin films undergoes a semiconductor-semiconductor transition near the reported structural transition temperature. It is also shown that the electrical behavior changed around the magnetic transition as well. A phenomenological model is proposed to model the physical behavior of the resistivity throughout the measured temperature range.

Resumen de Disertación Presentado a Escuela Graduada de la Universidad de Puerto Rico como requisito parcial de los Requerimientos para el grado de Maestría en Ciencias

ESTUDIOS ELÉCTRICOS DE PELÍCULAS DELGADAS DEL ÓXIDO DE VANADIO V₆O₁₃

Por

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Julio 2009

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 V_6O_{13} es uno de los compuestos de óxidos de vanadio entre VO_2 y V_2O_5 . Este material cambia su estructura cristalina alrededor de 150K, además sufre una transición magnética de paramagnético a antiferromagnético cerca de 55K. Mientras experimentos ópticos han mostrado que V_6O_{13} es un metal a temperatura ambiente, y que una brecha de energía aparece cerca de la temperatura de transición estructural, experimentos eléctricos en muestras de cristales sencillos y policristalinas han ofrecido resultados contradictorios. En este trabajo se estudiaron películas delgadas de V_6O_{13} que fueron fabricadas usando el método de "Pulsed Laser Deposition". Medidas de resistividad fueron hechas usando la técnica de los cuatro puntos en el rango de temperatura 30 - 280K. Se confirmó que las películas delgadas de V_6O_{13} sufren una transición de semiconductor a semiconductor cerca de la temperatura de transición estructural reportada. Además, se muestra que el comportamiento eléctrico de las películas delgadas también cambió cerca de la transición magnética. Un modelo fenomenológico es propuesto para modelar el comportamiento físico de la resistividad a través de todo el rango de temperatura medido. Copyright © 2009

by

Pedro Juan Sánchez Reyes

To God...The Mathematical Physicist.

To my grandmother, MamiMonin...for her love, I will always be grateful.

To my parents, Pedro and Bruni...because they formed the person I am today.

To my brothers, Carlos and Joel...because their successes are mine, and mine are theirs as well.

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CHAPTER 1 INTRODUCTION

1.1 Motivation

Vanadium oxides are part of the 3d-transition-metal-compound family. Most of the compounds in the vanadium-oxide system can be divided into two groups: V_nO_{2n+1} between $VO_2-V_2O_5$ and V_nO_{2n-1} which are between $VO_2-V_2O_3$. The former are named the Wadsley Phase and the later the Magneli Phase after their main investigators. Most of the vanadium family compounds present a variety of magnetic and electrical properties(various types of phase transformations) which makes them suitable for technological applications. From the knowledge point of view these materials provide the opportunity to study strong electron correlations, which in some of them are thought to drive the metal-semiconductor(**M-S**) transition. Thus, a closer study is important in order to gain a better physical understanding of the process involved in phase transitions.

 V_6O_{13} is one of the intermediate phase compounds between the more studied VO_2 and V_2O_5 . On its own, V_6O_{13} is worthy of study, since it exhibits a transition in the type of electrical transport around 150K and a magnetic phase transition approximately at 55K. There are several studies on single crystals and polycrystals of V_6O_{13} . The results have shown different types of electrical transitions, but there has not been a satisfactory explanation as to why the same material exhibits two different electrical transitions. In addition, very few studies of V_6O_{13} thin films have been conducted. We are only aware of two electrical studies. There is no theoretical work to explain the magnetic and electrical properties of V_6O_{13} thin films. It is the

purpose of this work to confirm the type of electrical transition occurring in thin films, and try to explain the transport process occurring in the material.

1.2 Literature Review

This section presents a concise review of the existent literature directly related to V_6O_{13} .

The crystal structure of V_6O_{13} was determined by Aebi in 1948. Later it was refined by Wilhelmi [19]. Near room temperature he found that the material has a monoclinic structure with lattice parameters

$$a = 11.922 \text{\AA}, b = 3.680 \text{\AA}, c = 10.138 \text{\AA}, \beta = 100.87^{\circ}$$

and space group symmetry C2/m. Crystallographically there are three non equivalent vanadium atoms and seven non equivalent oxygen sites in the structure, which can be regarded as three different distorted octahedra, connected by sharing borders and corners. It is best to visualize the 3-dimensional structure as two types of layers parallel to the ab-plane, see figure 1–1. The first is a single layer, where $V(1)O_6$ octahedra form single zig-zag strings by edge sharing, and by corner-sharing the strings link together to form the layer. The second sheet is actually a double layer, where $V(2)O_6$ and $V(3)O_6$ octahedra share edges to form zigzag strings. They are also joined by edge-sharing in the ac-plane actually forming double zig-zag strings along b. The double zig-zag strings form one sheet parallel to the ab-plane, and by joining a similar sheet in the ac-plane(by edge-sharing between the double zig-zag strings)the double layer is created. The single and double layer are connected by common corners in the ac-plane.

Subsequent crystallographical studies have confirmed that the crystal structure of V_6O_{13} at high temperature is monoclinic with space group C2/m, and below 150K the materials suffers a structural change losing a mirror plane and changes to space group symmetry C2[1] or alternatively $P2_1/a[9]$.



Figure 1–1: (a) The crystal structure of V_6O_{13} at room temperature, projected on the (010) plane. (b) and (c), two types of a-b planes, A and B, including zigzag chains running along b axis with mixed V^{4+} -like and V^{5+} -like, and with mono V^{4+} -like sites, respectively. Taken from reference [2].

Nuclear Magnetic Resonance(**NMR**) measurements in conjunction with crystallographical studies permit to say that V(1) and V(3) sites are V^{4+} -like, while V(2) site is more V^5 -like[4]. Below the structural change temperature, there is charge redistribution among the different ions with V(1) becoming more V^{5+} -like, and V(2) becomes more V^{4+} -like. One of the unsolved problems in V_6O_{13} is that the magnetic susceptibility starts to follow the Curie Weiss law above the structural change while being paramagnetic, both, above and below the structural transition. At the structural transition temperature, there is a decrease in the magnetic susceptibility which seems to be caused by spin pairing of some of the V^{4+} sites[4]. Around 55K, the materials undergo a magnetic phase transition (see figure 1–2) from paramagnetic to antiferromagnetic [4, 18]. The origin of the antiferromagnetic state has been explained as arising from an interaction among the unpaired V^{4+} sites along the *b*-axis, the antiferromagnetic spin is also parallel to this direction [6, 18]. It is noteworthy that the energy gain due to spin pairing appears to be considerable, since the pairing is thought to persist in the antiferromagnetic state.



Figure 1–2: Magnetic susceptibility vs temperature, and **NMR** intensity vs temperature measurements from Gossard et al. The decrease in the **NMR** is caused by the magnetic transition.

A band picture of V_6O_{13} , taking into account strongly correlated d-bands, seems to be adequate. Resonant photoemission spectra has shown strong hybridization between the lowest O2p bands and V3d[16]. V3d intraband transitions have also been seen in different experiments. The optical bands had been estimated to be around $2 - 3 \ eV[5, 12]$. Angular-resolved photoemission spectroscopy(**ARPES**) experimental studies have made clear that the material is highly anisotropic in the a-b plane, and that V_6O_{13} has a quasi-one dimensional structure along the *b*-axis[2]. This experiment has also revealed that a small band opening of aproximately 0.2eV begins across the structural change indicating that the material is metallic above the transition, and insulating below it.

Although optical experiments have confirmed that the transition is a Metalinsulator one, electrical measurements in the literature provide contradicting results, some implying semiconductor to semiconductor(**S-S**) transitions instead. For instance, see table 1–1 and associated figures. Finally, there are very few measurements on V_6O_{13} thin films, whereas all of the data have exhibited the semiconductorsemiconductor transition of polycrystals, although in a less pronounced way.



Figure 1–3: Conductance measurement, by Saeki et al.

Sample	Transition	Temperature (K)	Remarks	Reference
polycrystals	S-S	155	The change in the resis- tivity data is of one or- der of magnitude, and the data appears to show simple activated	Kachi et al.[7] (1963)
single crystals single crystals	M-S S-S	Not available. 149	behavior. Along the <i>b</i> -axis, con- ductivity changed by two orders of magni- tude. Hysteresis be- tween cooling and heat- ing was present, see fig-	K.K. Kanazawa[8](1967) Saeki et al.[13](1973)
single crystals	M-S	150	ure 1–3. Abrupt change in the resistivity along all crystallographic di- rection of more than	Kawashima et al.[10](1974)
single crystals	M-S, S-S	158	four orders of magni- tude(figure 1–4). M-S occurred only along <i>b</i> direction, with hysteresis present. The semi-conductive phases are described as roughly linear with $\frac{1}{2}$ see figure	Onoda et al.[11](2004)
thin film	S-S	123	1-5. Above the transition the resistivity seems to follow simple activated behaviour. The change is less than an order of magnitude and hystere- sis is present. See figure	Sahana et al.[15](2004)
thin film	S-S	145	1–6 The change is less than an order of magni- tude(see figure 1–7). It is claimed that a $M-S$ was seen in IR trans- mission experiment around $164K$.	C. Pitre[12](2006)

Table 1–1: Summary of electrical measurement results on V_6O_{13} .



Figure 1–4: Resistivity measurement, after Kawashima et al.



Figure 1–5: Resistivity measurement, from Onoda et al. The doted line in (a) is from a fit to the Bloch-Gr \ddot{u} neisen formula, the solid lines in (c) are fits from simple activated behavior.





Figure 1–7: Resistance measurement of V_6O_{13} thin film, taken from reference[12]

CHAPTER 2 SAMPLE'S GROWTH AND CHARACTERIZATION

For this work two sets of samples were made and measured. The V_6O_{13} thin film were prepared at the Physics Department's Materials Laboratory of the University of Puerto Rico in Mayaguez. The first set of samples was prepared by the method of DC-magnetron sputtering. The Pulsed Laser Deposition(**PLD**) method was used for making the second set of thin films. On this chapter, details of the sample preparation are presented. The characterization of the samples by x-ray and AFM images is also discussed.

2.1 V₆O₁₃ DC-magnetron Sputtering Thin Films

A detailed discussion of the sample preparation method used can be found in [12]. Here we will present only a brief overview.

2.1.1 Substrate

The substrate used was fused silica(SiO_2), which is amorphous. In addition, two more samples were prepared on $LaAlO_3$ crystalline substrates. The hexagonal structure of the crystal substrate below 25 °C, with lattice parameters a = 3.79 Å and c = 13.11 Å, was expected to help the V_6O_{13} crystals orient. All the substrate pieces were cleaned using a four step process:

- An immersion in an ultrasonic Trichloroethylene(**TCE**) bath for ten minutes to remove grease from the substrate.
- Immersion for ten seconds in an ultrasonic bath with acetone.
- Immersion for another ten seconds in an ultrasonic bath, this time with methanol.

• Finally, the sample is blown dry using gaseous nitrogen.

Pre-sputtering was performed on the target to remove impurities for $20 - 30 \ min$, in an atmosphere of Argon with a pressure between $20 - 30 \ mtorr$.

2.1.2 Thin Film Growth

As mentioned before, the method for growing the first set of V_6O_{13} thin films was DC-magnetron sputtering. The parameters used are presented on table 2–1. The samples were at a distance of 5 cm from the metallic Vanadium target(99.5% purity). Once the deposition was completed, the sample was left to cool to room temperature without any control. The thickness of the films was measured using a profilometer (Tencor Alphastep) at a step created in the corner of the samples. The average thickness was 100 nm.

Sample	Substrate	Temperature(°C)	Ar Flow(sccm)	O_2 Flow(sccm)	Deposition Time(min)
Vs41	SiO_2	400	18.7	0.8	28
Vs42	SiO_2	400	19.85	0.65	30
Vs44	SiO_2	400	19.85	0.54	30
Vs103	$LaAlO_3$	400	19.1	0.8	30
Vs108	$LaAlO_3$	400	19.1	0.8	60

Table 2–1: Table with the preparation parameters for the different V_6O_{13} thin film samples.

2.1.3 Crystal Structure

The crystal structure of the samples was determined with an x-ray diffractometer (Bruker AXS, D8 Discover). All the samples were found to be in the V_6O_{13} phase, no peaks from the VO_2 or V_2O_5 phases were seen in the x-rays. The data used to verify the structure of the films, was that of Kawada[9]. Also, the x-rays indicate that the samples grew preferentially in the (001) crystallographic direction. This is due to the greater packing density of the a - b plane, and the tendency for minimization of the surface energy[14]. As an example, the x-ray spectrum of the sample Vs41 are shown in figure 2–1. A broad peak around 22° can also been seen in the figure, which corresponds to the SiO_2 substrate.



Figure 2–1: X-ray data for Vs41 thin film sample.
2.2 V₆O₁₃ PLD Thin Films

The bulk of this work was done on the V_6O_{13} thin films fabricated by the Pulsed Laser Deposition method. So a more detailed analysis will be presented here and in subsequent sections and chapters.

2.2.1 Substrate

The substrate used with the **PLD** was amorphous SiO_2 . This was done in order to better compare the efficiency of the two methods in producing high quality V_6O_{13} thin films. The method for cleaning the substrates, was the same 4 step procedure described before, except that air was blown to the sample instead of gaseous nitrogen.

2.2.2 Thin Film Growth

Thin films were fabricated by ablating a rotating metallic Vanadium target with a pulsed KrF laser(Lambda Physik Compex110), see table 2–2 for the operational parameters.

Wavelength (nm)	Pulse $Duration(ns)$	Frequency of Pulsing(Hz)	Fluence $\left(\frac{J}{cm^2}\right)$
248	20	10	4

Table 2–2: Laser parameters used for the **PLD** technique.

All the samples were fabricated under identical conditions, varying only the total pressure. The details can be seen on table 2–4. The Argon and Oxygen flows were 10 and 15 *sccm*(standard cubic centimeters per minute) respectively. The color of the samples was a yellowish-green color, as was the case with the samples made by sputtering. The average thickness of the samples measured with the profilometer was 200nm.

Table 2–3: **PLD** parameters.

Sample	Substrate	Temperature(°C)	$P_T(mtorr)$	$P_{par}O_2(mtorr)$
V396	SiO_2	500	65	39
V397	SiO_2	500	60	36
V398	SiO_2	500	70	42
V399	SiO_2	500	80	48
V400	SiO_2	500	90	54
V401	SiO_2	500	140	83

Table 2–4: Growth parameters for the thin films fabricated with the **PLD** technique.

2.2.3 Crystal Structure

The x-ray data revealed that the V397 thin film sample was composed of two phases, VO_2 and V_6O_{13} . The crystal structure for the VO_2 phase was consistent with the crystal structure obtained by K.D. Rogers(file 82-0661 of **ICDD**). The (110) peak around 27° labeled as 1 in figure 2–2 is related to monoclinic VO_2 . The other phase present in the film is monoclinic V_6O_{13} . The sample V401 showed also two phases, the wide band gap semiconductor V_2O_5 and monoclinic V_6O_{13} . The V_2O_5 crystal structure was compatible with the **ICDD** file 41-1426, which ascribed the crystal structure to be orthorhombic with space group symmetry *Pmmn*. The three peaks in the x-ray data of figure 2–2 labeled as *I*, *II* and *III* correspond to the V_2O_5 phase. The positions of the peaks are approximately 20, 41 and 64, and are associated with the V_2O_5 crystallographic planes (001), (002) and (003) respectively. This shows preferential orientation for the V_2O_5 phase in the (00 ℓ) direction. The remaining samples(V396, V398, V399, V400) showed to be V_6O_{13} single phase. Evidence for the high orientation of the films also in the crystallographic direction (001) on all samples can be seen in figure 2–2, where only (00 ℓ) reflections are seen. In that figure, only V400 x-ray data are shown as an example of the V_6O_{13} single phase thin films. The other samples' x-ray data are similar.



Figure 2–2: X-ray data for V397, V400 and V401 samples.

2.2.4 Atomic Force Microscopy Images(AFM)

Sample	Phase(s)	RMS Roughness(\mathring{A})
V396	$V_6 O_{13}$	23
V397	$V_6O_{13} + VO_2$	32
V398	$V_{6}O_{13}$	69
V399	$V_{6}O_{13}$	84
V400	$V_{6}O_{13}$	46
V401	$V_6O_{13} + V_2O_5$	44

AFM images were taken for all the thin films. The measured root mean squared (**RMS**) roughness of the thin films can be seen in table 2-5.

Table 2–5: **RMS** roughness for the thin films samples.

It can be seen in figure 2–3, belonging to sample V396, that grains are formed. Because of the amorphous nature of the substrate, there is no evident in-plane orientation of the film, as was expected. It is apparent that the size of the grains varies, and there appears to be good connection between them.



Figure 2–3: **AFM** image of V396 on a 2μ m x 2μ m area.

For the V397 sample(image 2–4), which has two phases, there is an increase in the grain size. The good connection between the grains is obvious and no directional pattern can be seen.



Figure 2–4: **AFM** image of V397 on a $2\mu m \ge 2\mu m$ area.

AFM images 2–5 and 2–6 of samples V398 and V399 (both are single phase) respectively, are quite similar. For V399, it seems that the connection between the grains is not as good as the one in the V398 sample.



Figure 2–5: **AFM** image of V398 on a 3μ m x 3μ m area.

The single phase V400 thin film image 2–7, appears to have grains of similar size. A good connection between the different grains is not evident in the image.

Finally, on the figure 2–8, corresponding to the film V401, it is clear the formation of crystals. No discernible in-plane orientation was present in the image. The average size of the grains of these sample are smaller than the average size of the other films.



Figure 2–6: **AFM** image of V399 on a 2μ m x 2μ m area.



Figure 2–7: **AFM** image of V400 on a 3μ m x 3μ m area.



Figure 2–8: **AFM** image of V401 on a 5μ m x 5μ m area.

CHAPTER 3 ELECTRICAL-MEASUREMENT INSTRUMENTATION

3.1 General Overview

At the Magneto-Optics laboratory of the Physics' Department we have a superconducting magnet, which is contained in a cryostat (model JANIS 4TL-VT25-4KCCR). This magnet can produce magnetic fields from -40 to 40 KG. Because the magnet is operating temperature is 4.2 K we need to cool the system with a helium compression unit (CSW71C model of the SUMITOMO HEAVY INDUSTRIES) under a vacuum achieved with a VARIAN model DS102 mechanical pump and a VARIAN model V70 turbo-molecular pump. Inside the sample chamber Helium is used as a thermal contact gas between the sample space and the magnet space, the magnet space is cooled using with the compression unit that uses a Gifford-McMahon cycle. Once the magnet is at operating temperature, one atmosphere of Helium is introduced in the sample space. At that point the temperature can be cooled from room temperature down to 5 K.

We use a KEITHLEY 236 source/meter to supply the current to the sample and read the voltage across the sample. This unit is capable of providing current and measuring voltage at the nanoamp and nanovolt levels. To study the electrical properties we used the four-point-probe method in the temperature range: 5 - 300K.

3.2 Four-Point-Probe Technique

In figure 3–1, we have four collinear electrical probes which are separated by a distance s, over a thin film. The two outer contacts source current, while the inner ones measure voltage. To calculate the resistance one takes into account that the layer thickness (t) is much less than the space between the probes, and assume that the current propagates from the outer contacts in the form of rings(with area A). The resistance between the inner contacts is given by:

$$R = \int_{x_2}^{x_1} \frac{\rho}{A} dx = \int_{s}^{2s} \frac{\rho}{2\pi t} \frac{dx}{x} = \frac{\rho}{2\pi t} ln(2)$$

Expressing the resistance in terms of the measured current and the applied voltage, $R = \frac{V}{I}$, leads to the resistivity:

$$\rho = \frac{2\pi t}{\ln(2)} \frac{V}{I}$$

Because the sample is actually finite, a correction factor k that depends on the probes spacing and the dimensions of the samples must be added. Thus the more general expression for the resistivity using four point probes is

$$\rho = k \frac{\pi t}{\ln(2)} \frac{V}{I}$$



Figure 3–1: V_6O_{13} thin film sample with four collinear probes.

3.3 Experimental Set-up

The samples were cleaned with methanol to remove any dirt from them. Afterwards, four collinear probes were made on the samples by attaching gold wires with silver paint over the thin films, see figure 3-1. The advantage of using four collinear probes, is that the resistance of the cables is not included in the measurements, thus only measuring the materials resistence. The samples dimensions and inter-silver-point distance were measured, to later determine the appropriate correction factors. The correction factors used in this work, are the ones presented in the Haldor Topsoe book. The sample was placed on a copper finger at the bottom of the sample holder insert (see figure 3-2). For some samples there was a thin sheet of phenolic between the sample and the finger, in others they were in direct contact. The purpose of the phenolic sheet was to better electrically insulate the sample from the metal finger. In both cases, caution was taken that the thermal contact was a good one. The four gold wires were attached with silver paint to four copper electrodes, which were connected to the Keithley 236 source/meter. One of the conditions of the four-point-probe technique is that the electrical probes be ohmic. Therefore at room temperature, an I - V curve was taken to verify the ohmic behaviour. The column was then immersed inside the cryostat and proper care was taken to correctly seal the cryostat. A vacuum of 10^{-5} torr was achieved before starting to cool down the sample and the system. The cooling of the system took approximately 12 hours, but the samples were generally maintained at 5 K for 24 hours, to let the system achieve equilibrium. Using Labview software, data were acquired between 5-300 K, and displayed in real time using a computer. The current used was small enough (less than $1\mu A$), so no significant heating of the sample due to current took place. Also, to verify that no currents were present as a result of thermal gradients, measurements were done with zero current. The temperature ramp was chosen to allow a reliable measurement of the sample's real temperature.

For this, various measurements were done with different temperature ramps, and the more repeatable and stable through cooling and heating was selected. Various I-V curves as a function of temperature were measured, to verify the repeatability of the measurements. Finally the data was processed to obtain the resistivity using the formula described in section **3.2**.



Figure 3–2: V_6O_{13} thin film sample with four collinear probes, on top of the cryostat column.

CHAPTER 4 ANALYSIS AND DISCUSSION

4.1 Theory

The solution to the Boltzmann equation using the relaxation time approximation, can be found in many text books, for example see Ferry and Tritt. When the external driving force is an electric field \mathcal{E} , the distribution function is approximated to first order by:

$$f(E) = f_0(E) + e\tau \mathcal{E} \cdot v \frac{\partial f_0(E)}{\partial E}$$

where τ is the relaxation for the system to return to equilibrium. The current density is defined as the summation over all the electron states:

$$J = -e \int \rho(E) v f(E) dE$$

here, $\rho(E)$ is the density of states. Then, by substituting the distribution function

$$J = -e \int f_0(E)\rho(E)vdE + e^2 \int \tau\rho(E)v(\mathcal{E} \cdot v)\frac{\partial f_0(E)}{\partial E}dE = e^2 \int \tau\rho(E)v(\mathcal{E} \cdot v)\frac{\partial f_0(E)}{\partial E}dE$$

The first term vanishes because the equilibrium distribution function f_0 averages to zero in k-space. This equation can be rewritten as

$$J = -ne^{2} \mathcal{E} \frac{\int \tau \rho(E) v^{2} \frac{\partial f_{0}(E)}{\partial E} dE}{\int \rho(E) f_{0}(E) dE}$$

given that the number of carriers n in the semiconductor band is

$$n = \int \rho(E) f_0(E) dE$$

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to which we will return later. If the drift velocity is negligible compared to the thermal velocity (in a cubic crystal), then $v^2 = v_x^2 = \frac{2E}{3m^*}$, where m^* is the effective mass. Therefore, the equation can be simplified as

$$J = \frac{ne^2 < \tau >}{m^*} \mathcal{E}$$

Finally we recognize the resistivity from this expression

$$\rho = \frac{1}{ne\mu}$$

where the mobility is defined as $\mu = \frac{e < \tau >}{m^*}$. If we assume that the bands of the semiconductor are parabolic, then the number of carriers in a 3-dimensional conductor reduces to:

$$n = \frac{4}{\sqrt{\pi}} \left(\frac{2\pi m^*}{h^2}\right)^{\frac{3}{2}} (k_B T)^{\frac{3}{2}} e^{\frac{E_g}{k_B T}}$$

for a nondegenerate semiconductor. Accordingly, the resistivity can be re-writen in a simplified form as:

$$\rho = AT^{\alpha} e^{\frac{E_g}{k_B T}}$$

where the term A represents all the constant terms. The temperature dependence of the carrier concentration depends on the dimensions of the system, while the temperature dependence of the mobility (or relaxation time) depends on the type of scattering mechanism, although it may not be a power law dependence necessarily. The temperature dependence of the pre-exponential term will be a combination of the aforementioned dependencies.

4.2 Phenomenological Model for the S-S Transitions

The resistivity calculated from raw data was acquired from I-V curves as was described in the previous chapter. To better process the data, running averages were used. The smoothed data were compared with the original to verify that artifacts were not introduced. The resistivity of V_6O_{13} thin films made by DC sputtering revealed that the electrical behavior corresponded to that of a semiconductor throughout the measured temperature range (typically 50 - 300K). The temperature dependence of the log of the resistivity was roughly linear with $\frac{1}{T}$. An analysis of the different V_6O_{13} thin films made by DC sputtering was not done. The reason being that films made under the same conditions exhibited different behavior. This may be explained as a consequence of the method employed to fabricate them, since it is difficult to control the amount of partial oxygen pressure during fabrication. And as can be see in figure 4–1, this quantity affects the behavior of the resistivity.

Since the **PLD** method offers a better control of the oxygen pressure during fabrication, various samples were fabricated using this method. The details can be seen on table 2–4 of chapter 2. The raw data was processed as described before. The resistivity for the different samples is shown in figure 4-1. The data for sample V397 is not present, since it was not possible to measure it, because its resistance exceeded the measurement capacity of the Keithley 236 source/measure unit. It can be seen in the figure how the samples become less resistive with increasing oxygen pressure during fabrication, except for the V401 sample. It is natural to expect this, since this sample contains also the wide band gap semiconductor V_2O_5 . Although small, there is a perceivable hysteresis between the cooling and heating runs. It is also apparent that the films are semiconductive throughout the measured temperature range. For V_6O_{13} single-phase samples V398, V399 and V400, it is very clear that changes in the slope start to occur around 177K, with V400 being the most obvious and interesting among them. For the same samples, it can be seen how the concavity of the resistivity curve changes two times. The first, as mentioned before, is around 177K, and may be associated to the **S-S** transition. The temperature of the second change in the concavity tends to lower values, as the oxygen pressure is increased, until for sample V400 it is very near the reported magnetic transition around 55 K. All of these observations serve as evidence that the data have at least three regions where the physical behavior is different. If the information in the literature is taken

into account, one has to assume that the changes in the concavity are related to the two phase transitions reported to occur in V_6O_{13} . Thus, a change in the resistivity which may be associated to the magnetic transition has been seen in V_6O_{13} for the first time. Measurements with samples with intermediate composition between V400 and V401 could not be done, since the **PLD** equipment broke down and could not be repaired in time for this work. But one could speculate that a sharp **S-S** transition could occur at higher oxygen concentration if the tendency continues, and films of V_6O_{13} single phase continue to form.



Figure 4–1: Arrhenius plot for the different samples of V_6O_{13} thin films fabricated under different partial oxygen pressures.

To understand the transport properties of V_6O_{13} , different models for the resistivity of the form:

$$\rho = AT^{\alpha} e^{\frac{B}{T^n}} \tag{4.1}$$

were tried. It was found that none of the different models could fit the data over the complete measured range. In view of the absence of a satisfactory fit which could be associated to a particular physical model, we tried to fit the resistivity in different temperature intervals. The segmentation of the data was done by using, as a reference, the different transition temperatures (i.e. electric and magnetic) reported in the literature on table 1–1 of chapter 1. The temperature intervals are:

- $\mathbf{I} = \mathbf{T}_{Lowest} 55K$
- II = 55-150K
- III = 150-300K

Again, the different models tried could not fit the data in the temperature intervals I, II, and III. This indicates that the transport mechanism occurring in V_6O_{13} films are more complicated than the resistivity behavior of the bulk material or single crystals, as can been appreciated in the Resistivity vs Temperature figures on chapter 1. Usually, in a semiconductor at high temperature, scattering with phonons is the main scattering mechanism. While at low temperatures, scattering with impurities is the dominant one. The Debye temperature (θ_D) of a material can be used as the criterion of what is high and low temperature for a material. At approximately $T = \frac{\theta_D}{10}$ one can safely say that it is low temperature and usually the relevant scattering mechanism will be by impurities. The only reported value for the Debye temperature of V_6O_{13} is $\theta_D = 400K$, although the authors are uncertain of its validity [11]. The Debye temperature for V_2O_5 is around 790K, and for VO_2 it is between 477 - 685K. Taking the magnitudes of these temperatures, we can say that for most of the measured temperature intervals, both electron-phonon scattering and impurity scattering need to be taken into account. So we have a material where there are possibly two or more relevant scattering mechanism operating in the same temperature range.

In view of the complicated resistivity data, and the fact that it did not adjust to any of the conventional models, another approach to adjust and analyze the data was

Parameter	V398H	V399H	V400H	V401H
$A_1(K)$	136(2)	80(17)	199(88)	146(10)
$A_2(K)$	401(30)	307(4)	251(2)	563(16)
$A_3(K)$	972(84)	1148(57)	1146(38)	1512(183)
B_1	-8.13(0.09)	-10.8(0.78)	2.59(6.36)	-15.7(0.24)
B_2	-2.42(0.48)	-2.04(0.08)	-0.715(0.039)	-6.63(0.21)
B_3	4.41(0.62)	7.69(0.47)	9.93(0.31)	3.9(1.4)
$C_1 \ (1/K)$	-0.051(9E-4)	-0.109(0.009)	0.119(0.111)	-0.077(0.002)
$C_2 \ (1/K)$	-0.02(0.002)	-0.023(4E-4)	-0.024(2E-4)	-0.028(7E-4)
$C_3 (1/K)$	3.96E-4(0.001)	4.92E-3(1E-3)	7.19E-3(6E-4)	1.69E-3(3.7E-3)
$T_1(K)$	92(2)	55(1)	33(2)	105(0.7)
$T_2(K)$	187(4)	188(2)	190(1)	210(3)
$dT_1(K)$	5.33(0.78)	3.17(0.56)	5.41(0.12)	3.4(0.44)
$dT_2 (K)$	16.2(1.19)	16.57(1.23)	14(0.6)	8.13(0.82)
R. Chi-Sqr	1.16E-5	3.8E-5	2.88E-5	$9.35\text{E}{-5}$
Adj. R Sqr.	1	1	1	0.99999

Table 4–1: Table with the parameters for the different V_6O_{13} samples on heating(H), obtained by fitting the Ln(Resistivity) vs Temperature data with model 4.2. The standard deviation appears in parenthesis.

taken. The Ln(Resistivity) vs Temperature data for different V_6O_{13} samples during cooling and heating was fitted(see tables 4–1 and 4–2) using a phenomenological model:

$$Ln(\rho) = A(T)/T - B(T) + C(T) * T$$
(4.2)

where

$$A(T) = A_1 + \frac{A_2 - A_1}{e^{\frac{-(T - T_1)}{dT_1}} + 1} + \frac{A_3 - A_2}{e^{\frac{-(T - T_2)}{dT_2}} + 1}$$

$$B(T) = B_1 + \frac{B_2 - B_1}{e^{\frac{-(T - T_1)}{dT_1}} + 1} + \frac{B_3 - B_2}{e^{\frac{-(T - T_2)}{dT_2}} + 1}$$

$$C(T) = C_1 + \frac{C_2 - C_1}{e^{\frac{-(T - T_1)}{dT_1}} + 1} + \frac{C_3 - C_2}{e^{\frac{-(T - T_2)}{dT_2}} + 1}$$

This model offers the advantage that the data do not need to be segmented to adjust it. All the physics are included in the model. Initially a more traditional fit,

Parameter	V396C	V398C	V399C	V400C	V401C
$A_1(K)$	109(416)	37(8)	82(9)	96(63)	122(6)
$A_2(K)$	644(722)	370(13)	302(1)	251(4)	536(11)
$A_3(K)$	935(1037)	993(39)	1207(39)	1087(53)	1378(112)
B_1	-16(15)	-11.8(0.4)	-10.4(0.4)	-4.95(4.6)	-16.2(0.2)
B_2	-6.41(5.31)	-2.74(0.2)	-1.96(0.04)	-0.512(0.081)	-6.85(0.15)
B_3	-3.05(7.36)	4.56(0.3)	8.21(0.33)	9.47(0.42)	2.82(0.86)
$C_1 (1/K)$	-0.066(0.15)	-0.089(0.005)	-0.104(0.005)	-0.014(0.082)	-0.082(0.001)
$C_2 \ (1/K)$	-0.023(0.014)	-0.021(7E-4)	-0.023(2E-4)	-0.023(4E-4)	-0.028(5E-4)
$C_3 (1/K)$	-0.013(0.013)	6.0E-4(6.0E-4)	5.99E-3(7E-4)	6.31E-3(8E-4)	-5.80E-4(0.002)
$T_1(K)$	93(105)	70(2)	54(1)	35(3)	102(0.5)
$T_2(K)$	168(2)	189(2)	182(3)	189(1)	206(3)
$dT_1(K)$	26.5(17.9)	7.06(0.8)	0.26(1.37)	7.16(0.34)	3.06(0.37)
dT_2 (K)	0.30(1.9)	13.4(0.8)	16.8(1.11)	16.03(0.73)	7.67(0.75)
R. Chi-Sqr	2.35E-4	9.98E-6	4.43E-5	2.32E-5	7.07E-5
Adj. R Sqr.	0.99997	1	0.99999	1	0.99999

Table 4–2: Table with the parameters for the different V_6O_{13} samples on cooling(C), obtained by fitting the Ln(Resistivity) vs Temperature data with model 4.2. The standard deviation appears in parenthesis.

equivalent to equation 4.1

$$Ln(\rho) = Ln(A) + \alpha Ln(T) + \frac{B}{T^n}$$

was adjusted to the data, but the fit was not a satisfactory one. Instead, equation 4.2, provided a better fit to the data. Before analyzing the fit results and the parameters value, let's discuss equation 4.2. Due to the different transitions that the material goes through it should be expected that the parameters vary with temperature. One way to introduce the temperature dependence is to assume that in the interval I the values of the parameters are constants equals to A_1 , B_1 , and C_1 . Then in interval II, they abruptly change their values to the new constants A_2 , B_2 , and C_2 . Finally, over the electrical and structural transitions parameters A, B, and C change their values to constants A_3 , B_3 , and C_3 (for an example see figure 4–2). Since the Fermi-Dirac function occurs naturally in semiconductor physics to represent an abrupt transition, it was modified (see figure 4–3) and used to accomplish the goal stated above. The modified Fermi-Dirac function allows A, B, and C to remain constant in intervals

I, II, and III, but also allows to change their values between the different intervals. This would reflect the changes in the resistivity behavior and transport properties with temperature in a natural way, while at the same time having only one coherent picture describing the system. Equation 4.2 with A, B, and C constant was used to fit the $Ln(\rho)$ data in the intervals I, II, and III to obtain initial parameters for the fit of equation 4.2. Then the natural logarithm of the data was fitted using the Levenberg-Marquardt non-linear least square algorithm implemented in Origin.



Figure 4–2: Example of how the parameters change their values between the different intervals of temperature.

The adjusted $Ln(\rho)$ data for samples V396, V398, V399, V400, and V401 during cooling, is presented on figures 4–4, 4–5, 4–6, 4–7 and 4–8 respectively. A visual inspection of the fit shows that equation 4.2, describe the data accurately.

The discussion of parameters $A_{i=1,2,3}$, $T_{j=1,2}$, and $dT_{j=1,2}$ is left for later, since their assignment is straightforward and provides physical evidence of the correctness of the model. Inside each temperature interval **I**, **II**, **III** the resistivity, according to the model, can be written as:

$$\rho = e^{-B} e^{CT} e^{\frac{A}{T}} = B' e^{CT} e^{\frac{A}{T}} = D(T) e^{\frac{A}{T}}$$



*

Figure 4–3: Modified Fermi-Dirac distribution.

Since the parameters B and C are probably coupled we do not intended to provide a direct physical meaning for them. Instead, the parameter C can be associated with the relaxation time of the material. Still, in the absence of more transport measurements, the information obtained from these parameters should be used carefully and used more as a qualitative description of the physics of these parameters. Using a classical description of the resistivity, one must say that the parameter B include all the constant terms of the mobility, the carrier concentration, and the temperature dependence of the carrier concentration. Some of the values of B' at low temperatures are quite high, but since this value is coupled to C, the magnitude that should be considered are the product of both terms (denoted as D(T)). The behavior of B and C can be seen in figures 4-9 and 4-10. Although the values for the different samples differ, it is safe to say that there is a tendency for the parameter B to increase from one interval to the other when the temperature rises. Consequently, the value for B' decreases. In the case of parameter C, it should be associated with the temperature dependence of the mobility or what is the same, with the relaxation time. The reason of this type of exponential dependence is unknown. The tendency of the parameter C is to increase also, when going from one interval to other as



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Figure 4–4: $Ln(\rho)$ vs*Temperature* for sample V396 on cooling. The solid red line is the fit to the data based on the phenomenological model.



Figure 4–5: $Ln(\rho)$ vs*Temperature* for sample V398 on cooling. The solid red line is the fit to the data based on the phenomenological model.

was the case with parameter B. Now, there are actually two cases that need to be described in the different temperature intervals for the behavior of C, and therefore of the product D(T). When C is negative, this product will decrease in the interval, but when it is positive the product will increase inside the interval as is the case of region III. So the physical behavior of the mentioned product D(T) is that it starts at a value, then it continues to decrease rapidly(due to the magnitude of parameter



Figure 4–6: $Ln(\rho)$ vs*Temperature* for sample V399 on cooling. The solid red line is the fit to the data based on the phenomenological model.



Figure 4–7: $Ln(\rho)$ vs*Temperature* for sample V400 on cooling. The solid red line is the fit to the data based on the phenomenological model.

B) inside the temperature interval **I**. Then, at the magnetic transition, the product changes its behavior, but continues to decrease, although more slowly because of the smaller magnitude of B. And finally, at the **S-S** transition and inside interval **III** it changes the behavior again, and starts increasing slowly. The reason of the variance between the parameters is that as can be seen in figure 4–1, the behavior for the different samples are different. Which is consistent with the fact that the



Figure 4–8: $Ln(\rho)$ vs*Temperature* for sample V401 on cooling. The solid red line is the fit to the data based on the phenomenological model.

oxygen concentration is not the same for all. Moreover, one of the samples also contains V_2O_5 . The other reason for this variance is that when fitting, these two parameters are the least relevant ones. Although all the parameters were treated with the same weight, it should be expected that in the fitting process the parameters $A_{i=1,2,3}$, $T_{j=1,2}$, and $dT_{j=1,2}$ are more important. That is the reason why B and C should only be used as to extract qualitative information(i.e. the tendency of these parameters to increase or decrease). It is interesting that the value of C_2 is almost constant in all the films. This can mean that for this parameter the approximate value of -0.023 is the correct one.

Lets discuss now the meaning of the parameters $A_{i=1,2,3}$, $T_{j=1,2}$, and $dT_{j=1,2}$. The behavior of the parameter A can be see more clearly in figure 4–11. It is quite clear that parameter A is associated with the activation energy of the distinct phases of the semiconductor. Its value changes to higher ones with temperature as is expected for temperature activated behavior and are reasonably physical values. T_1 and T_2 are the values associated with the temperatures where the transitions occur. Except for V396 and V401 the values for T_1 are near 55K as expected, remembering



Figure 4–9: Parameter B vs Temperature.

that all the parameters where set free, it is reassuring that the fitted value of T_1 is consistently near the reported magnetic transition. The values for T_2 are close to 188K for the different single phase V_6O_{13} thin films, except for sample V396. Since V396 is composed of a single phase (V_6O_{13}) , it is puzzling why the fitted values of the parameters differ from the other single phase films. The large standard deviations for this sample's parameters indicate that the phenomenological model might not be adequate to explain the observed resistivity data. The data measured during heating could not be adjusted with the model either. The reason may be that V396 appears to be the only V_6O_{13} single-phase sample that didn't show either of the two electric transitions as can be seen in figure 4-1. Although the values for the parameter T_2 of all the samples are somewhat far from the reported value, the fact that the values for the parameters are very close, indicates that it should be associated to the transition. Moreover, since it is an S-S transition, the fact that the value for V401is different is consistent with this sample being composed of more than one phase. Finally, the parameters dT_1 and dT_2 should provide information about how broad are the transitions at temperatures T_1 and T_2 . On average the difference between the temperature width between the two transitions appears to be 10K. Again, for



Figure 4–10: Parameter C vs Temperature.

samples V398, V399 and V400, the results are very similar. This reinforces the fact, that although the films were fabricated under different partial oxygen pressures, they are single phase V_6O_{13} . This suggest, that for near-stoichiometric V_6O_{13} thin films, the **S-S** and magnetic transitions are similar to bulk transitions. The derivative of the fit for the data taken while heating is presented on figure 4–12, there it can be appreciated that the magnetic transition is a narrower one. Also, it can be seen how minima which can be related to the transitions are shifted from one sample to other, although they are close.

The figures of the fit's derivatives are also presented individually, with the transition temperature and respective width on them. For sample V400, which is the one who presents the most drastic change, it can be seen that the parameter T_1 is somewhat misplaced from where one would believe should be the transition(see figures 4–18 and 4–19). A higher value, nearer the peak seen at approximately 44K would yield values nearer the reported value. On figure 4–14, it also seems that the parameter T_1 overshoot the real value of the transition. The value depicted in figure 4–15 seems a more reasonable value, and also is nearer the reported value of 55K and the values seen in the other V_6O_{13} single phase films. An inspection of figures



Figure 4–11: Parameter A vs Temperature.

4–13 and 4–17 appears to indicate that the value for dT_1 for V399C and dT_2 for V396C respectively, are too small. The value for V399H during heating seems to be a more reasonable result.

From the statistics point of view the fits are valid, since the Reduced chi squared values are very small, and the values of adjusted R are practically equal to one. Although, the proposed model has 13 parameters, the values for all of them were proven to be physically feasible. For instance the values of the parameters related to the S-S transition and magnetic transition are similar to those reported in the literature, see table 1–1 of chapter 1. Also, as expected the values of the parameters for sample V401 differ from the other films, but still present the change of behavior associated with the electric and magnetic transitions. This reflects, the dual phase composition of this thin film. All of these evidence, suggest that the model presents a physically coherent picture. Given that there are practically no transport data for V_6O_{13} single crystals nor the bulk material, it is difficult to obtain more information from the resistivity measurements alone. More transport data, or information from other experiments would permit to fix some of the phenomenological model



Figure 4–12: $\frac{dLn(\rho)}{dT}$ vs *Temperature* for the different measured samples on heating. parameters and possibly remove the few parameters values for some films that do not agree with the bulk of other values.

4.3 Closing Comments

A phenomenological model for explaining the resistivity behavior of V_6O_{13} thin films was presented in this chapter. The model is based primarily on the resistivity formula for a thermal activated semiconductor, and uses the properties of a modified Fermi-Dirac distribution for representing the electric transitions that seemed to occur in the data. The main advantage of the model is that it allows a fit of the data throughout the whole measured temperature range, without the need to segment the data. The values resulting from the fit for the **S-S** transition temperature



Figure 4–13: $\frac{dLn(\rho)}{dT}$ vs *Temperature* for V396 on cooling.



Figure 4–14: $\frac{dLn(\rho)}{dT}$ vs *Temperature* for Figure 4–15: $\frac{dLn(\rho)}{dT}$ vs *Temperature* for V398 on heating. V398 on cooling.

at high temperature are higher than the reported values in the literature (see table 1–1). The temperatures of the second **S-S** transition are near the reported value of the magnetic transition at 50 K in V_6O_{13} .



Figure 4–16: $\frac{dLn(\rho)}{dT}$ vs *Temperature* for V399 on heating.



Figure 4–17: $\frac{dLn(\rho)}{dT}$ vs *Temperature* for V399 on cooling.





Figure 4–18: $\frac{dLn(\rho)}{dT}$ vs *Temperature* for V400 on heating.

Figure 4–19: $\frac{dLn(\rho)}{dT}$ vs *Temperature* for V400 on cooling.

0.00



T₂=206K,dT₂=7.7K

Figure 4–20: $\frac{dLn(\rho)}{dT}$ vs *Temperature* for V401 on heating.

Derivative of Ln(Resistivity) Fit

Figure 4–21: $\frac{dLn(\rho)}{dT}$ vs *Temperature* for V401 on cooling.

Temperature

CHAPTER 5 CONCLUSION AND FUTURE WORK

5.1 Conclusion

Various V_6O_{13} thin films made using the **PLD** technique were studied. All the measured films underwent a **S-S** transition, contrary to the mostly reported **M-S** transition in single crystals. A change in the electrical resistivity near the reported magnetic transition in the literature was also seen in all the measured samples. It was shown that samples grown under various partial oxygen pressures exhibited different physical behavior. As the pressure increased, the thin films presented less electrical resistance, and the **S-S** became more evident with a constant transition temperature for all the samples. The temperature of a second **S-S** transition, which may be related to the known magnetic transition that occurs in V_6O_{13} , decrease with an increasing oxygen pressure. A phenomenological model was proposed to model the resistivity. The model suggests that the temperature for the **S-S** transition at high temperature is around 188K. It was seen that the temperature of the low temperature **S-S** transition is different for each sample, but the model indicates to be in the range 30 - 60 K for the V_6O_{13} single phase films.

5.2 Future Works

All the measurements need to be repeated using magnetic fields. Thin films grown under partial oxygen pressures from 54 to 83 *mtorr* need to be made and measured. It is possible that these films will exhibit a more pronounced high temperature **S-S** transition as the oxygen pressure increases, if the tendency observed in this work continues. Samples that are grown on crystalline substrates can show

in-plane alignment, which can be important for a **M-S** to happen, since V_6O_{13} is a quasi-one dimensional conductor. Thus, measurements of V_6O_{13} thin films to study how the resistivity varies as a function of substrate or sample thickness are very desirable.

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ELECTRIC STUDIES OF VANADIUM OXIDE (V_6O_{13}) THIN FILMS

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